INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

University Microfilms International
300 North Zeeb Road
Ann Arbor, Michigan 48106 USA
St John's Road, Tyler's Green
High Wycombe, Bucks, England HP10 8HR

77-7867

BEDFORD, Clifford Douglas, 1948-
REACTIONS OF A TRIAZOLYL CARBENE WITH ALKYL BENZENES, AND EFFECTS ON THE NORCARADIENE-CYCLOHEPTATRIENE ISOMERIZATION.

The University of Michigan, Ph.D., 1976
Chemistry, organic

Xerox University Microfilms, Ann Arbor, Michigan 48106

REACTIONS OF A TRIAZOLYL CARBENE WITH ALKYL BENZENES, AND EFFECTS ON THE NORCARADIENE-CYCLOHEPTATRIENE ISOMERIZATION

by

Clifford Douglas Bedford

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Chemistry)
in The University of Michigan
1976

Doctoral Committee:

Professor Peter A. S. Smith, Chairman
Professor Arthur J. Ashe, III
Professor Joseph H. Burckhalter
Professor Richard G. Lawton
Associate Professor Ralph Rudolph
Assistant Professor David Weiss

To Adeline, Clifford and Denise for their confidence, friendship and love

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to the "Boss," Dr. Peter A. S. Smith, for his friendship during times of indecision, confidence during times of questioning and guidance through the course of this research when my zeal overcame common sense.

I would also like to express my appreciation to the members of my doctoral committee and the organic staff at The University of Michigan for their helpful suggestions, interest and advice throughout the course of this investigation.

Financial assistance in the form of Teaching Fellowships in the Department of Chemistry during the academic years of 1972-1976 and of a Rackham (Spring Half 1974) and an Eastman-Kodak (Spring Half 1975) Summer Fellowships are gratefully acknowledged.

Finally, I wish to thank Mr. Frank Parker for expert instruction for the operation of the C-13 NMR instrument.

TABLE OF CONTENTS

DEDICATION ii

ACKNOWLEDGEMENTS iii

LIST OF TABLES vi

LIST OF FIGURES ix

CHAPTER I: THE SYNTHESIS AND DECOMPOSITION OF 5-DIAZOMETHYL-1,4-DIPHENYL-1,2,3-TRIAZOLE IN POLYSUBSTITUTED AROMATIC SUBSTRATES 1

1. Introduction 1
2. Statement of the Problem 12
3. Results and Discussion 13
   A. 5-Diazomethyl-1,4-Diphenyl-1,2,3-triazole 13
   B. 5-(1-Diazoethyl)-1,4-diphenyl-1,2,3-triazole 18
   C. The Reaction of 1,4-Diphenyl-1,2,3-Triazolylcarbene with Aromatic Substrates 20
      (1) Thermolysis in o-Xylene 25
      (2) Thermolysis in m-Xylene 26
      (3) Thermolysis in p-Xylene 28
      (4) Thermolysis in Indan 30
      (5) Thermolysis in Mesitylene 31
      (6) Thermolysis in Durene 34
      (7) Thermolysis in p-Ethyltoluene 36
      (8) Thermolysis in 4-tert-Butyltoluene 38
      (9) Thermolysis in p-Cymene 41
      (10) Thermolysis in Naphthalene 43
      (11) Thermolysis in Thiophene 46
      (12) Thermolysis in p-Diisopropylbenzene 52
      (13) Thermolysis in p-Di-tert-butylbenzene 52
      (14) Interpretive Discussion 52
4. Experimental 69
   A. Preparation of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole 70
   B. Preparation of 5-(1-Diazoethyl)-1,4-diphenyl-1,2,3-triazole 73
   C. Decomposition of 5-Diazomethyl-1,4-diphenyl-triazole in Aromatic Solvents 77
5. Spectra 95
6. References 109

CHAPTER II: THE NORCARADIENE/CYCLOHEPTATRIENE PROBLEM 114

1. Introduction 114
2. Statement of the Problem 118
3. Discussion and Results 119
   (1) Mesitylene Case 119

(2) The Durene Case 128
(3) The Xylene Series 130
(4) The p-Substituted Toluene Series 132
(5) Interpretive Discussion 142
4. References 145

CHAPTER III: THE THERMAL REARRANGEMENTS OF 1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL ADDUCTS OBTAINED BY DECOMPOSITION OF 5-DIAZOMETHYL-1,4-DIPHENYL-1,2,3-TRIAZOLE IN POLYSUBSTITUTED AROMATIC SUBSTRATES 147

1. Introduction 147
2. Statement of the Problem 151
3. Results and Discussion 151
A. Thermal Rearrangement of 1,3,5-Trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-norcaradiene 151
B. Thermal Rearrangement of 1,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene 161
C. Thermal Rearrangement of 2,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene 168
D. Thermal Rearrangement of 1-tert-Butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene 175
E. Thermal Rearrangement of 1,3,4,6-Tetramethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene 181
4. Experimental 185
A. Thermal Rearrangement of Selected 1,4-Diphenyl-1,2,3-triazol-5-yl Adducts 185
B. Kinetics of the Thermal Rearrangement of Selected 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole Adducts 189
5. Spectra 191,208
6. References 211

APPENDIX 213

LIST OF TABLES

Table		Page
I	Syn:Anti Distribution of Cyclopropanes Formed by Arylcarbenes and Arylcarbenoids Addition to cis-2-Butene	6
II	Syn:Anti Distribution of Cyclopropanes Formed by Diarylcarbenes and Diarylcarbenoids Addition to Cyclopentadiene	7
III	Selectivity in Addition to Olefins of p-Tolylcarbenoid	9
IV	Effect of Aromatic Substituents on the Positional Selectivity of Carbene Attack in Monosubstituted Benzenes	23
V	Effect of Aromatic Substituents on the Positional Selectivity of Carbene Attack, Comparison of Copper-catalyzed Decomposition of Diazomethane and Thermal Decomposition of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole in Disubstituted Benzenes	54
VI	PMR Spectrum of 1,3,5-Trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene Compared with Known Norcaradiene Adducts	120
VII	^{13}CMR Spectrum of 1,3,5-Trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene	121
VIII	^{13}CMR Spectrum of C_1, C_6 and C_7 Carbon Atoms of 7-Aryl-7-carbomethoxynorcaradienes	122
IX	PMR Spectrum of 1,3,4,6-Tetramethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene Compared with Mesitylene Adduct	129
X	^{13}CMR Spectrum of 1,3,4,6-Tetramethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene	130
XI	PMR Spectra of Adducts Resulting from the Thermal Decomposition of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole in the Xylene Series	131
XII	PMR Spectra of Adducts Resulting from the Thermal Decomposition of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole in p-Ethyltoluene, p-Cymene and 4-tert-Butyltoluene	135

XIII	Comparison of Chemical Shifts of the H_6 and H_7 Protons of Known Norcaradienes and Adducts Obtained from the Thermal Decomposition of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole in Disubstituted Aromatic Substrates	136
XIV	^{13}CMR Spectrum of 1-tert-Butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene	136
XV	Kinetic Parameters for Some Intramolecular 1,5-Hydrogen-transfer Reactions	149
XVI	^{13}CMR Spectrum of 1,4,6-Trimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene	152
XVII	Kinetics of the Thermal Rearrangement of 1,3,5-Trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene to the Conjugated Tropilidene Isomer	160
XVIII	Activation Parameters for the Thermal Isomerization of the Mesitylene Adducts to their Conjugated Tropilidene Isomers	160
XIX	Kinetics of the Thermal Rearrangement of 1,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene to 1,5-Dimethyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene	171
XX	Activation Parameters for the Thermal Isomerization of 1,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene to 1,5-Dimethyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene	171
XXI	Kinetics of the Thermal Rearrangement of 2,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene to 1,6-Dimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene	174
XXII	Activation Parameters for the Thermal Isomerization of 2,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene to 1,6-Dimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene	174
XXIII	Kinetics of the Thermal Rearrangement of 1-tert-Butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene to 1-Methyl-5-tert-butyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene	182

XXIV Activation Parameters for the Thermal Isomerization of 1-tert-Butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene to 1-Methyl-5-tert-butyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene 182

XXV Relative Rates for the Thermal Rearrangement of Selected 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole Adducts 192

LIST OF FIGURES

Figure		Page
1.	^{13}CMR spectrum of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene	33
2.	Schematic representation of reactions energetics of the norcaradiene/cycloheptatriene system	65
3.	Variable temperature PMR spectra of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-norcaradiene	124
4.	Variable Temperature ^{13}CMR spectra of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-norcaradiene	126
5.	Variable Temperature PMR spectra of 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene	137
6.	Variable temperature ^{13}CMR spectra of 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene	139
7.	Schematic representation of the chemical non-equivalence generated by the hindered rotation of the diphenyltriazole moiety past the vicinal substituent	155
8.	Schematic representation of the possible reaction pathways for thermal isomerization of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene to 1,4,6-trimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cyclo-heptatriene	156
9.	Kinetics for the thermal isomerization of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene	157
10.	Energy of Activation for the thermal isomerization of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene and 1,3,5-trimethyl-2,4,6-trideuterio-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene	158
11.	Kinetics for the thermal isomerization of 1,3,5-trimethyl-2,4,6-trideuterio-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene	159

12. Variable temperature PMR spectra of 1,5-dimethyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene 164

13. Schematic representation of the chemical non-equivalence generated by the hindered rotation of the diphenyltriazole moiety past the vicinal substituent 166

14. Kinetics for the thermal isomerization of 1,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene 169

15. Activation parameters for the thermal isomerization of 1,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene and 2,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene 170

16. Kinetics for the thermal isomerization of 2,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene 173

17. Kinetics for the thermal isomerization of 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene 179

18. Activation parameters for the thermal isomerization of 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene 180

CHAPTER I

THE SYNTHESIS AND DECOMPOSITION OF 5-DIAZOMETHYL-1,4-DIPHENYL-1,2,3-TRIAZOLE IN POLYSUBSTITUTED AROMATIC SUBSTRATES

1. Introduction

Caution 1.

> "Diazomethane is toxic and prone to cause development of specific sensitivity; in addition, it is potentially explosive. Hence one should wear heavy gloves and goggles while performing this experiment and should work behind a safety screen or a hood door with safety glass. Also, it is recommended that ground joints and sharp surfaces be avoided. . . . Furthermore, at least one explosion of diazomethane has been observed (hopefully from a distance) at the moment crystals (sharp edges!) suddenly separate from a supersaturated solution. Stirring by means of a teflon-coated magnetic stirrer is greatly to be preferred to swirling the reaction mixture by hand, for there has been at least one case of a chemist whose hand was injured by an explosion during the preparation of diazomethane in a hand-swirled reaction vessel. . . ."[1]

This rather morbid account preceding the Organic Syntheses (Collective Volume VI) directions for the preparation of diazomethane indicates the difficulties facing the physical organic chemist who attempts to elucidate the complex behavior of reactive intermediates. Though the preparation of diazomethane has become rather routine with the development of several stable precursors,[2] the high frequency of its appearance in the chemical literature indicates that numerous chemists are continually exposed to this very unpredictable material. In light of the myriad

other diazo compounds available for carbene precursors, many of which are remarkably stable and innocuous, it is curious that so many carbene chemists continue to expose themselves and others to the dangers of diazomethane. One such carbene precursor, 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I), was selected for this study, because it is: (1) not overly toxic; (2) a stable crystalline solid, mp 104-106°C; (3) can be stored in the refrigerator for an indefinite period; (4) fairly easy to prepare, and (5) does not send refrigerator doors flying down chemistry building hallways.

A tremendous growth and wide interest has developed in carbene chemistry in the past two decades, though the subject is not new. Dumas and Péligot,[3] in 1835, suggested that pure methylene could be made by the pyrolysis of methyl chloride at the proper temperature.*

Distinct progress unraveling the complex nature of carbene reactions has been made, although one area, the addition of carbenes to aromatic substrates, has remained an enigma.[5] Carbene intermediates are generally influenced by the following factors: (1) mode of generation; (2) the relative energetics of the divalent intermediate; (3) the

---

* It should be noted that since the atomic weight of 12 for carbon was not generally accepted until after 1862, in some of the early suggestions methylene was given such formulas as C_2H_2 instead of CH_2.[4]

electronic factors on the carbene species; (4) the electronic effects of the substrate molecule; (5) steric interactions between the carbene and substrate, and (6) the spin state.

Of the four common reaction intermediates permeating the organic literature, carbonium ions, carbanions and free radicals possess a tricoordinate carbon atom. Their behavior is now sufficiently well understood that it is generally predictable. The fourth type, carbenes, derivatives of divalent carbon, are the most reactive. Once a carbene is formed, its high energy results in a probability of reaction at subsequent collisions. This situation minimizes the selectivity between competitive reaction pathways, with the result that a large number of products may be formed in substantial amounts. In addition, the chemistry of carbenes has to contend with the ambiguities imposed by the many methods used for their generation, which may introduce a large variety of materials into the reaction medium or impart varying amounts of excess energy to the intermediate carbene.

Carbene intermediates may be formed in many ways: by photolysis or pyrolysis of diazo compounds,[6] from halides or dihalides by the action of powerful bases,[7] from halogenated alkyl mercurials,[8] by pyrolysis of the alkali salts of tosylhydrazones,[9] from diazo compounds by decompositions catalyzed by metals or metal salts,[10] by the action of organolithium compounds on alkyl halides,[11] by pyrolysis

of diazirines,[12] and from organometallic halides, of which the Simmons-Smith reagent has been very widely used.[13] Such a wide variety of possible precursors and the often drastic means used for their production has led to a wide spectrum of selectivities and reactions. The method of generation also influences the subsequent chemical behavior of the carbene intermediates, even towards aromatic substrates. The photolysis of diazomethane in a benzene solution resulted in a 4.8:1 ratio of addition product to insertion product,[14] whereas the copper-catalyzed decomposition afforded only addition product uncontaminated with toluene.[15] A classical example of how the mode of carbene generation influences its reactivity was obtained from a comparison of the photolytic vs. copper-catalyzed thermal decomposition of ethyl diazoacetate in cyclohexene. Photolysis of ethyl diazoacetate in cyclohexene gives 26% norcarane (product of addition reaction) and 21% of the isomeric carboethoxycyclohexenes (product formed by insertion reaction). Thermolysis in the presence of metallic copper yielded only 7-carboethoxynorcarane.[16] Not only were the insertion reactions quenched, as in the benzene case above, by the use of a copper catalyst, but also the stereoselectivity of the intermediate as implicated by the exo/endo ratios of the product norcaranes increase ten-fold: 1.6 from the photolysis and 16 from the catalyzed reaction. Furthermore, a comparative study of the reactivities of a series of olefins towards the intermediates generated by

photolysis of aryldiazomethanes and by the treatment of benzal bromides with organolithium compounds established that the two reactions led to different intermediates.[17]

The stereochemistry of olefin cyclopropanation resulting from carbenes and carbenoids (a term now widely used for divalent carbon species that are in some way complexed with the catalyst employed for their generation) has been a particularly active topic of research. Useful concepts believed to influence the electronic interactions between the carbene intermediates and the olefinic substrate, and the steric limitations placed on various reaction pathways have been proposed. Representative examples of these effects and how they influence the relative stereoselectivity of cyclopropanation are shown in Tables I and II.

Clearly, the more reactive monoarylcarbenes exhibit a much lower stereoselectivity than the metal catalyzed monoarylcarbenoids. It is believed that a positive charge is induced on the olefin substrate during the attack of the electrophilic carbenoid or "free" carbene which is further enhanced by interactions with the aromatic π electrons, as represented by transition states IIa and IIb. This energetically favorable interaction is possible only with a <u>syn</u> arrangement of carbenic and olefinic substituents.[17]

Diarylcarbene and diarylcarbenoid reactions shown in Table II indicate that the major product formed has the electron rich aryl group <u>endo</u> (a direct result of <u>syn</u> attack) to the olefinic substrate. In addition, very

Table I

Syn:Anti Distribution of Cyclopropanes Formed by Arylcarbenes[a] and Arylcarbenoids[a] Additions to Cis-2-butene[17]

	Phenyl Substituent				
	H	p-Cl	m-Cl	p-CH_3	p-OCH_3
Arylcarbene	1.1[c]	1.1	1.2	1.7	2.8
Arylcarbenoid	2.4(21)[b]	2.9(21)	3.7(41)	4.5(22)	8.1(55)

(a) Method of generation, arylcarbenes, from photolyses of aryldiazomethanes; arylcarbenoids, from the action of alkyllithiums on benzal halides or from the metal halide catalyzed decomposition of aryldiazomethanes.

(b) Yields of isolated products in parentheses.

(c) Yields of isolated products ranged from 10-40%.

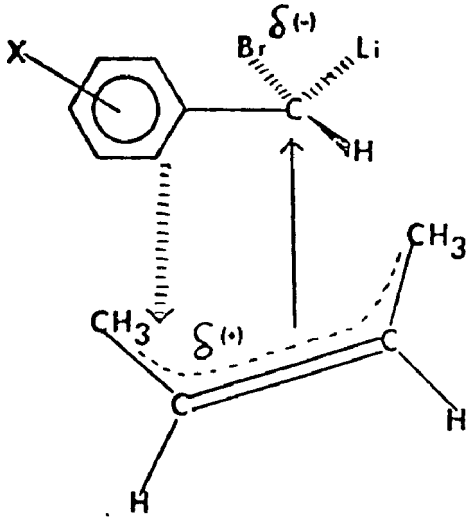
Table II

Syn:Anti Distribution of Cyclopropanes Formed by Diarylcarbenes[a] and Diarylcarbenoids[a] Additions to Cyclopentadiene[18]

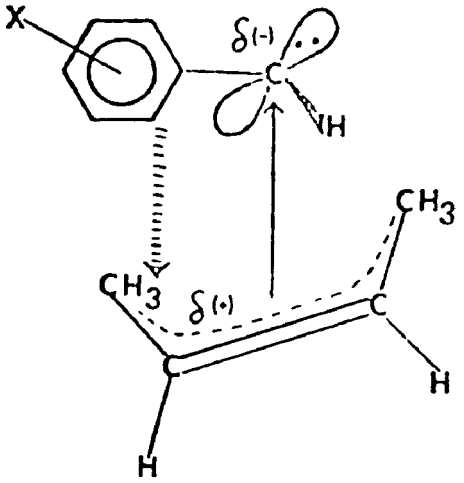
	Aryl substituent [Ar(Ph)-X]				
	p-CN	p-Br	H	p-CH_3	p-OCH_3
Diarylcarbene	0.31(32)[b]	0.28(25)	- -	1.2(14)	≥20(15)
Diarylcarbenoid	0.4(37)[b]	0.28(31)	- -	2.0(12)	≥20(11)

(a) Method of generation, diarylcarbenes, from photolyses of diaryldiazomethanes; diarylcarbenoids, from the metal halide catalyzed decomposition of diaryldiazomethanes.

(b) Isolated yields of products.

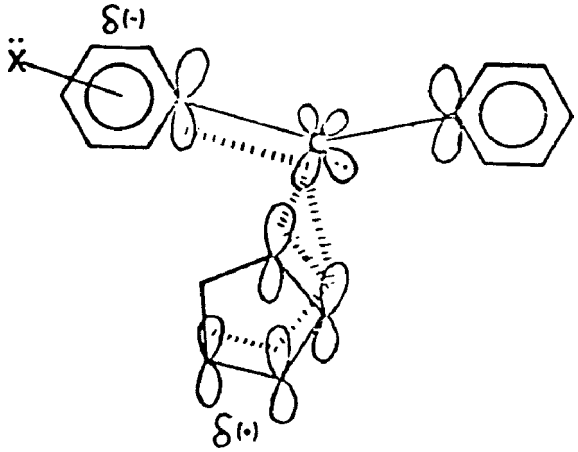


IIa (Carbenoid)



IIb (Free Carbene)

little difference in the stereoselectivity is observed between "free" carbene and carbenoid reactions. A mechanism similar to that presented for arylcarbenes can be invoked to interpret these observations. Furthermore, the developing positive charge on the olefinic substrate is further stabilized by conjugation with the diene system, represented by transition state III.



III

However, a possible spin inversion to the triplet diarylcarbene resulting in a long-lived transition state would allow for thermodynamic equilibration. The energetically favored arrangement of the electronically rich portion of the carbene adding syn to the olefinic substrate could result. Although diarylcarbenes are triplet in a rigid media,[20] mixtures of triplet and singlet states have been implicated in various diphenylcyclopropanations.[21]

These Coulombic interactions between carbenic and olefinic substituents generally offset accompanying unfavorable steric interactions and entropy effects. However, in a recent probe of steric hindrance, as it affects carbene additions, Moss,[19] Table III, increased the alkyl sub-

Table III

Selectivity in Addition to Olefins of p-Tolylcarbenoid[(a)19]

R in $R-CH=CH_2$	Stereoselectivity	Rate of Carbenoid Addition to $R-CH=CH_2$*	
	Syn:Anti	syn mode	anti mode
C_2H_5	2.7	0.99	0.37
i-C_3H_7	1.9	0.46	0.24
t-C_4H_9	0.42	0.071	0.17

(a) Method of generation, p-tolylcarbenoid, from p-methylbenzal iodide and butyllithium in pentane, -10°C.

(b) Relative to trans-butene. All rates have been normalized to the standard by multiplication by 2.

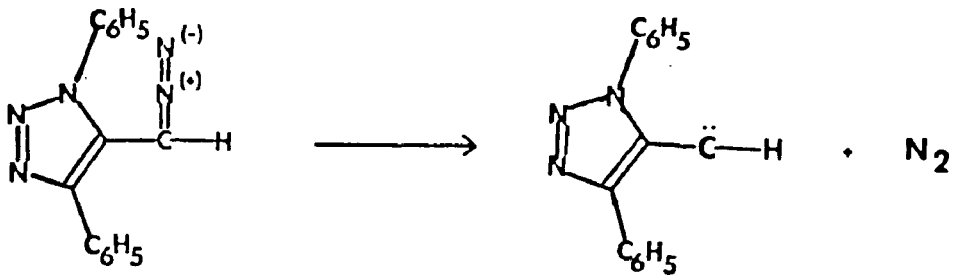
stituents on ethylene and observed a preferential anti addition product for the t-butylethylene case. Clearly,

the resonance donation from the aryl group and the secondary Coulombic interactions with the olefin substrate were overcome by steric factors, resulting in this preference for anti addition product.

A major handicap facing both aryl- and diaryl carbenes or their corresponding carbenoid analogs is the relatively low yields of cyclopropanation products. Extension of these systems to aromatic substrates has met with little success.

In order to investigate the electronic and steric interactions between aromatic substrates and carbenes it was first necessary to find a carbene intermediate with the following characteristics: (1) the carbene precursor should offer an opportunity to explore the nature of a "free" carbene, with no interference from metal complexation or other internal contaminate; (2) the method of generation of the carbene should be as mild as possible. Even in "free" carbene systems, differences in the product ratios have been noted,[22] due particularly to varying amounts of excess energy imparted to the intermediate[23]; (3) the carbene intermediate must undergo addition reactions with aromatic substrates, cleanly and in high yields. Many factors have been found which influence the reaction and selectivity of carbene intermediates; however, the discovery and development of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I), the direct precursor of 1,4-diphenyl-1,2,3-triazole-5-ylcarbene, met all the required conditions stipu-

lated for this investigation. Smith and Wirth[24,25] found



I

that thermolysis at 40-50°C of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I) generated a carbene that was totally immune to intramolecular reactions, but which in the presence of benzene gave high yields of addition products uncontaminated with any insertion products. The unusually low temperature at which this carbene may be generated makes it particularly suited as a model for the study of "free" and relatively stable carbenes. Smith and Bruckmann[26,27] extended the investigations on this model carbene precursor. They demonstrated that 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I) reacts with monosubstituted benzenes at 40-50°C to give 72-90% yields of mixtures of 7-(1,4-diphenyltriazol-5-yl)tropilidene in which the predominant isomer has the substituent in the 3-position. The relative reactivities of monosubstituted benzenes toward the carbene from I were determined, and indeed confirmed that this is an electrophilic carbene. The high selectivity is believed to result, in part, from electronic stabilization of the carbene by the triazole ring.

In light of all the progress to unravel the complex

nature of carbene reactions it seems odd that only one area, first reported by Buchner and Curtius in 1885,[28] the addition of carbenes to aromatic substrates, has remained an enigma. Over 90 years have passed since the first reactions of carbenes, probably the most unique of carbene reactions, with aromatic substrates were discovered, and yet even today little is known about the effects which influence these reactions. For this reason the following work on the decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in arene substrates remains an important contribution to the field of carbene chemistry.

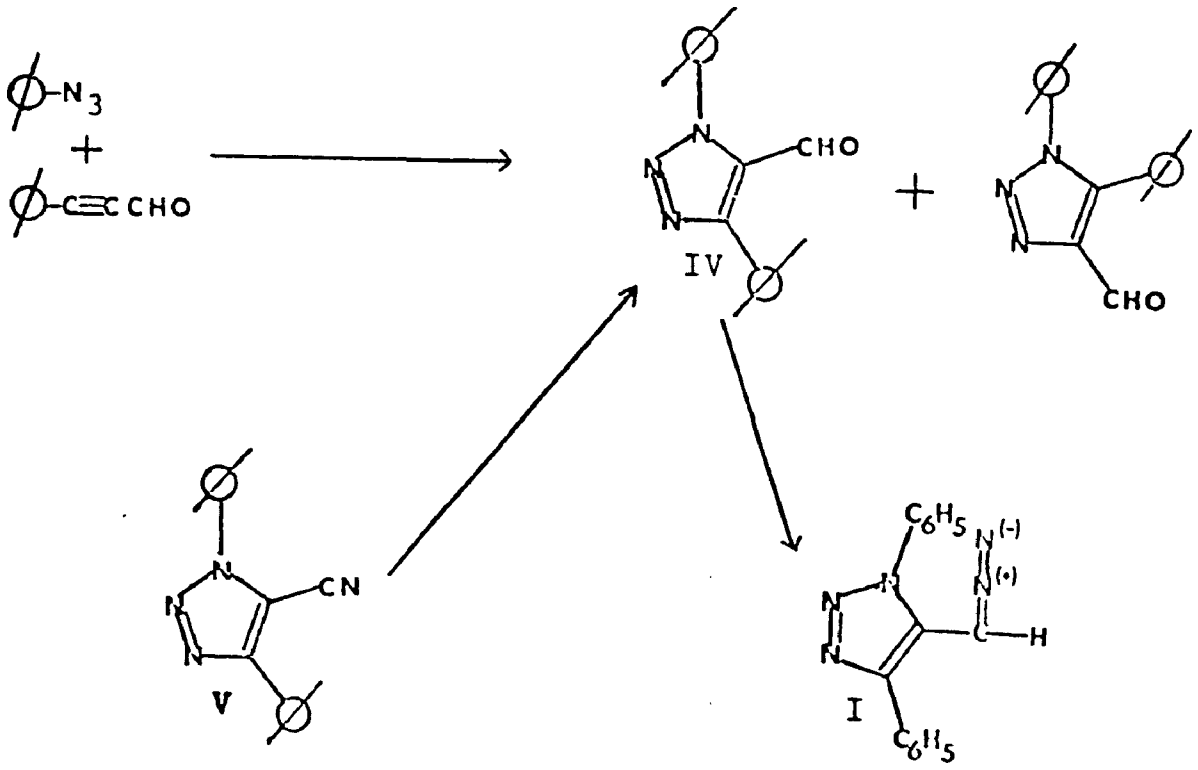
2. Statement of the Problem

In order to investigate the effects of alkyl substituents on the carbene addition to polysubstituted arene substrates a practical synthesis of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole, the desired carbene precursor, was undertaken. A comparison between the alkyl group's size, number and positioning on the arene nucleus, and the site of carbene attack was interpreted in terms of the current theories on electronic and steric interactions between carbene and substrate moieties. In addition, the isolated product norcaradienes and/or tropilidenes are related to these same factors.

3. Results and Discussion

A) 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole (I).

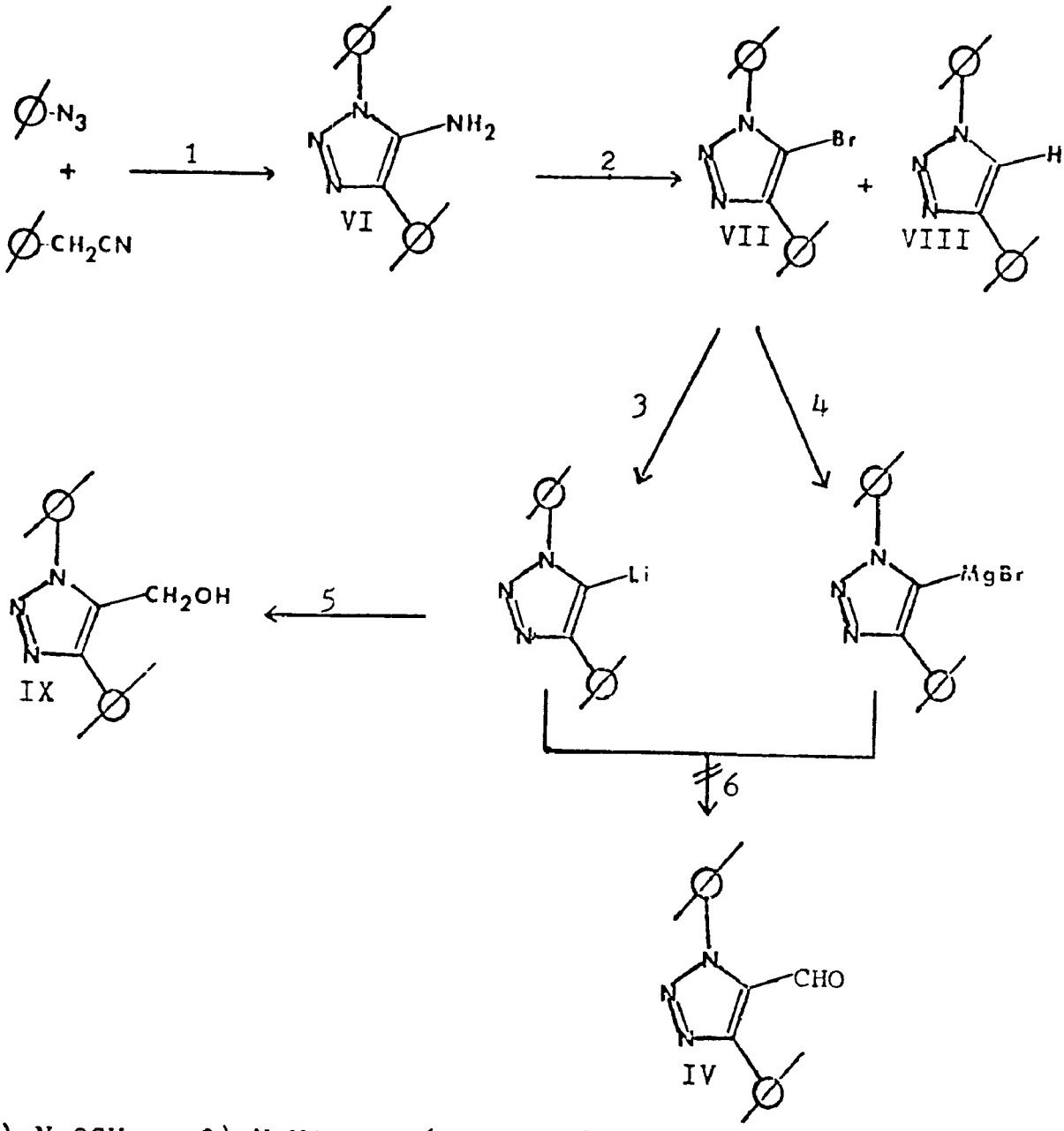
The desired starting material required for the preparation of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I) is the corresponding 1,4-diphenyl-1,2,3-triazole-5-carbonaldehyde (IV). The aldehyde IV had previously been synthesized by the 1,3-dipolar reaction of phenyl azide[29] and phenylpropargaldehyde,[30] by an established route,[31] or by Raney nickel reduction of 1,4-diphenyl-1,2,3-triazole-5-carbonitrile (V).[32] But the time consumption and overall low yields for both above methods left much to be desired.



Apparently simple 1,3-dipolar additions of phenyl azide to acetylenic compounds resulted in preferential formation of

the 4-substituted isomeric triazole instead of the desired 5-substituted triazole.[33] However, the base catalyzed 1,3-dipolar cycloaddition reactions of phenyl azide, requiring some type of activated methylene group, generally gave high yields of 5-substituted triazoles uncontaminated with the 4-isomer.[34] Attempts to prepare carboxaldehyde IV by simple chemical transformations of appropriately substituted triazoles were undertaken.

One such compound prepared by the condensation of phenyl azide with benzyl cyanide in a methanol/sodium methoxide solution gave consistently high yields of 5-amino-1,4-diphenyl-1,2,3-triazole (VI).[35] Treatment of the 5-amino compound VI with hydrogen bromide under Sandmeyer conditions yielded the corresponding 5-bromo-1,4-diphenyl-1,2,3-triazole (VII), mp 191-193°C. Under a variety of conditions the diazotization proceeded in only a 30 to 40% conversion and resulted in a mixture of starting material, 5-bromotriazole VII and a third material which proved to be identical to an authentic sample of 1,4-diphenyl-1,2,3-triazole (VIII), mp 184-185°C.[32] Conversion of the 5-bromo compound VII to either the lithium species by treatment with n-butyllithium at -78°C or the Grignard reagent by reaction with activated magnesium[36] was essentially quantitative. Subsequent treatment of these compounds with various formylating agents[37] resulted only in the formation of compound VIII and polymeric tars. The lithium species did, however, react with formaldehyde and water to yield

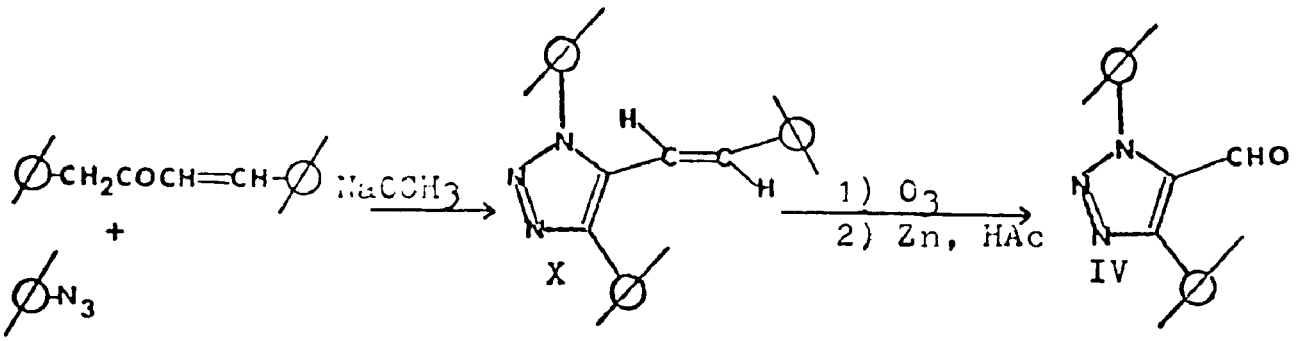


1) $NaOCH_3$; 2) $NaNO_2$, 50% HBr; 3) n-BuLi, THF, -78; 4) Mg, THF; 5) CH_2O; 6) HCO_2Et.

1,4-diphenyl-5-hydroxymethyl-1,2,3-triazole (IX), mp 167-169°C,[38] and 1,4-diphenyl-1,2,3-triazole VIII, respectively, but the low conversion of the 5-amino triazole VI to the 5-bromo triazole VII, coupled with the relative inert behavior of the lithium and magnesium species towards formylating reagents, rendered this reaction sequence unacceptable for further study. A reasonable explanation

for the lack of reactivity of these organometallic triazoles is the imposed steric hindrance at the 5-position by the 1 and 4 phenyl substituents.

The second method used for the preparation of carboxaldehyde IV started with the base condensation of benzyl styryl ketone[39] with phenyl azide. Treatment of the ketone with phenyl azide in the presence of sodium methoxide resulted in a 25% yield of 1,4-diphenyl-5-styryl-1,2,3-triazole (X), mp 193-195°C. Ozonolysis of compound V followed by a reductive workup resulted in a quantitative conversion to the carboxaldehyde IV, identical with authentic sample. However, because of the difficulties in preparing benzyl styryl ketone and the low yields of the styryl triazole X this route was also abandoned.

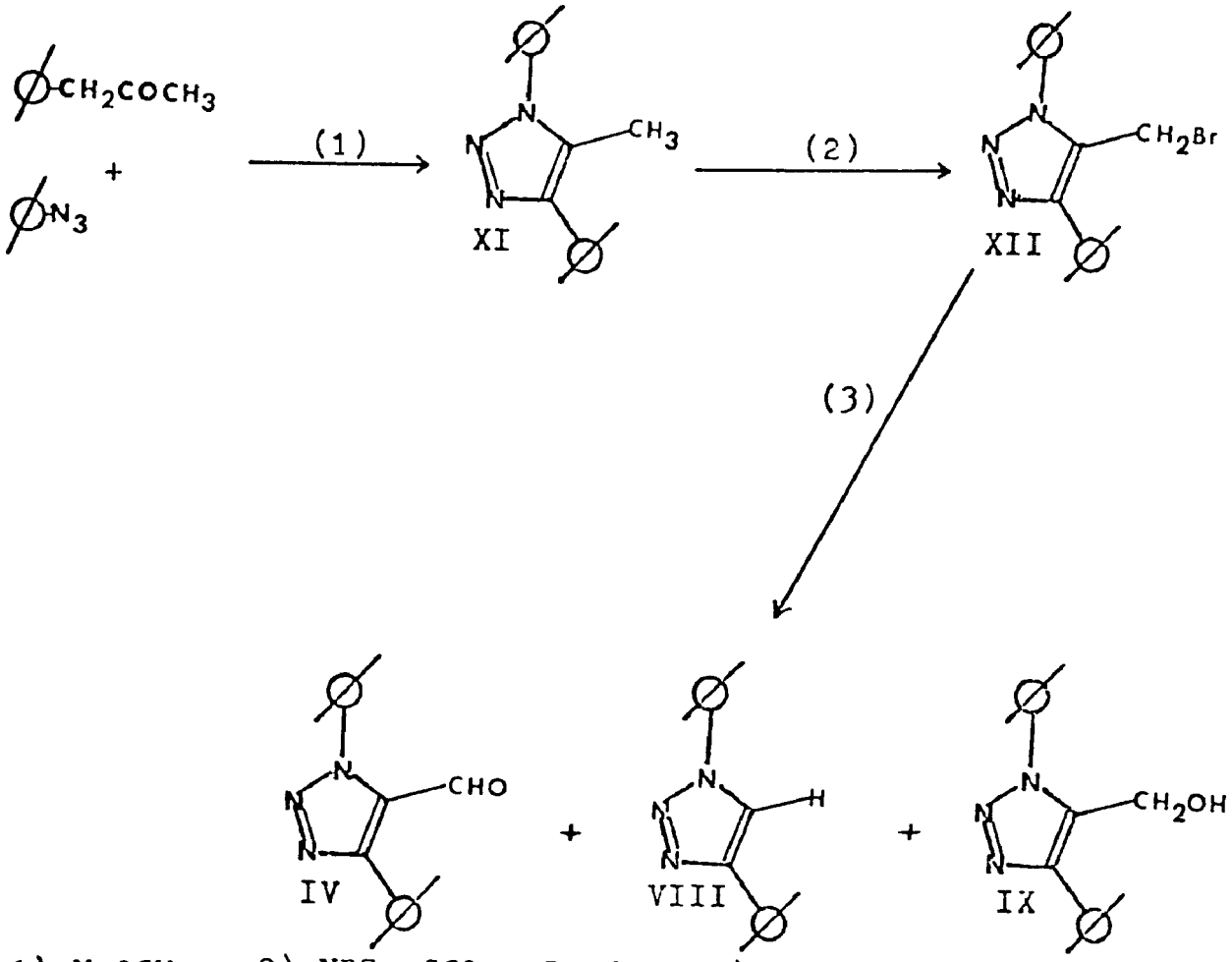


The final route attempted, which has become the standard method for the preparation of carboxaldehyde IV, involves oxidation of 5-bromomethyl-1,4-diphenyl-1,2,3-triazole (XII) by dimethyl sulfoxide (Moffatt reaction).[40] The base catalyzed condensation of phenyl azide with phenyl acetone gave consistent yields, 80% or better, of 1,4-

diphenyl-5-methyl-1,2,3-triazole (XI), mp 158-160°C.[41] Conversion to the monobromide XII, mp 94-96°C, was accomplished by free-radical bromination of the methyl triazole XI with N-bromosuccinimide (in better than 70% yield). The dimethyl sulfoxide oxidation in the presence of anhydrous $NaHCO_3$ resulted in a mixture of three new compounds, which were easily separated by column chromatography. The first material proved to be the desired carboxaldehyde IV in yields ranging from 40 to 60%. The second fraction was shown to be 1,4-diphenyl-1,2,3-triazole (VIII), believed to result from decarbonylation of the carboxaldehyde IV under the reaction conditions. Prolonged heating or high reaction temperatures caused a substantial increase in the amount of compound VIII formed. The final product, which generally amounted to 10 to 20% of the material balance (based on 100% conversion to the carboxaldehyde IV) was shown to be identical to 1,4-diphenyl-5-hydroxymethyl-1,2,3-triazole (IX), mp 168-169°C.[38]

This synthetic design gave consistent overall yields of 40% or better of the desired carboxaldehyde IV. It was now possible to stockpile larger quantities of the diazo compound I than could conveniently be generated with the previously reported preparative routes. As previously described,[26,27] treatment of the carboxaldehyde IV with anhydrous hydrazine followed by oxidation of the hydrazone with phenyliodoso acetate gave consistent yields (50%) of the carbene precursor 5-diazomethyl-1,4-diphenyl-1,2,3-

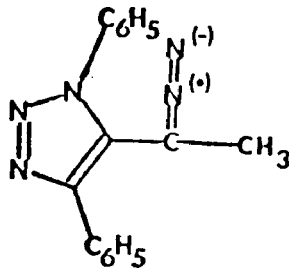
triazole (I).



1) $NaOCH_3$; 2) NBS, CCl_4, Bz_2O_2; 3) DMSO, $NaHCO_3$.

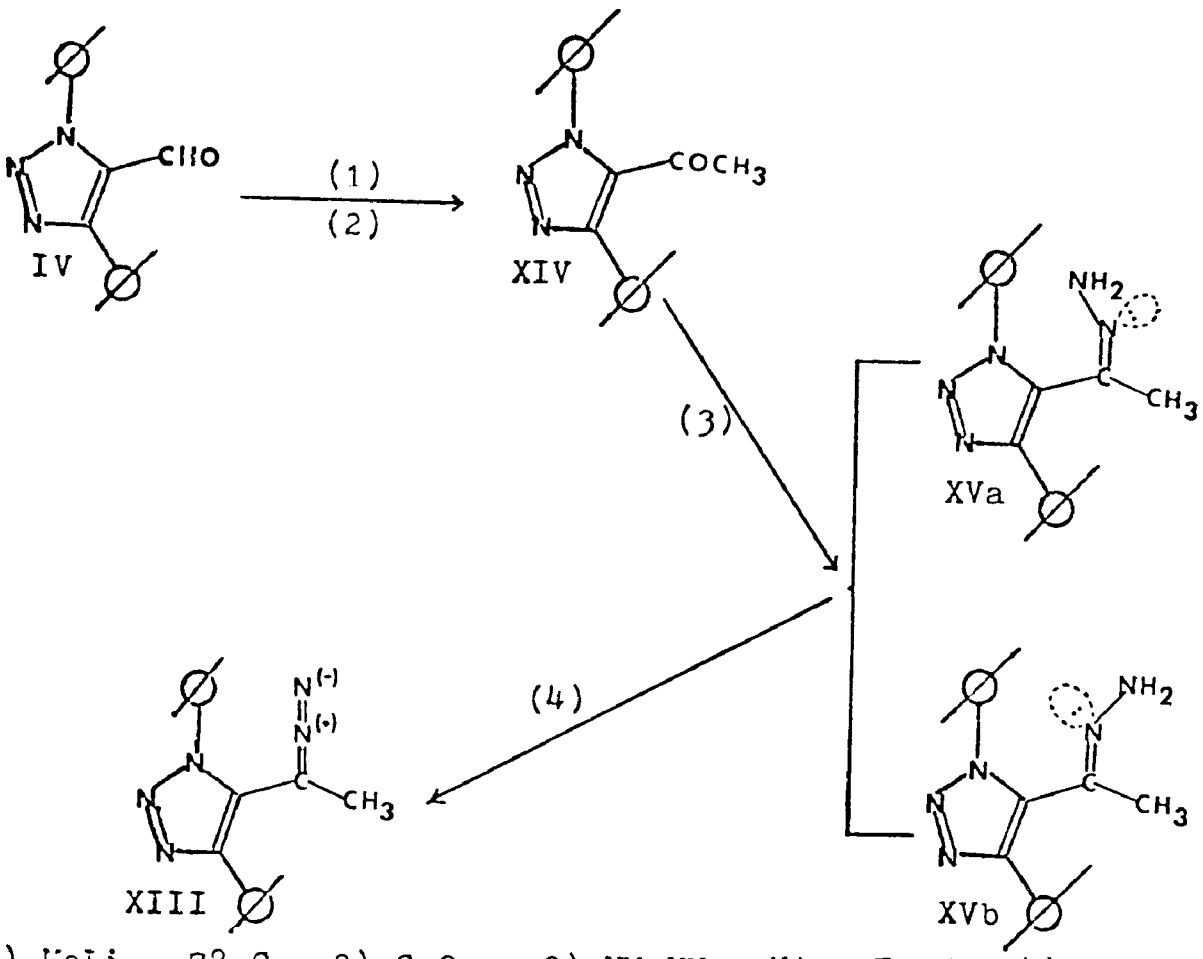
B) 5-(1-Diazoethyl)-1,4-diphenyl-1,2,3-triazole (XIII).

Because 5-diazobenzyl- and 5-diazomethyl-1,4-diphenyl-1,2,3-triazole show typical carbene behavior upon thermolysis,[24-27] the analogous 5-(1-diazoethyl)-1,4-diphenyl-1,2,3-triazole (XIII) was prepared. Applying the sequence of carbonyl compound-hydrazone-diazo compound to the preparation of diazo compound XIII seemed a logical extension, in view of the success experienced in the formation of diazo



XIII

compound I. Therefore, the carboxaldehyde IV was treated with methyllithium and the resulting alcohol, without further purification, was oxidized with Jones reagent, yielding 50% of the corresponding 5-acetyl-1,4-diphenyl-1,2,3-triazole (XIV), mp 121-121.5°C. Conversion to the hydrazone was accomplished by treatment of the ketone XIV with anhydrous hydrazine in an acidic medium. The initial PMR spectra revealed the ten hydrogen multiplets typical of the 1,4-diphenyl-1,2,3-triazole moiety centered at δ 7.50, a two proton, broad singlet, centered at 5.50 assigned to the NH_2 group of the hydrazone, and two singlets, amounting to one and a half protons each, at 1.98 and 1.72 ppm assigned to the methyl protons. Thin-layer chromatography of this oil showed two new compounds, in about a 1:1 ratio, were formed during the preparation of the hydrazone. They were separated by column chromatography and proved to be the <u>syn</u> and <u>anti</u> geometric isomers of 5-acetyl-1,4-diphenyl-1,2,3-triazole hydrazone (XVa and XVb), mp 190.5-192 and 159-164°C, respectively.[42]



1) MeLi, -78 C; 2) CrO_3; 3) NH_2NH_2, HAc, EtOH; 4) Ph-I$(OAc)_2$, CH_2Cl_2.

Treatment of the combined hydrazones with phenyliodoso acetate yielded 67.5% of the desired diazo compound XIII, mp 114-115°C.

C) The Reaction of 1,4-Diphenyl-1,2,3-triazole-5-ylcarbene with Aromatic Substrates.

In earlier studies on the chemistry of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole[24-27] it was concluded that this

compound is an "unusual clean carbene source." This was manifested in the high yields of material obtained from the interaction of the carbene with a number of given substrates, in particular the addition to aromatic rings. In addition, an addition/insertion ratio of 25:1 derived from a product analysis of decompositions conducted in mixtures of cyclohexene/cyclohexane displayed its remarkable selectivity. In cyclohexene alone, addition predominated over insertion by about 10:1. By comparison phenylcarbene[43] and carboethoxycarbene,[44] whose selectivities were found to be 1:1 and 2:1, respectively, for the same reaction, suggested that the stability of diphenyltriazolylcarbene far surpasses that observed for other carbene systems.

The preference for double over single bonds should constitute a valid measure for electrophilic carbenes. A quantitative measure of the selectivity in terms of well-defined parameters was established by decomposition of diazo compound (I) in monosubstituted benzenes. The electrophilicity was found to be intermediate between that of carboethoxycarbene[45] and carboethoxynitrene.[45] A Hammett value of $\underline{p} = -1.01$[26] indicates that diphenyltriazolylcarbene nearly matches the selectivity of carboethoxynitrene ($\underline{p} = -1.38$) with respect to cycloadditions to aromatic bonds. This observed higher selectivity confirmed the hypothesis that the mild conditions used for the generation of diphenyltriazolylcarbene greatly increases its relative stability and consequently, its selectivity.

The addition of carbenes to aromatic rings is, of course, no novelty; it was first reported by Buchner and Curtius in 1885,[46] and its synthetic utility has been fully explored.[47] Many carbenes, i.e., diaryl-, aryl- and halocarbenes are either inert or only slightly reactive towards addition reaction on aromatic substrates, whereas others react in a well-defined manner. Factors, such as, relative energetics, spin state and stability are proposed to account for these differences in reactivity towards aromatic nuclei. Little has been made of the potential to provide quantitative or even qualitative correlations for the effects that govern the carbene attack on aromatic rings. Alder and coworkers[48] reported isomer distributions for the cycloheptatrienes produced in the reaction of photolytically generated methoxycarbonylcarbene with a series of substituted benzenes. The data revealed a dominance of steric over polar effects. However, since the isomer ratios were determined by diene additions to the tropilidenes followed by pyrolysis of the adducts, they probably did not correspond to the kinetically controlled ratios.[49] Subsequently, Müller and coworkers[15] investigated the copper-catalyzed decomposition of diazomethane in substituted benzenes. A comparison between their observations and those obtained from the thermal decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole[26] are presented in Table IV. It should be noted that the decomposition of diazo compound (I) resulted in substantially higher yields of tropilidene products. The ratio of product dis-

Table IV

Effect of Aromatic Substituents on the Positional Selectivity Carbene Attack in Monosubstituted Benzenes

Substituent R	%Conversion diazomethane[a]	% Isomerization			% Conversion diazo (I)[b]	% Isomerization		
		1,2	2,3	3,4		1,2	2,3	3,4
CH_3^-	75%	21.0	43.0	36.0	90.6%	22.7	27.3	50.0
$C_2H_5^-$	68	20.0	38.0	42.0	- -	- -	- -	- -
$\underline{i}\text{-}C_3H_7^-$	64	17.0	37.0	46.0	- -	- -	- -	- -
F^-	41	23.0	25.0	52.0	72	26.5	23.5	50.0
Cl^-	50	15.0	43.0	42.0	- -	- -	- -	- -
CH_3O	75	30.0	25.0	45.0	94	26.4	38.8	34.8
$\underline{i}\text{-}C_3H_7O^-$	- -	- -	- -	- -	92	- -	- -	- -

(a) Methylene, generation from copper-catalyzed decomposition of diazomethane.[15]

(b) 1,4-Diphenyl-1,2,3-triazol-5-ylcarbene, generated by thermolysis of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole.[26]

tribution vary somewhat from strict statistical values, probably due to steric interactions between the ortho substituent and the carbene moiety.

These isolated reports indicated that both electronic and steric factors influence carbene addition to aromatic rings. The ultimate goal of the present study was to investigate the effect of size of alkyl substituents, their number and their relative positioning on the aromatic substrate, and the effects exerted on the mode of carbene addition and product type (tropilidene or norcaradiene).

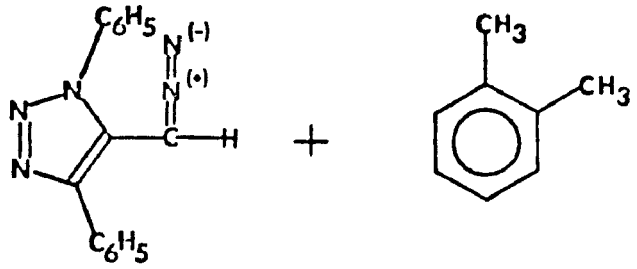
The carbene precursor, 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I), was decomposed thermally at 45-55°C in a variety of polysubstituted alkylbenzenes, selected on the basis of three criteria. The first, was the relative positioning of the alkyl groups (methyl substituents) on the aromatic ring and their effect on site selectivity of carbene attack. Secondly, the number of methyl substituents were increased to investigate their effect on product isolation. Increased steric hindrance introduced by an ever increasing number of alkyl substituents might lead to alternative reaction pathways for the carbene intermediate. Finally, the effect of alkyl substituent size and its influence on product type and site selectivity of carbene attack was explored. To this aim, the following benzene derivatives were chosen as reaction partners for the diphenyltriazolylcarbene: o-xylene, m-xylene, p-xylene, indan, mesitylene, durene, p-ethyltoluene, p-cymene, p-

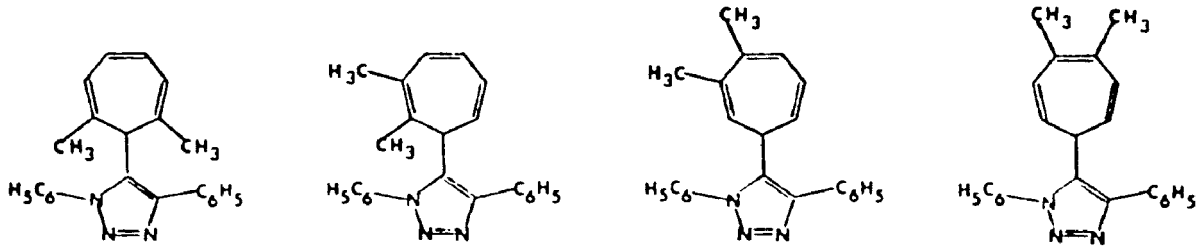
tert-butyltoluene, naphthalene, thiophene, triethylbenzene, p-diisopropylbenzene and p-di-tert-butylbenzene.

(1) Thermolysis in o-Xylene

Decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I) in o-xylene gave after appropriate workup a 73% yield of a white crystalline material, mp 160-161°C. The PMR spectrum readily permitted its identification as a single adduct of 1,4-diphenyl-1,2,3-triazol-5-ylcarbene to o-xylene. Of the four positional isomers of x-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl) cycloheptatriene (XVII-a-d) possibly formed during the decomposition, the 3,4-dimethyl structure (XVII d) was assigned to the compound, based on the PMR spectrum. The aromatic region was typical of the 1,4-diphenyl-1,2,3-triazole moiety; a two-proton multiplet shifted downfield to δ 7.70 from the large, complex multiplet centered at 7.32 ppm. Of the four olefinic hydrogens, two were centered at δ 5.81 a doublet (J = 9.0 cps) and assigned to the internal olefinic hydrogens, the other two hydrogens were centered at 4.61 ppm a doublet of doublets ($J_{1,2}$ = 9.0 cps and $J_{1,7}$ = 5.5 cps) and was assigned to the terminal olefinic hydrogens.[51] The 7-hydrogen of compound XVIId appeared as a triplet centered at 2.82 ppm ($J_{7,1}$ = 5.5 cps), shifted downfield by the adjacent triazolyl ring and the six methyl hydrogens appeared as a singlet at 1.82 ppm. The remarkable symmetry

of the PMR spectrum reinforced the structural assignment of cycloheptatriene (XVIId) as the adduct formed from the decomposition of diazo compound (I) in o-xylene.





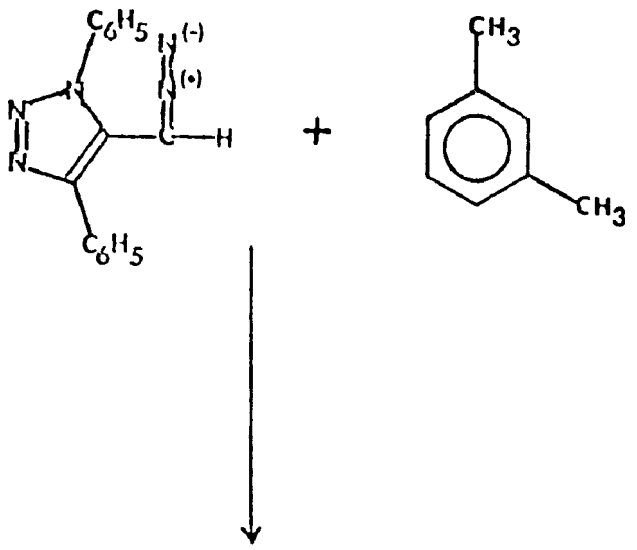
XVIIa XVIIb XVIIc XVIId

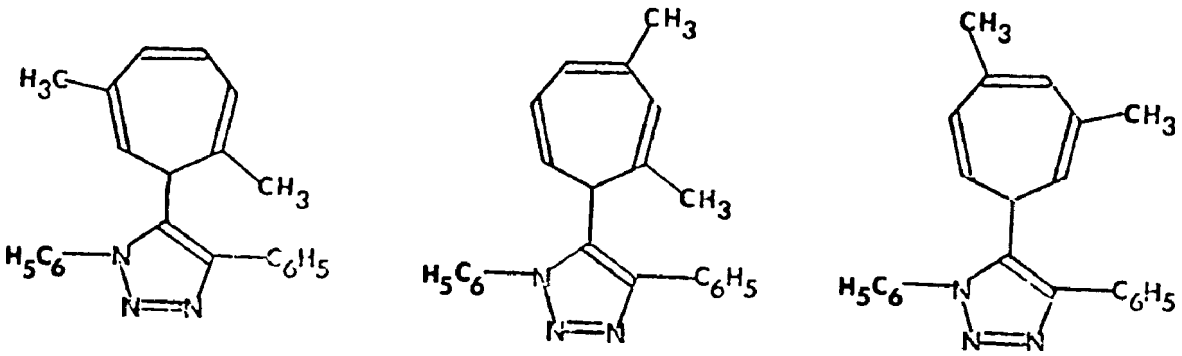
(2) Thermolysis in m-Xylene

Decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I) in m-xylene afforded a crystalline adduct in 58% yield. The PMR spectrum readily permitted its identi-

fication as a single adduct of the three possible positional isomers of x-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XVIIIa-c) formed during the decomposition. The 2,4-dimethyl structure (XVIIIc) was assigned to the compound, based on the PMR spectrum. The presence of the 1,4-diphenyl-1,2,3-triazole group was established by the characteristic two-proton and eight-proton multiplets centered at δ 7.71 and 7.39 ppm, respectively. The four olefinic hydrogens appeared at δ 6.13, a singlet for the hydrogen between the two methyl groups, a doublet centered at 5.80 for the other internal olefinic hydrogen and two multiplets centered at 4.67 and 4.37 ppm corresponding to the two terminal olefinic hydrogens. The 7-hydrogen of compound XVIIIc appeared as a triplet centered at δ 2.96 shifted downfield by the adjacent triazole ring and the two methyl groups appeared as singlets at 1.93 and 1.75 ppm, respectively.

The two other tropilidene isomers XVIIIa and XVIIIb were isolated from the mother liquor and purified by column chromatography on Florisil. The PMR spectrum, however, did not allow identification of the two adducts due to signal overlap in the vinylic region. The four methyl singlets which appeared at δ 1.518, 1.638, 1.768 and 1.844 ppm indicate that the remaining isomeric tropilidenes are present in a 60:40 ratio, however all attempts to separate these isomers failed.



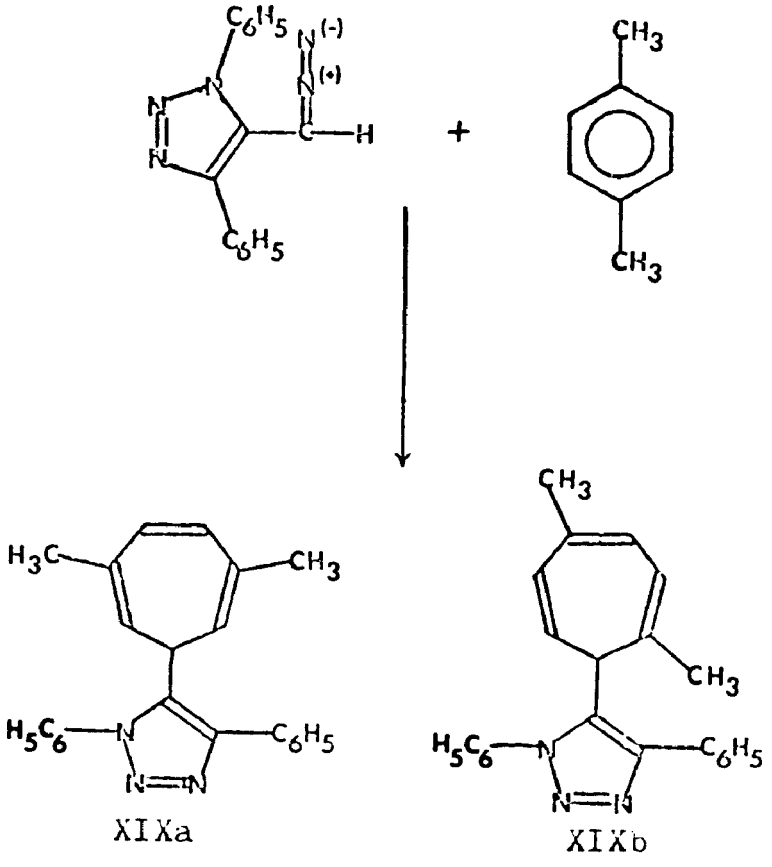


XVIIIa XVIIIb XVIIIc

(3) Thermolysis in p-Xylene.

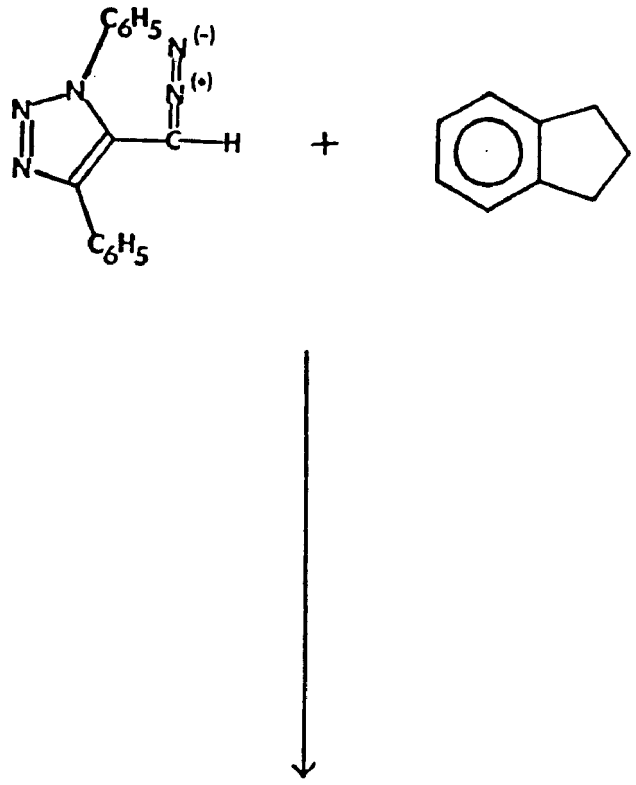
When diazo compound I was either thermolyzed or photolyzed in p-xylene, a 75% yield of the substituted tropilidene was isolated, derived from addition of 1,4-diphenyl-1,2,3-triazol-5-ylcarbene to the aromatic ring. The structure proof rests on spectral identification. On the basis of the PMR spectrum, compound (XIXb) was identified as 1,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cyclohepta-

triene, mp 171-173°C. The ten aromatic protons formed the two characteristic multiplets at δ 7.75 and 7.40 ppm. Three of the four olefinic hydrogens centered at δ 6.05 (J = 6 cps), 5.91 (J = 9 cps) and 5.64 ppm (J = 9 cps), respectively, were assigned to the internal olefinic hydrogens. The fourth vinylic hydrogen, assigned to the terminal olefinic hydrogen appeared at δ 4.81 ppm as a doublet of doublets ($J_{5,6}$ = 6 cps and $J_{6,7}$ = 6 cps). The 7-hydrogen of compound XIXb appeared as a doublet centered at δ 3.17 shifted downfield by the adjacent triazole ring and the two methyl groups appeared as singlets at 1.83 and 1.78 ppm, respectively.



(4) Thermolysis in Indan.

Indan proved to be a very reluctant reaction partner for 1,4-diphenyl-1,2,3-triazol-5-ylcarbene. The product mixture from decomposition of diazo compound I contained many components, from which only one, in about 15% yield, could be isolated. Of the four positional isomers of X,Y-trimethylene-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XXa-d) possibly formed during the thermal decomposition, the 3,4-trimethylene structure XXd was assigned to the compound, based on the PMR spectrum. The ten aromatic hydrogens of the diphenyltriazole moiety formed two characteristic multiplets centered at δ 7.80 and 7.45 ppm, two and eight protons respectively. Of the four olefinic hydrogens, two were centered at δ 6.21 a doublet (J = 9.0 cps) and assigned to the internal olefinic hydrogens; the other, terminally olefinic hydrogens were centered at 5.27 ppm and appeared as a doublet of doublets ($J_{1,2}$ = 9.0 cps and $J_{1,7}$ = 5.0 cps). The 7-hydrogen appeared as a triplet centered at δ 3.38 ($J_{7,1}$ = 5.0 cps) shifted downfield by the adjacent triazolyl ring and the six methylene hydrogens appeared as a triplet (four hydrogens) centered at 2.65 and a quartet (two hydrogens) centered at 2.00 ppm. The remarkable symmetry of the PMR spectrum reinforced the structural assignment of cycloheptatriene XXd as the adduct isolated from decomposition of diazo compound I in indan.

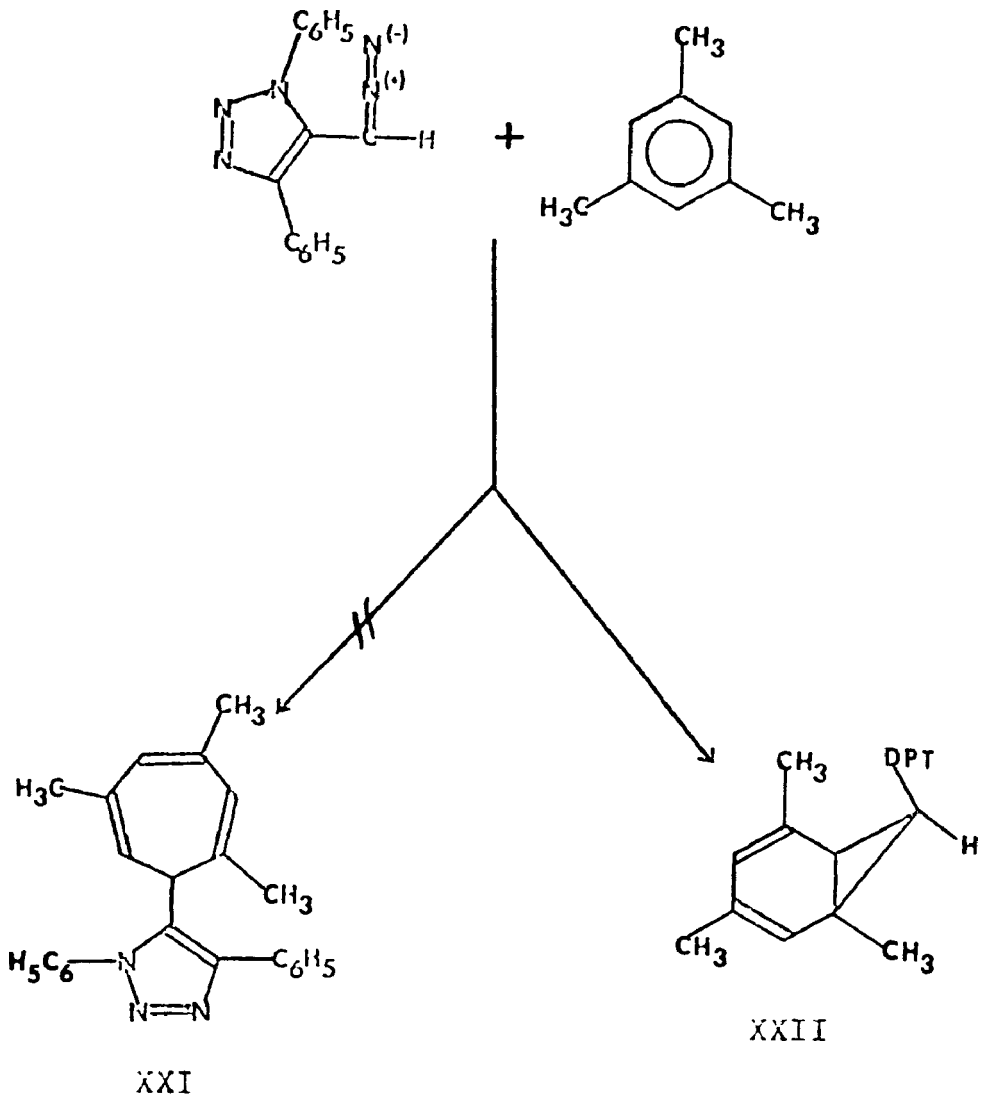


XXa XXb XXc XXd

(5) Thermolysis in Mesitylene.

The reaction of 1,4-diphenyl-1,2,3-triazol-5-ylcarbene with mesitylene has been described elsewhere.[27] The PMR spectrum of the initial material isolated indicates that the tropilidene XXI, which had been expected in analogy to the adducts previously described, had not been formed.

Instead, 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (XXII) was assigned the structure.



XXI XXII

Conclusive structural assignment of norcaradiene XXII was obtained from the ^{13}CMR spectrum (Figure 1). Assignments were made on the basis of relative signal intensities and with the aid of coupled spectra. The ^{13}CMR spectrum clearly indicates that six alkyl-type carbon atoms are present. The three methyl carbons appeared as quartets at

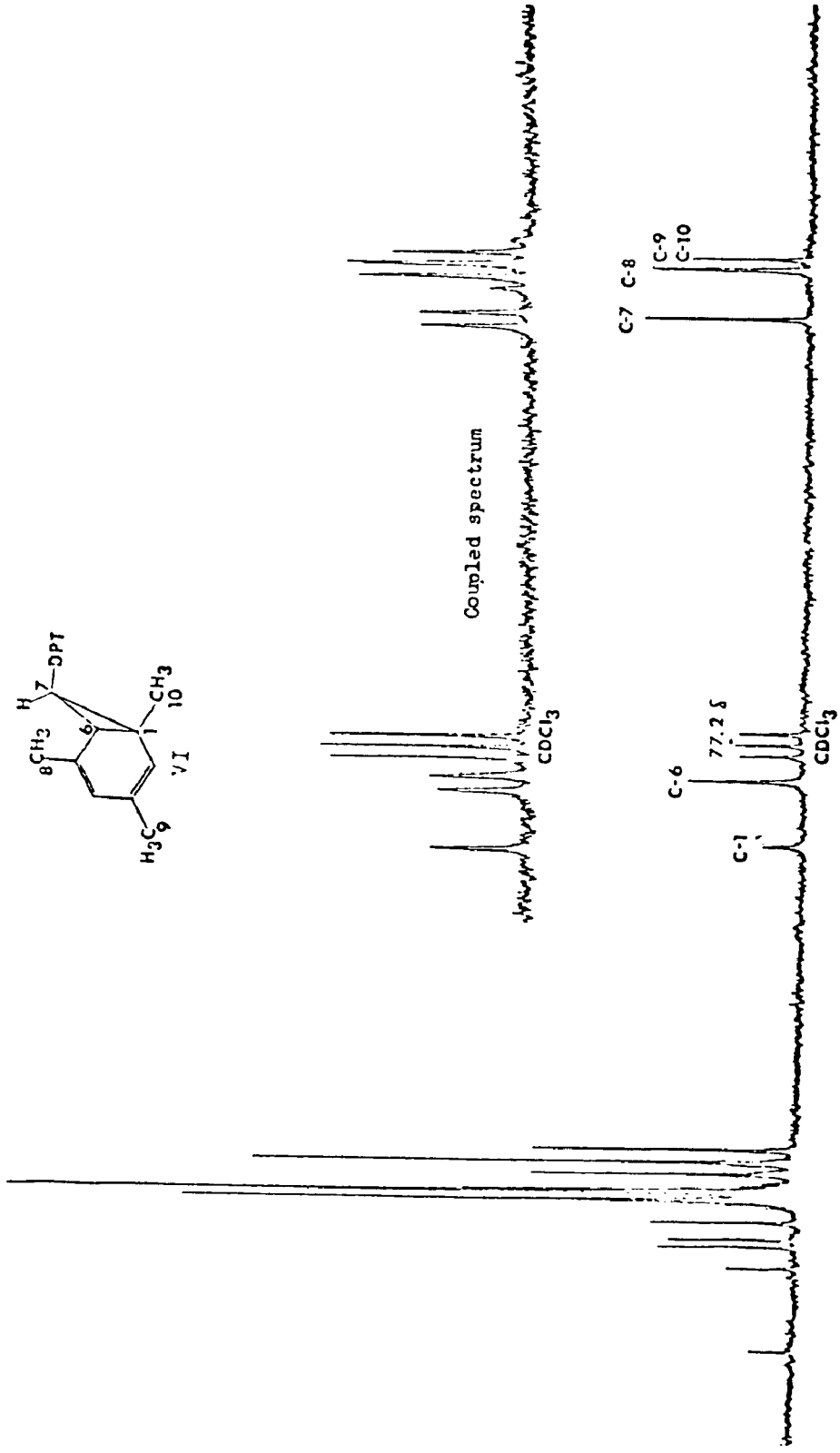


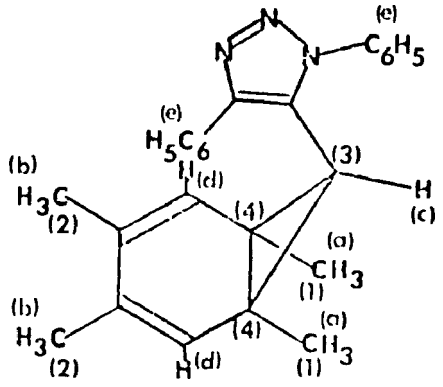
Figure 1. ^{13}CMR spectrum of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene.

δ 21.809, 22.962 and 22.964 ppm, respectively. The C_7-cyclopropyl carbon atom appeared as a doublet centered at δ 28.604 ppm. The C_1- and C_6-cyclopropyl carbon atoms appeared at δ 81.326 and 88.789 ppm as a doublet and singlet, respectively. The extremely high values for the C_1- and C_6-cyclopropyl carbon atoms are explained in fuller detail in Chapter II (page 119). By comparison, all possible thirteen tropilidene isomers would possess only four alkyl carbon atoms. Therefore, the above ^{13}CMR spectrum coupled with the PMR spectrum[27] illustrates compound XXII as the isolated product from decomposition of diazo compound I in mesitylene.

(6) Thermolysis in Durene.

Decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in a durene/dichloromethane solution afforded the adduct of carbene and substrate in 56% yield. The major isomer was separated by crystallization and identified as 1,3,4,6-tetramethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-norcaradiene (XXIIIa), based upon PMR and ^{13}CMR spectra. The observed symmetry reinforced the assignment of norcaradiene XXIIIa as the major isomer formed from decomposition of diazo compound I in durene.

The minor adduct, approximately 11% yield, proved to be the isomeric norcaradiene XXIIIb based on the PMR spectrum. The four methyl groups appeared as singlets at δ 1.63, 1.36, 1.30 and 0.99 ppm. The C_7-H cyclopropyl hydro-



PMR spectrum (δ relative to TMS)

(a)	1.38	singlet	6 hydrogens
(b)	1.46	singlet	6 hydrogens
(c)	2.87	singlet	1 hydrogen
(d)	4.72	singlet	2 hydrogens
(e)	7.51	multiplet	10 hydrogens

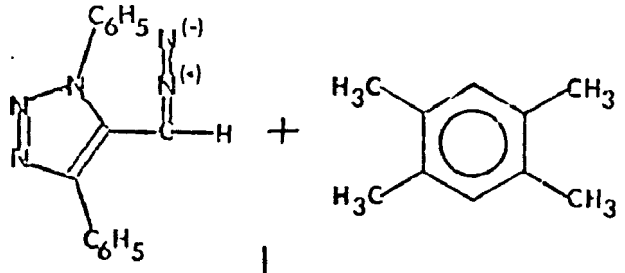
^{13}CMR spectrum (δ relative to TMS)

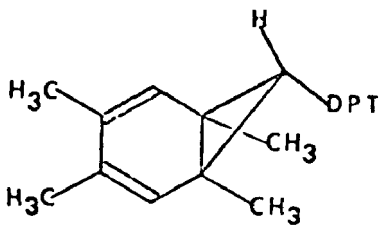
(1)	19.200	quartet	2 carbon atoms
(2)	22.719	quartet	2 carbon atoms
(3)	27.269	doublet	1 carbon atom
(4)	63.368	singlet	2 carbon atoms

aromatic and vinyls = 124.523 to 147.638

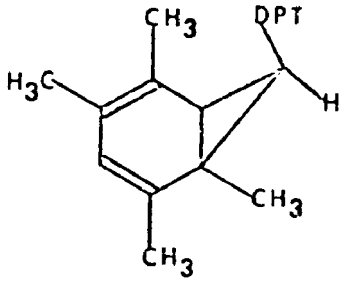
gen appeared as a doublet centered at δ 2.10 ($J_{7,6}$ = 6 cps) and the C_6-H cyclopropyl hydrogen appeared as a doublet

centered at 2.49 ppm. The lone olefinic hydrogen appeared at δ 5.57 as a singlet and finally, the presence of the intact 1,4-diphenyl-1,2,3-triazole group was established by the characteristic aromatic signals, a two-proton multiplet centered at 7.80 and an eight-proton multiplet centered at 7.50 ppm.





XXIIIa



XXIIIb

(7) Thermolysis in p-Ethyltoluene.

Decomposition of diazo compound (I) in p-ethyltoluene gave after appropriate workup a 68% yield of a white crys-

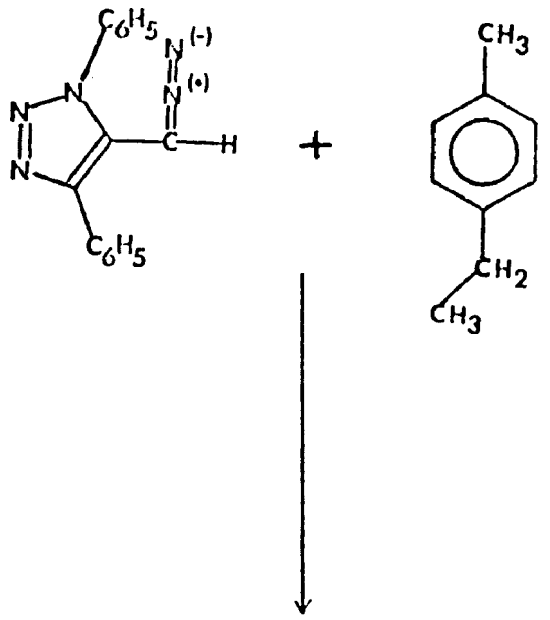
talline material, mp 129-130°C. The PMR spectrum revealed two isomeric tropilidenes were formed, which could not be separated by conventional techniques. PMR and decoupled spectra of the mixed material allowed identification of the isolated adducts. Of the three positional isomers (XXIV-a-c) possibly formed during the decomposition of diazo compound (I) in p-ethyltoluene, compound XXIVb and XXIVc were assigned the structures based on the PMR spectrum. The two isomers were present in approximately a 1:1 ratio. Compound XXIVb was assigned the 1-methyl-4-ethyl structure based on the following PMR spectrum. The spectrum contained the characteristic ten hydrogen multiplets of the diphenyltriazole moiety in addition to a singlet at δ 1.71 assigned to the methyl group and a broad quartet centered at 2.12 and broad triplet centered at 0.92 ppm assigned to the ethyl group. The three internal olefinic hydrogens appeared at δ 5.90 as a doublet ($J_{2,3}$ = 8 cps), 5.62 as a doublet ($J_{3,2}$ = 8 cps) and at 5.72 ppm another doublet ($J_{5,6}$ = 7 cps). The remaining terminal olefinic hydrogen appeared as a doublet of doublets centered at δ 4.75 ppm ($J_{6,5}$ = 7 cps and $J_{6,7}$ = 6 cps). The assignment of the 1-methyl-4-ethyl isomer (XXIVb) was further supported by a comparison of the terminal olefinic hydrogen of compounds XVIIIb and XIXb. In both compounds the terminally olefinic hydrogens appeared as a doublet of doublets centered at δ 4.80 and 4.81 ppm, respectively. The 7-hydrogen of compound XXIVb appeared as a doublet centered at δ 3.07 ppm

shifted downfield by the adjacent triazole ring.

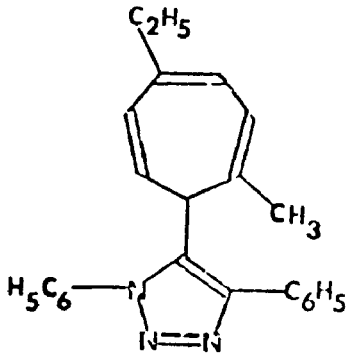
The other isomeric tropilidene (XXIVc) was assigned the 1-ethyl-4-methyl structure based on the PMR spectrum. The diphenyltriazole moiety appeared as two multiplets centered at δ 7.55 and the methyl and ethyl groups appeared at 1.71 a singlet, 2.12 a broad quartet and 0.92 ppm a broad triplet, respectively. The three internal olefinic hydrogens appeared as three doublets centered at δ 6.05 ($J_{3,2}$ = 7 cps), 5.82 ($J_{2,3}$ = 7 cps) and 5.40 ppm ($J_{5,6}$ = 8 cps), respectively. The 7-hydrogen of compound XXIVc appeared as a doublet centered at δ 2.86 ppm shifted downfield by the adjacent triazole ring. The remaining terminal olefinic hydrogen appeared as a broad triplet centered at δ 3.91 ppm, a rather bizarre value, even for a terminally olefinic hydrogen. This unusual observation is dealt with in Chapter II (p. 133).

(8) Thermolysis in 4-tert-Butyltoluene:

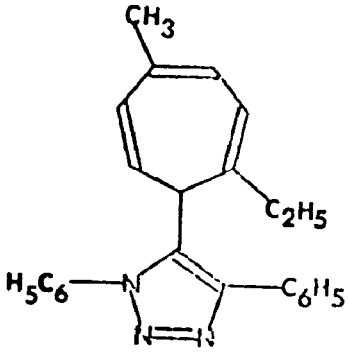
When diazo compound (I) was thermolyzed in 4-tert-butyltoluene, a 75% yield of the substituted tropilidene was isolated, derived from the addition of 1,4-diphenyl-1,2,3-triazol-5-ylcarbene to the aromatic ring. The structure proof rests on spectral identification. On the basis of the PMR spectrum, compound XXVc was identified as 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene, mp 154-155.5°C, the sole product isolated from the decompcsition. The ten aromatic protons of the diphenyl-



XXIVa



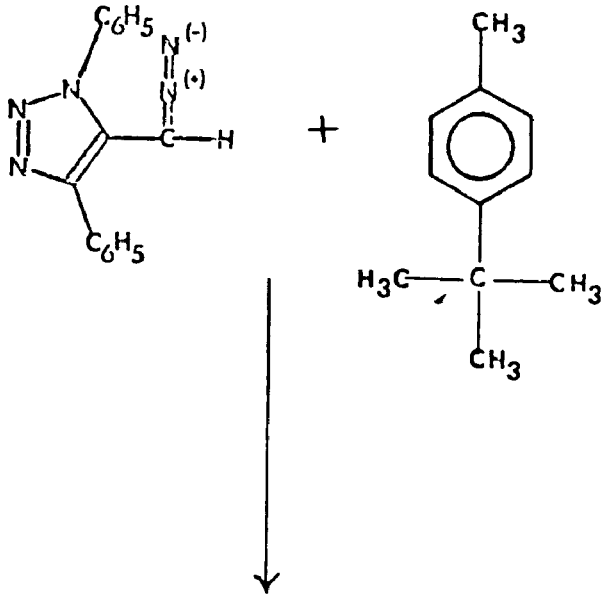
XXIVb

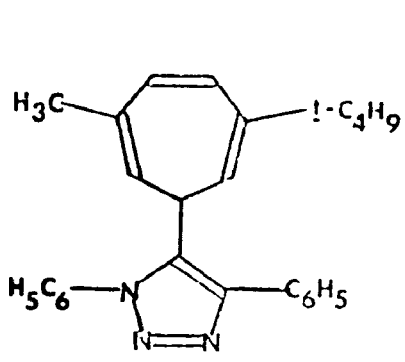


XXIVc

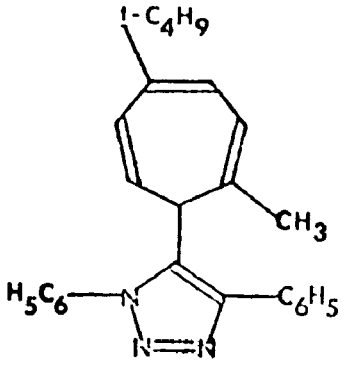
triazole moiety formed two characteristic multiplets centered at δ 7.65 and 7.30 ppm. The three internal olefinic hydrogens appeared as doublets centered at δ 5.98 ($J_{3,2}$ = 8 cps), 5.66 ($J_{5,6}$ = 8.5 cps) and 5.46 ppm ($J_{2,3}$ = 8 cps). The methine 7-hydrogen of compound XXVc appeared as a doublet centered at δ 2.87 ($J_{7,6}$ = 7 cps) shifted downfield by the triazole moiety, and the methyl and tert-butyl groups appeared as singlets at 1.55 and 0.92 ppm, respectively.

The terminal olefinic hydrogen appeared as a triplet centered at δ 4.07 ppm. Comparison with compound XXIVc whose terminal olefinic hydrogen also appeared as a triplet centered at δ 3.91 ppm gave further credence to the structural assignment of compound XXVc as the 1-tert-butyl-4-methyl isomer. Again, the discussion of the unusual chemical shift observed for the terminal olefinic hydrogen of compound XXVc is differed to Chapter II, p. 133.

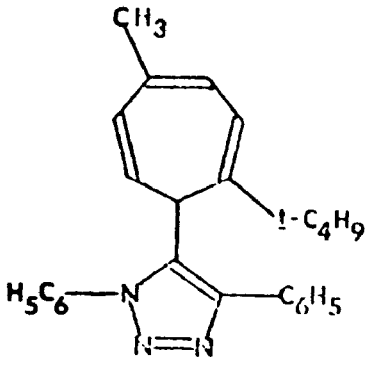




XXVa



XXVb

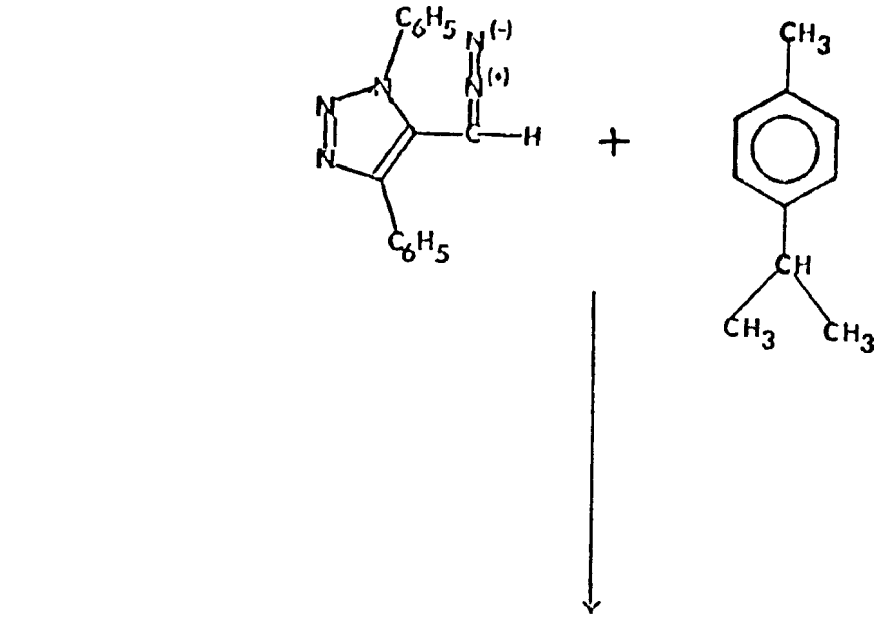


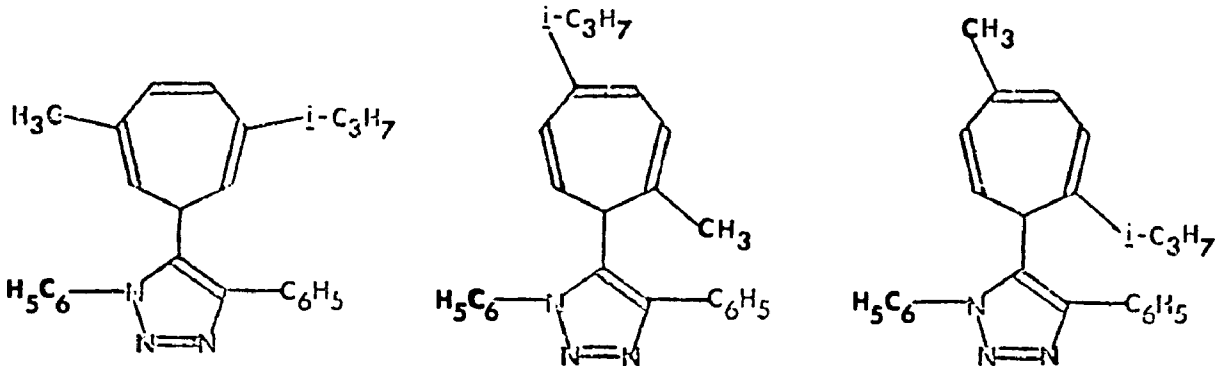
XXVc

(9) Thermolysis in p-Cymene:

Decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in p-cymene afforded the adduct of carbene and substrate in 87% yield. On the basis of the PMR spectrum, compound XXVIb was identified as 1-methyl-4-isopropyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (39% yield). The ten aromatic protons formed the two characteristic multiplets centered at δ 7.83 and 7.40 ppm. Three of the four olefinic hydrogens centered at δ 5.75 a doublet (J = 8 cps) and 5.68 ppm two olefinic hydrogens (J = 8 cps) respectively were assigned to the internal olefinic hydrogens. The fourth vinylic hydrogen, assigned to the terminal olefinic hydrogen by comparison to compounds XIXb, XVIIIb and XXIVb, appeared at δ 4.63 ppm as a doublet of doublets ($J_{5,6}$ = 8 cps and $J_{6,7}$ = 6.5 cps). The 7-hydrogen of compound XXVIb appeared as a doublet centered at δ 3.05 shifted downfield by the adjacent triazole ring and the methyl group appeared as a singlet at 1.70 ppm. The isopropyl methine appeared as a complex multiplet centered at δ 2.25 and the isopropyl methyls appeared as two doublets centered at 0.92 and 0.90 ppm, respectively.

A second isomeric tropilidene XXVIc was isolated in 48% yield and was purified by preparative thin-layer chromatography. Based on the PMR spectrum and with the aid of decoupled spectra, compound XXVIc was assigned the 1-isopropyl-4-methyl structure. The diphenyltriazole moiety appeared as two multiplets centered at δ 7.68 and 7.45 ppm,





XXVIa XXVIb XXVIc

respectively. The three internal olefinic hydrogens appeared as doublets centered at δ 5.77 ($J_{3,2}$ = 8.4 cps), 5.33 ($J_{2,3}$ = 8.4 cps) and 5.12 ppm ($J_{5,6}$ = 6.5 cps). The terminal olefinic hydrogen appeared as a triplet centered at δ 3.59 ppm ($J_{6,5}$ = 6.5 cps and $J_{6,7}$ = 8 cps). This unusual chemical shift is similar to the observations made on the p-tert-butyl toluene and p-ethyltoluene adducts and is dealt with in fuller detail in Chapter II (p. 133). The 7-hydrogen of compound XXVIc appeared as a doublet centered

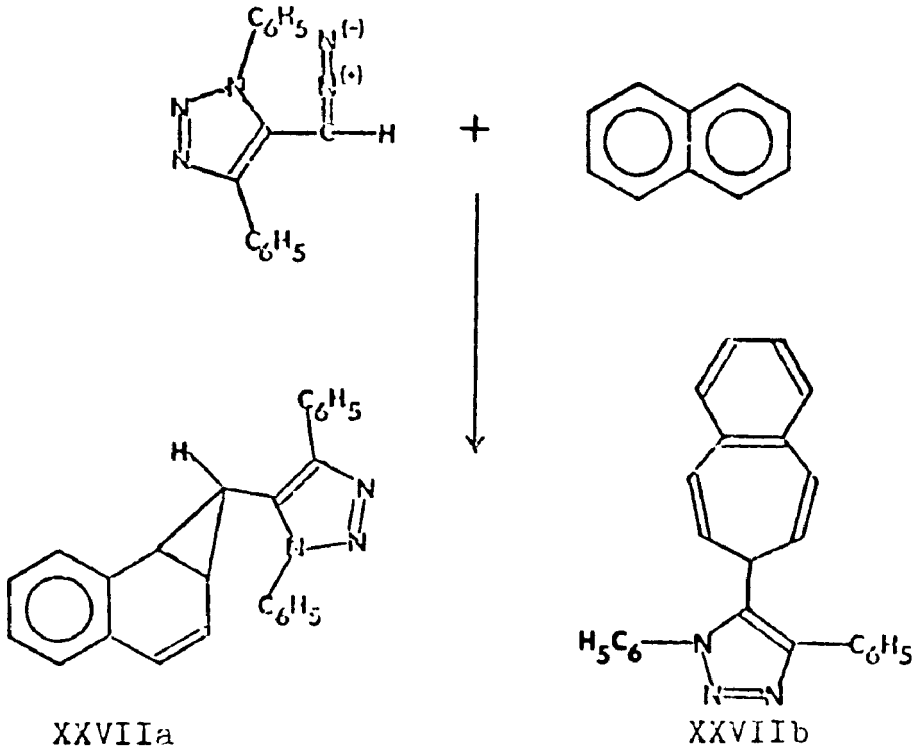
at δ 3.13 ppm ($J_{6,7}$ = 8 cps) shifted downfield by the adjacent triazole ring. The methyl group appeared as a singlet at δ 1.62, the methine hydrogen of the isopropyl group appeared as a multiplet centered at 1.77 and the isopropyl methyl groups appeared as two doublets (J = 6.2 cps) centered at 0.80 and 0.70 ppm.

(10) Thermolysis in Naphthalene.

Decomposition of diazo compound I in a naphthalene/dichloromethane solution gave, after appropriate workup, a 91.5% yield of isomeric adducts. The PMR spectrum readily permitted the identification of compounds XXVIIa and XXVIIb as the adducts of 1,4-diphenyl-1,2,3-triazol-5-ylcarbene to naphthalene. The 5,6-benzonorcaradiene structure XXVIIa which was separated from the mixture by crystallization in 58.5% yield was assigned to the compound based on the PMR spectrum. The aromatic region was typical of the 1,4-diphenyl-1,2,3-triazole moiety; a two-proton multiplet shifted downfield to δ 7.83 from the large complex eight-proton multiplet centered at 7.50 ppm. The benzo-ring appeared as a multiplet centered at δ 7.06, and the two olefinic hydrogens appeared as a doublet centered at 6.29 ($J_{3,4}$ = 9.5 cps) for the internal olefinic hydrogen and a doublet of doublets centered at 5.90 ppm ($J_{4,3}$ = 9.5 cps and $J_{4,2}$ = 5.5 cps) for the terminally vinylic hydrogen. The three cyclopropyl hydrogens appeared as a quartet centered at δ 2.26 for the C_1-hydrogen, a multiplet centered

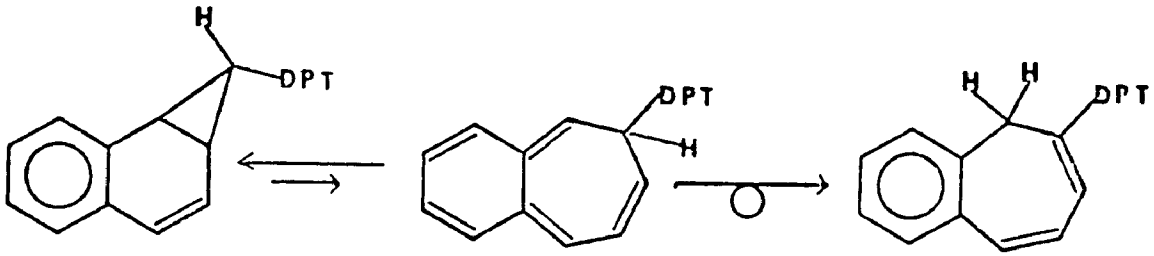
at 1.75 for the C_6-hydrogen and a triplet centered at 1.35 ppm assigned to the C_7-hydrogen.

The 3,4-benzocycloheptatriene structure XXVIIb, obtained in 41.5% yield, was established based on the following PMR spectrum. The ten aromatic hydrogens of the diphenyltriazole group formed the two characteristic multiplets centered at δ 7.90 and 7.40 ppm, two and eight protons respectively. The four olefinic hydrogens appeared as a doublet centered at δ 5.75, the internal two olefinic hydrogens and a doublet of doublets centered at 4.85 ppm assigned to the terminally vinylic hydrogens. The 7-hydrogen appeared as a triplet centered at δ 2.90 shifted downfield by the adjacent triazolyl ring, and the benzo-hydrogens appeared as a multiplet centered at 7.05 ppm. Again, the prevailing symmetry of the adduct XXVIIb aided in the assignment of the structure.



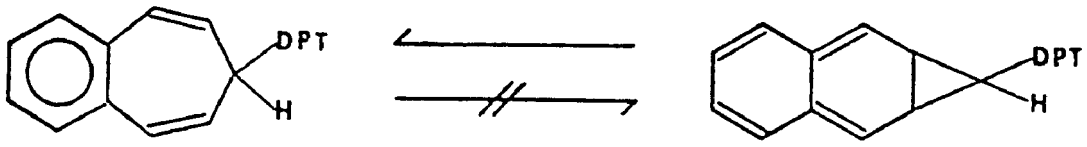
XXVIIa XXVIIb

The isolation of adduct XXVIIa results from added stabilization imparted into the norcaradiene system by incorporation of one of the double bonds in a benzene ring system. The subsequent transition into the cycloheptatriene derivative XXVIIc involves dearomatization of the benzene ring. Consequently, the isomerization takes place only at elevated temperatures, and on rearomatization XXVIIc would most likely be converted into XXVIId by a hydrogen shift.[52]



XXVIIa XXVIIc XXVIId

Likewise, if one of the double bonds of the tropilidene adduct belongs to a benzene ring, only the triene form is stable. Thus tropilidene XXVIIb would not be expected to enter into a dynamic equilibrium with its isomeric norcaradiene derivative XXVIIe.[53]



XXVIIb XXVIIe

The formation of a quinoid ring from a benzoid ring is a

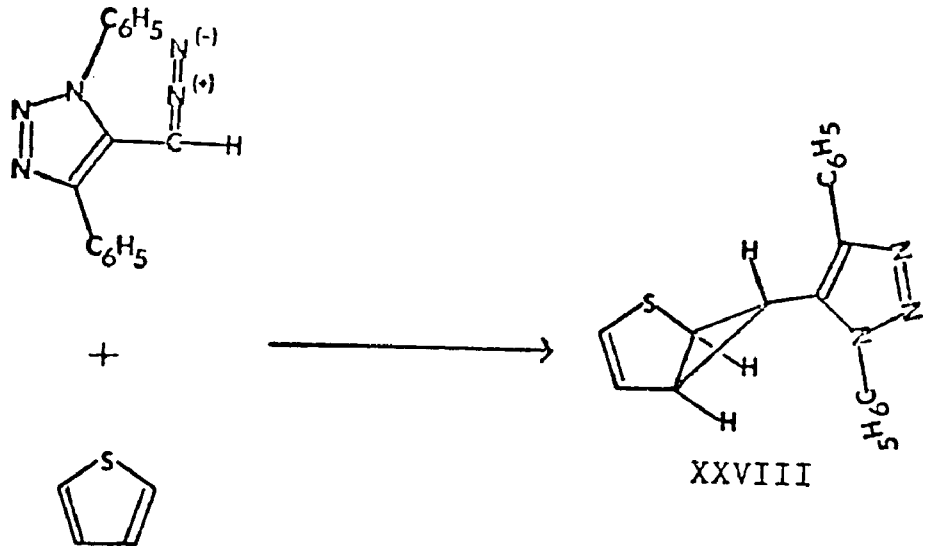
costly energy process and compounds of the type XXVIIe, the initial adduct formed during the decomposition of diazo compound I in naphthalene, spontaneously isomerize to the benzocycloheptatriene XXVIIb.[54]

A coupling constant of 4.7 cps for the C_1-C_7- and C_7-C_6-hydrogens clearly demonstrates a trans relationship.[66] This trans relationship between the cyclopropyl hydrogens indicates that the large diphenyltriazole moiety has added in an anti manner with respect to the naphthalene ring. The anti selectivity shown by 1,4-diphenyl-1,2,3-triazol-5-ylcarbene towards aromatic nuclei indicates that the principles which govern the addition of carbenes to olefinic substrates does not hold for the addition of carbenes to aromatic substrates.[55]

(11) Thermolysis in Thiophene:

Decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I) in redistilled thiophene afforded a crystalline adduct in 55% yield. The PMR spectrum readily permitted its identification as a single adduct, assigned to the cyclopropyl thioline structure XXVIII based on the PMR spectrum. The presence of the 1,4-diphenyl-1,2,3-triazole group was established by the characteristic two-proton and eight-proton multiplets centered at δ 7.75 and 7.43 ppm, respectively. The two vinylic hydrogens of the thiophene ring appeared as a doublet centered at δ 6.00 ($J_{3,4}$ = 6.0 cps) and a doublet of doublets centered at 5.58 ppm ($J_{4,3}$

= 6.0 cps and $J_{4,5}$ = 3.0 cps). The three cyclopropyl hydrogens appeared as a doublet of doublets centered at δ 2.70 ($J_{1,6}$ = 3.0 cps and $J_{1,5}$ = 8.0 cps) assigned the C_1-hydrogen, a multiplet centered at 2.34 for the C_5-hydrogen and a triplet centered at 1.62 ppm ($J_{6,1}$ = $J_{6,5}$ = 3.0 cps) assigned to the C_6-hydrogen.



XXVIII

Coupling constants of 3.0 cps for the C_1-C_6- and C_6-C_5-hydrogens clearly demonstrates a <u>trans</u> relationship.[56] This <u>trans</u> relationship between the cyclopropyl hydrogens indicates that the large diphenyltriazole moiety has added in an <u>anti</u> manner with respect to the thiophene ring. Like the naphthalene case, XXVIIa, the <u>anti</u>-steriochemical selectivity shown by 1,4-diphenyl-1,2,3-triazol-5-ylcarbene towards aromatic nuclei indicates that the principles which govern the addition of carbene to olefinic substrates does not hold for the addition of carbenes to aromatic

substrates, at least in this case and that of ethyl diazoacetate.[55] This relationship will become increasingly important to the interpretations set forth in the following chapters.

(12) Thermolysis in p-Diisopropylbenzene:

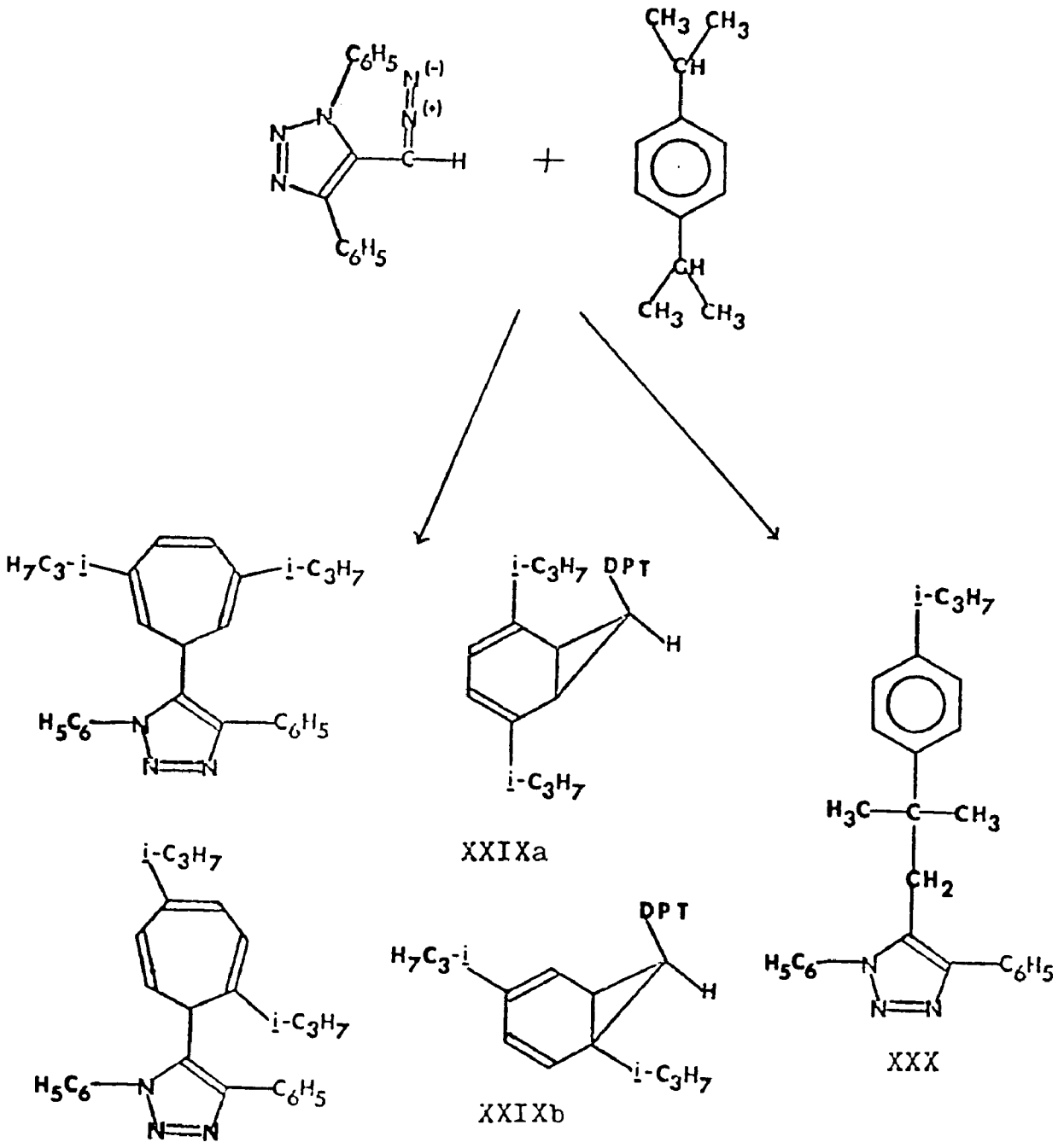
Decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I) in p-diisopropylbenzene afforded an oily adduct in 80% yield. The crude material, after column chromatography, crystallized as a white solid, mp 151-153°C. The PMR spectrum of an analytically pure sample of the product revealed that two 1:1 adducts were formed during the decomposition, which were inseparable by common chromatographic techniques. The norcaradiene XXIXb resulting from addition across the C-C bond of the aromatic nucleus and compound XXX resulting from C-H insertion of the carbene moiety into the methine C-H bond of the isopropyl group, were assigned to the compounds, based on the PMR and ^{13}CMR spectra. Assignments were made on the basis of relative signal intensities and with the aid of decoupled spectra. The presence of the 1,4-diphenyl-1,2,3-triazole group was established by the characteristic two-proton and eight-proton multiplets centered at δ 7.70 and 7.50 ppm, respectively. The three olefinic hydrogens of norcaradiene XXIXb appeared as a doublet centered at δ 5.69 ($J_{3,2}$ = 9.0 cps) assigned to the internal olefinic hydrogen, a doublet centered at 5.18 ($J_{2,3}$ = 9.0 cps) and a

doublet centered at 5.13 ppm ($J_{5,6}$ = 7.0 cps) assigned to the two terminal olefinic hydrogens. The C_6-H cyclopropyl hydrogen appeared as a triplet centered at δ 3.34 and the C_7-H cyclopropyl hydrogen appeared as a doublet centered at 3.07 ppm ($J_{7,6}$ = 8.0 cps). The two isopropyl methine hydrogens appeared as a complex multiplet centered at δ 2.06 and the isopropyl methyls appeared as a doublet centered at 0.74 (J = 7.0 cps) assigned to the four position of compound XXIXa and two doublets centered at 0.77 and 0.79 ppm (J = 6.5 cps) assigned to the isopropyl methyl attached to the C_1 position of the cyclopropyl group. The remarkable similarity displayed by norcaradiene XXIXb and adduct XXVIc obtained from the decomposition of diazo compound I in p-cymene reinforced the spectral assignments.

Conclusive structural assignment of norcaradiene XXIXb was obtained from the ^{13}CMR spectrum. The absorptions of the C_6- and C_1-carbon atoms of norcaradiene XXIXb appeared at δ 65.35 and 65.00 ppm, respectively, as a doublet and singlet. These chemical shifts are similar to those observed for the mesitylene and durene adducts and reinforce the structural assignment of adduct XXIXb as the norcaradiene isomer.

The isomeric compound XXX, a result of C-H insertion of the carbene moiety into the methine hydrogen of an isopropyl group, could not be isolated in pure form. Assignment of its structure is based on the following PMR and ^{13}CMR absorptions. The diphenyltriazole moiety was

established by the characteristic two-proton and eight-proton multiplets centered at δ 7.65 and 7.50 ppm, respectively. The benzene nucleus appeared as a complex multi-



plet centered at δ 7.0 ppm and accounted for four-protons. The methylene group of compound XXX appeared as a singlet at δ 3.34 and the isopropyl methine hydrogen appeared as a multiplet centered at 2.80 ppm. The isopropyl methyls

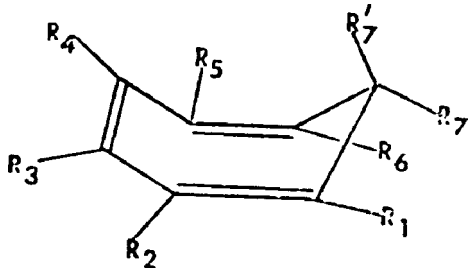
appeared as a doublet centered at δ 1.19 ppm and integrated for six hydrogens. The other methyl signals appeared as a singlet at δ 0.922 ppm and also integrated for six hydrogens. Conclusive structural assignment of 1,1-dimethyl-1-(p-isopropylbenzene)-2-(1,4-diphenyl-1,2,3-triazol-5-yl)-ethane (XXX) as the isomeric material isolated from decomposition of diazo compound I in p-diisopropylbenzene was obtained from the ^{13}CMR spectrum. The methylene carbon atom appeared at 36.67 as a triplet and thus confirmed the assignment.

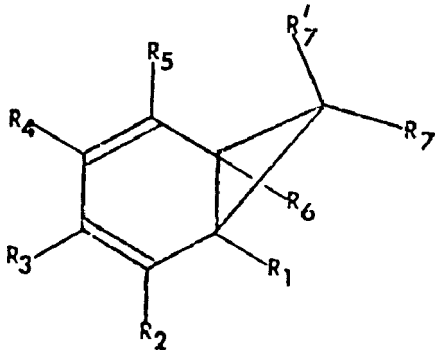
It is interesting to note that the increased steric interactions between carbene and substrate, introduced by the two isopropyl groups, caused a change in the reaction pathway. Any hypothesis concerning the cause for this change in reaction pathway remains purely speculative. However, it is tempting to postulate that the added steric hindrance presented to the attacking carbene moiety by the isopropyl groups forced C-H insertion over C-C addition. Two factors favored C-H insertion. First, the increased steric interactions between carbene and substrate substituents may not allow product formation upon every collision, and secondly, tertiary C-H bonds are known to be more reactive towards C-H insertion reactions of carbenes. A combination of these factors are believed responsible for the isolation of adduct XXX.

(13) Thermolysis in p-Di-tert-butylbenzene:

Decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in p-di-tert-butylbenzene proved to be completely futile. The product mixture contained at least six components, and most of these were present in comparable amounts. Two of the materials isolated from this mixture proved to be identical to 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde (IV) and the azine, both synthesized by unambiguous routes.[24,25] The remaining fractions were scrutinized by PMR after partial purification was achieved by preparative tlc. No indications that any products arising from the cycloaddition of diazo compound I to p-di-tert-butylbenzene were found.

(14) Interpretive Discussion:





Early work on the generation of 1,4-diphenyl-1,2,3-triazol-5-ylcarbene in monosubstituted benzenes, reported by Smith and Bruckmann,[26] indicated that electronic factors overshadowed any steric interactions between carbene and substrate molecule during the cycloaddition reactions. This effect was also demonstrated for the copper-catalyzed

decomposition of diazomethane in aromatic substrates as presented in Table IV.[15] The decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in disubstituted benzenes affords high yields of substituted cycloheptatrienes, formed by electrophilic addition of the carbene across an aromatic carbon-carbon bond, followed by bond reorganization of the initially formed norcaradiene adduct. However, unlike the monosubstituted adducts which afforded all three position isomers in approximately statistical proportions the disubstituted substrates generally formed only one positional isomer contaminated with only trace quantities of the other positional isomers, as may be seen from Table V.

Examination of the major isomers obtained from the xylene series clearly demonstrates that electronic factors of the aromatic nucleus no longer totally govern the course of the reaction. A subtle interation between the electronic effects of the aromatic nucleus, steric interactions between the alkyl substituents and the large 1,4-diphenyl-1,2,3-triazol-5-ylcarbene moiety, and the mode of carbene addition, <u>syn</u> or <u>anti</u> on the aromatic nucleus all effect the site selectivity of carbene attack and type of product, tropilidene or norcaradiene, isolated. The first evidence that steric interactions influence product orientation (or site selectivity) appeared in the ortho- and meta-xylene cases. The highest electron density in both systems is either next to or between the alkyl substituents.[57] How-

Table V

Effect of Aromatic Substituents on the Positional Selectivity of Carbene Attack, Comparison of Copper-Catalyzed Decomposition of Diazomethane[15] and Thermal Decomposition of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole in Disubstituted Benzenes

Substrate	Yield of[a] Adduct Diazo Compound (I)	Position of Alkyl Substituents	Isomer Distribution Found	Yield of[b] Adduct Diazomethane	Isomer Distribution Found	Statistical[e] Distribution
o-Xylene	80%	1,2	c		15%	17%
		2,3	c		62%	33%
		3,4	~90%	50%	23%	33%
		1,6	c		--	17%
m-Xylene	75%	1,3	d		23%	33%
		1,5	d		32%	33%
		2,4	~80%	70%	45%	33%
p-Xylene	75%	1,4	~100%		41%	67%
		2,5	- -	62%	60%	33%
Indan	15%	1,2	- -			17%
		2,3	- -			33%
		3,4	100%	- -	- -	33%
		1,6	- -			17%

Table V continued.

Substrate	Yield of[a] Adduct Diazo Compound (I)	Position of Alkyl Substituents	Isomer Distribution Found	Yield of[b] Adduct Diazomethane	Isomer Distribution Found	Statistical[e] Distribution
p-Ethyltoluene	68%	1,4 2,5 4,1	50% - - 50%	- -	- -	33% 33% 33%
p-Cymene	87%	1,4 2,5 4,1	36% - - 64%	- -	- -	33% 33% 33%
4-tert-Butyltoluene	75%	1,4 2,5 4,1	- - - - 100%	- -	- -	33% 33% 33%

[a] Total yield of isomeric adducts from 1,4-diphenyl-1,2,3-triazol-5-ylcarbene.

[b] Total yield isolated from decomposition of diazomethane.

[c] Trace quantities of other isomeric adducts were found, however their exact configuration could not be determined by PMR spectroscopy.

[d] The two remaining isomers were present in about a 60/40 mixture, however their assignment was impossible.

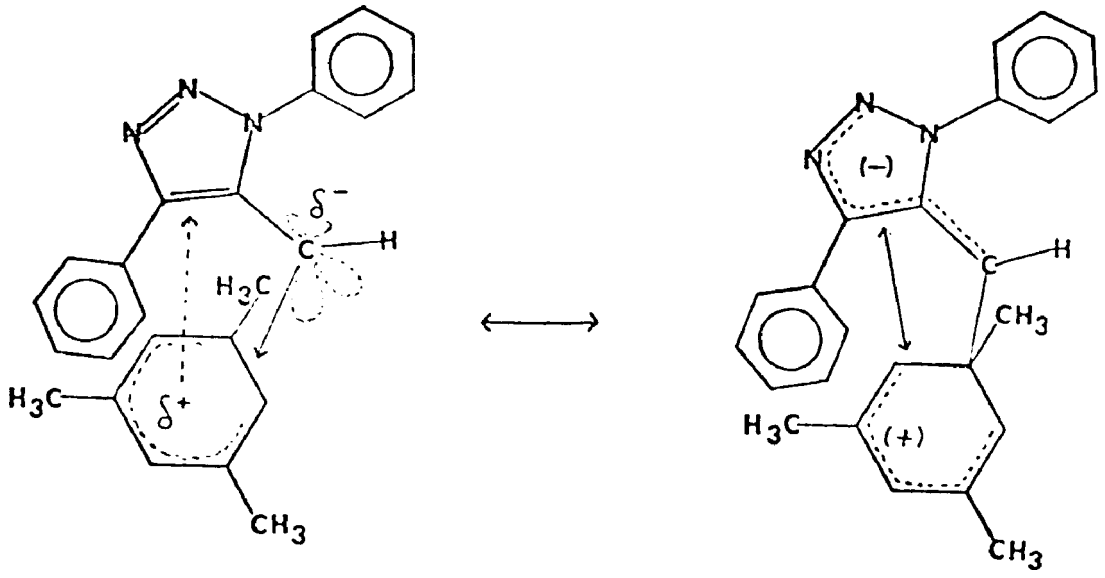
[e] Statistical proportions were obtained by allowing equal probability for carbene attack at any C-C bond of the aromatic substrate.

ever, because of large steric interactions between the carbene moiety and the alkyl substituents on the aromatic nucleus the attacking site of the carbene was altered. At least 73% of the isolated tropilidenes from o-xylene and 58% of the isolated tropilidenes from m-xylene stemmed from para-attack. Likewise, decomposition of I in indan yielded a product resulting from carbene addition away from the alkyl substituents at the para-position. These results indicate that the site selectivity of 1,4-diphenyl-1,2,3-triazol-5-ylcarbene is markedly influenced by steric interactions between substrate substituents and carbene. However, the electronic factors still influence the site selectivity by directing the electrophilic carbene moiety towards alternative areas of high electron density on the substrate molecule, i.e., the para positions.

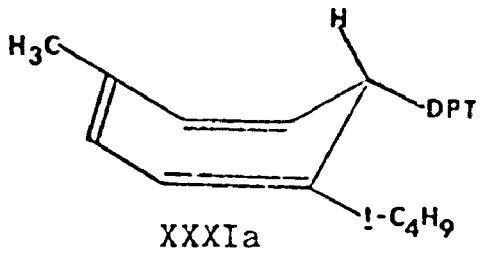
The results obtained from the decomposition of diazo compound I in p-xylene clearly showed that the electronic factors still played a major role in site selectivity. The only product obtained was a result of carbene attack at the C_1-C_2 bond of the aromatic ring. This result prompted the investigation of other 1,4-disubstituted benzenes. The effect of increasing the size of the alkyl substituent and its influence on carbene site selectivity and mode of addition, syn or anti was elucidated by decompositions of I in p-ethyltoluene, p-cymene and 4-tert-butyltoluene. In all substrates, only products arising from attack at the C_1-C_2 or C_3-C_4 bond of the aromatic

nucleus were formed, however, the isomer distribution changed radically, as may be seen from Table V. These results were quite surprising, since the o- and m-xylene cases indicate that the carbene moiety preferred to attack the ring at positions of least steric crowding. Table V shows that increased steric size of the alkyl substituent resulted in higher yields of tropilidenes resulting from addition next to the larger alkyl group, in direct contrast to the dimethyl cases.

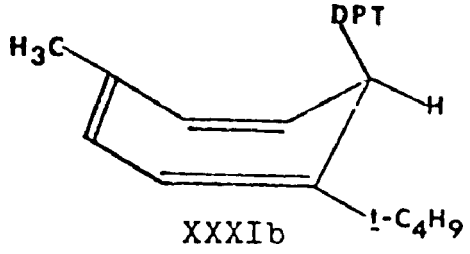
The addition of carbenes to aromatic substrates is a well documented reaction; however, unlike the carbene additions to olefins, the mode of attack, syn or anti, has not been established. It is reasonable to assume that the same factors that influence the geometrical orientation of carbene additions to olefins[58] will also hold for carbene additions to aromatic nuclei. During the transition state it is believed that the olefinic carbons develop some positive charge, which is in part dispersed throughout the molecule. One might well expect strong Coulombic interactions to result between carbenic and olefinic substituents, perhaps sufficient to overcome non-bonding repulsions between the two species. The addition of diphenyltriazol-5-ylcarbene to aromatic substrates could conform to this interpretation, especially in light of the possible additional charge stabilization by the aromatic nucleus.



The results for the naphthalene and thiophene adducts, however, clearly indicate that the mode of addition was anti, with respect to the aromatic substrate. The 4-tert-butyltoluene case indicates that addition occurred exclusively at the C_3-C_4 bond. If we assume anti addition, as demonstrated in the naphthalene and thiophene cases, the tropilidene product would have a geometric conformation represented by XXXIa.

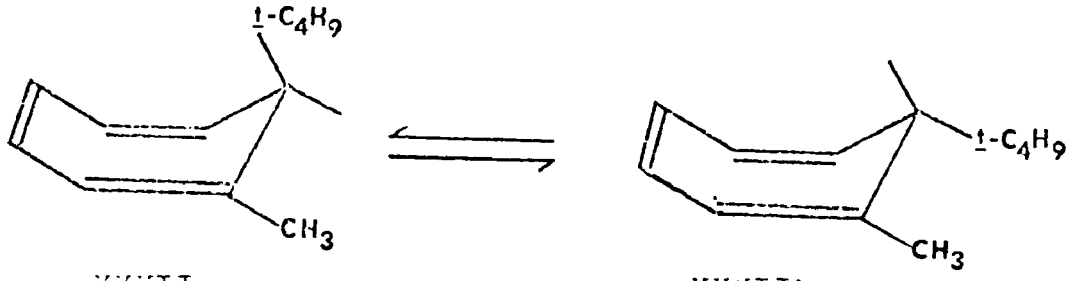


XXXIa



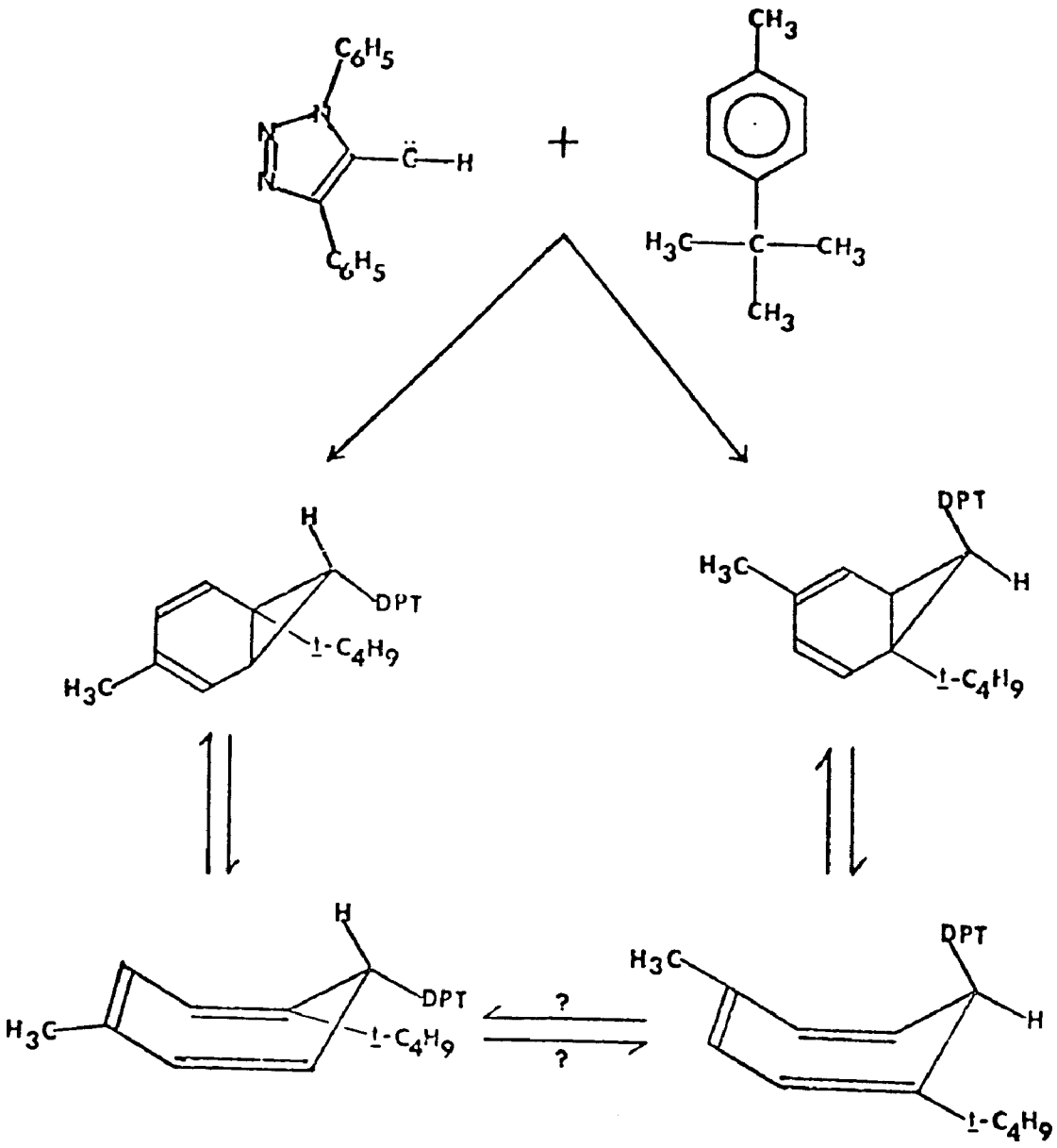
XXXIb

C. A. Capus and coworkers[59] extensively studied the behavior of 7-tert-butyl-1-methylcycloheptatriene, and reported on the observed barrier to interconversion of the nonplanar ring conformers XXXIIa ⇄ XXXIIb.



XXXIIa XXXIIb

They found an activation energy of 19.5 kcal/mole for ring inversion, and that the "axial" 7-tert-butyl group was the preferred conformation, from which facts they inferred the existence of nonbonded interactions between the 7-tert-butyl group and the 1-methyl substituent. Likewise, the interaction between diphenyltriazole moiety and the 1-tert-butyl group of compound XXXIa would be expected to cause an increase in the energy required for ring interconversion, as models clearly demonstrate. Therefore, it is reasonable to assume that the tropilidene isolated from the decomposition of diazo compound I in 4-tert-butyltoluene has a configuration represented by XXXIb with an "axial" diphenyltriazol moiety, a result of syn addition of the diphenyltriazol-5-ylcarbene to the substrate molecule. It is also unlikely that the large diphenyltriazole moiety would add to the same side as the tert-butyl group as would have to



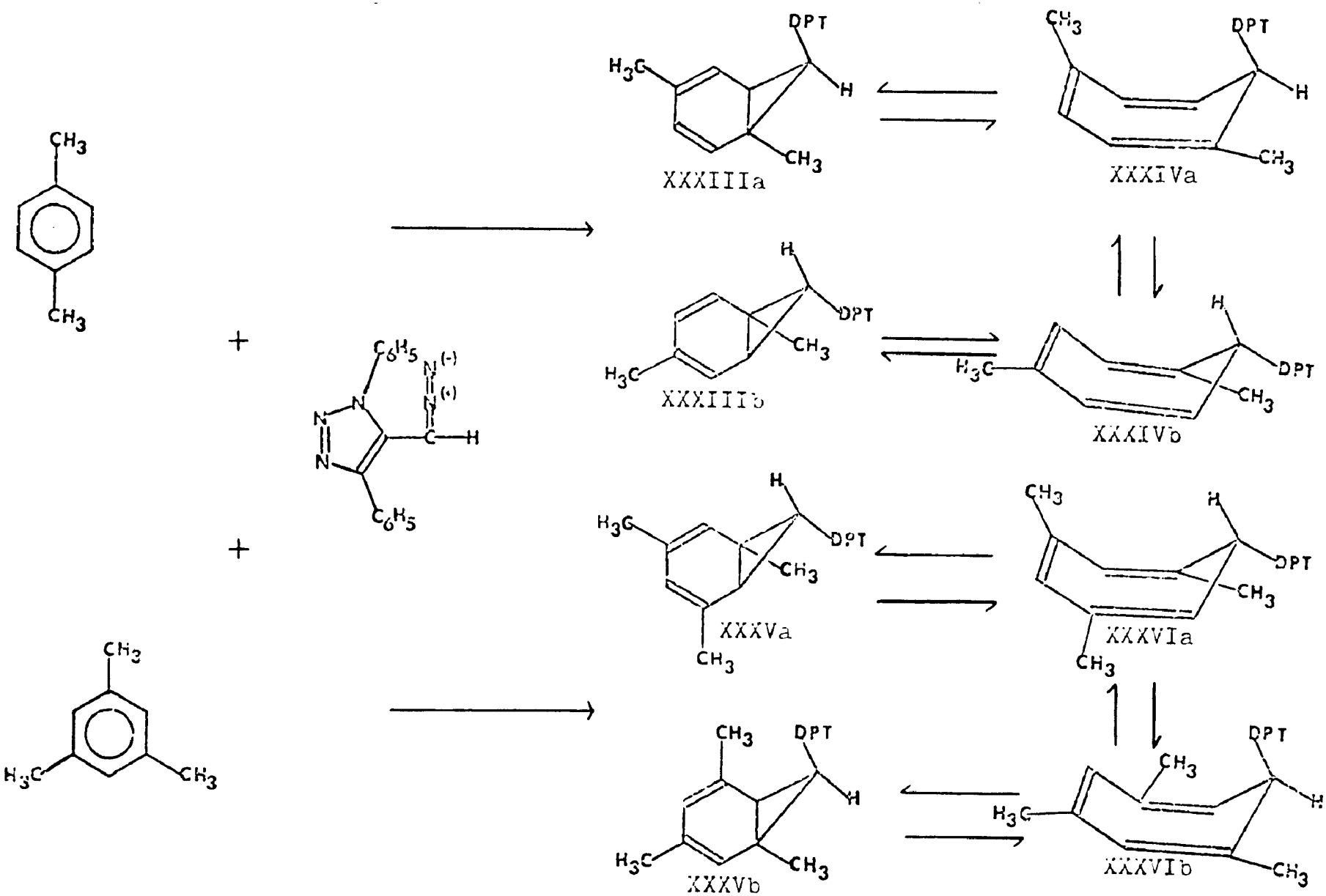
be the case if anti addition occurred.

Two factors reinforce the postulation of syn selectivity for the carbene addition to 4-tert-butyltoluene: (1) an observed equilibrium of the norcaradiene-tropilidene type, demonstrated by low-temperature PMR spectroscopy, contrary to the ring inversion of nonplanar tropilidene conformers reported by C. A. Capus and coworkers for the 7-tert-butyl-1-methylcycloheptatriene system (discussed in

fuller detail in Chapter II), and (2) the fact that the activation energy required for subsequent thermal rearrangements of XXXIb, discussed in Chapter III, is extremely low.

Additional evidence for a change in selectivity of 1,4-diphenyl-1,2,3-triazol-5-ylcarbene addition, syn or anti, to aromatic substrates stems from a comparison of the products obtained from p-xylene and mesitylene substrates. As in the 4-tert-butyltoluene case the p-xylene and mesitylene substrates offer two pathways for carbene addition.

Decomposition of diazo compound I in mesitylene clearly resulted in the isolation of a norcaradiene adduct. Low-temperature PMR revealed that the norcaradiene was in dynamic equilibrium with its tropilidene valence-isomer, discussed in Chapter II. One possible explanation for the observed change in product formation in the mesitylene case is that the diphenyltriazole moiety is interacting with a 1-methyl substituent and thus hindering the Cope rearrangement of XXXVb to XXXVIb, or possibly that this interaction causes a change in the relative ground state free-energies between the norcaradiene XXXVb and tropilidene XXXVIb favoring the norcaradiene form. Examination of the product resulting from the decomposition of I in p-xylene indicates that only the tropilidene isomer is isolated. Low-temperature PMR studies of this adduct showed no changes in the spectrum down to -100°C. This


XXXIIIa
XXXIVa
XXXIIIb
XXXIVb
XXXVa
XXXVIa
XXXVb
XXXVIb

result demonstrates that no norcaradiene-tropilidene equilibrium exists for either XXXIVa or XXXIVb and also indicates that there is either no or a very low barrier to the interconversions of tropilidenes XXXIVa and XXXIVb. Therefore, assuming that the steric interactions between the 1-methyl substituent and the diphenyltriazole moiety are altering the ground state free-energies of the norcaradienes the same interactions postulated for the isolation of norcaradiene XXXVb should hold for norcaradiene XXXIIIb. However, this is not the case.

It is reasonable to assume that the mode of carbene addition to the substrate molecule has been altered by increased steric interactions, especially in light of the 4-tert-butyltoluene example. The addition to p-xylene is most likely anti, similar to that observed for the naphthalene and thiophene case. However, the increased steric interactions presented to the attacking carbene moiety in mesitylene and 4-tert-butyltoluene may result in syn addition. The increased steric interactions may allow for additional time during the transition state complex. This additional time would allow the carbene moiety to align itself in the favorable syn orientation and fully develop the Coulombic interactions hypothesized for the olefinic cycloaddition reactions. The end result is a shift in the dynamic equilibrium from the interconversion of the two tropilidene boat conformers of the p-xylene case to a norcaradiene-tropilidene equilibrium observed in the

mesitylene and 4-tert-butyltoluene cases.

An alternate explanation can be offered to explain the observed results. If the steric interactions between the diphenyltriazole moiety and the 1-substituent is large, it is possible to substantially alter the ground state free-energies of the isolated adducts and their isomers (Figure 2).

Case I represents a normal energy pathway for the norcaradiene-cycloheptatriene valence bond rearrangement. The activation energy for the norcaradiene-cycloheptatriene isomerization is approximately 11 kcal/mole, whereas the interconversion of the nonplanar tropilidenes requires approximately 8 kcal/mole.[60] The ground state free-energy, ΔG°, between the exo and endo tropilidenes is approximately zero indicating a 50/50 mixture of two forms. A ΔG° of 3 kcal/mole between tropilidene and norcaradiene isomers would insure that 99+% of the dynamic equilibrium would exist in the tropilidene form. This picture would represent typical norcaradiene/tropilidene equilibria, and is consistent with the results obtained from decomposition of diazo compound I in monosubstituted benzene.

Case II represents a norcaradiene/tropilidene dynamic equilibrium in which all possible isomers are present. The ΔG° between any two components in this equilibrium must be less than 1 kcal/mole to insure detection by ordinary spectroscopic methods. Once again the norcaradiene/tropilidene activation energy would be approximately

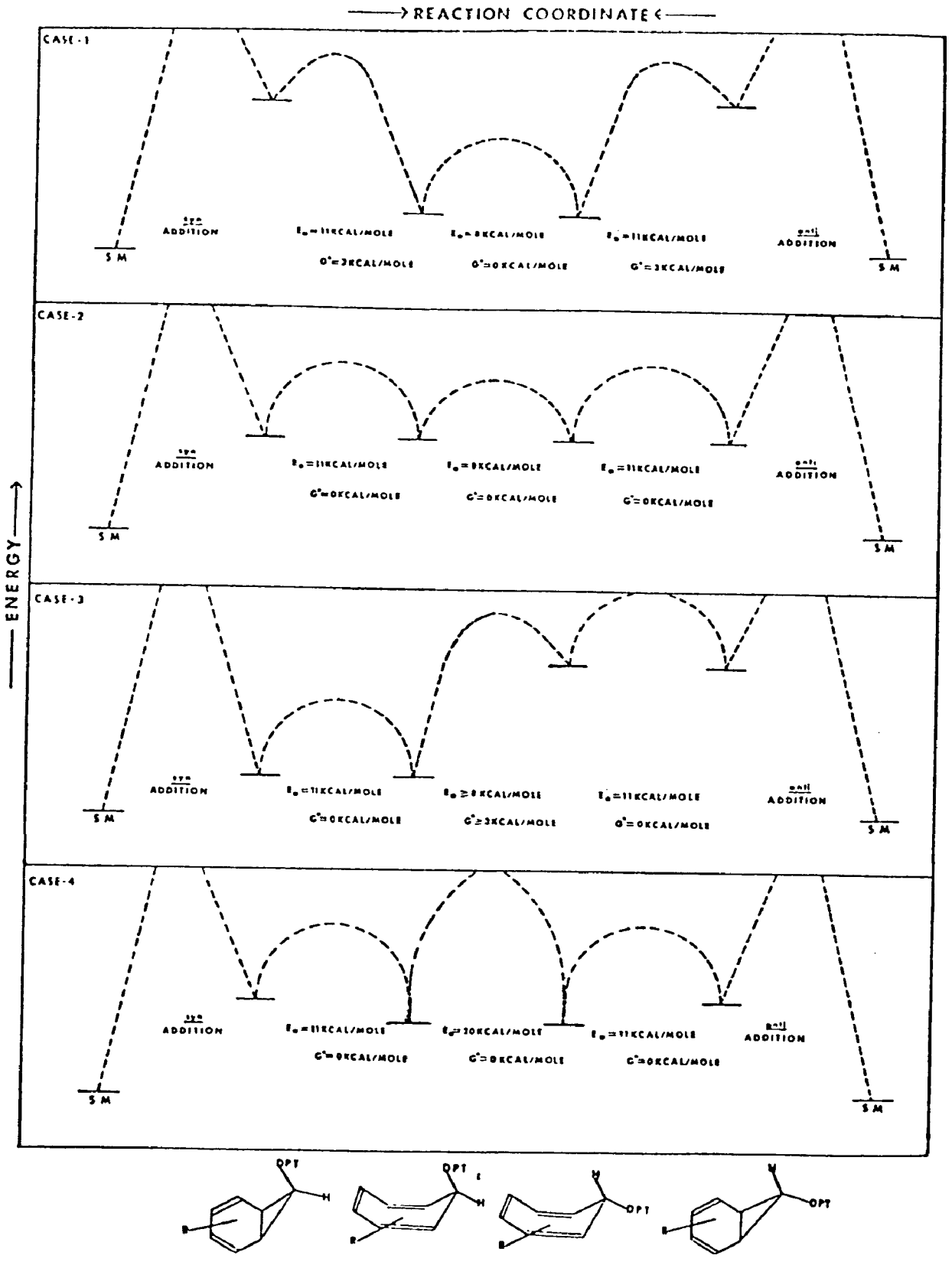


Figure 2. Schematic representation of reaction energetics of the norcaradiene/cycloheptatriene system.

11 kcal/mole and the activation energy for interconversion of the nonplanar tropilidenes would be approximately 8 kcal/mole. This type of energy profile is indicative of the 7-phenylnorcaradiene-7-carboxylate/7-phenyl-1,3,5-cycloheptatriene-7-carboxylate series, examined by Günther,[61] Roberts,[62] and others.[63]

The fourth case represents a norcaradiene/tropilidene system where the ΔG° between the norcaradiene and tropilidene forms is 3 kcal/mole, but the activation energy between the two tropilidene isomers is large, i.e., greater than 15 kcal/mole. C. A. Capus reported that 7-tert-butyl-1-methyl-cycloheptatriene fits this energy description. Their findings also showed that the ΔG° between tropilidene and norcaradiene must be at least 3 kcal/mole since none of the norcaradiene isomer was detected, even down to temperatures of -100°C. This description, however, does not fit the results obtained in the present discussion.

The final energy profile, case III, requires that the ΔG° between the two tropilidene forms be at least 3 kcal/mole. With an activation energy of only 8 kcal/mole the equilibrium concentration would be 99+% of the "axial" tropilidene. If the ΔG° between the syn norcaradiene and the "axial" tropilidene is 1 kcal/mole or less a dynamic equilibrium between the two forms would be observed. This type of energy profile amply represents the observations for the mesitylene and 4-tert-butyltoluene adducts. Of

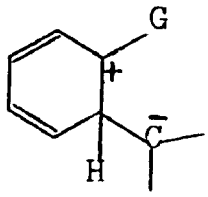
course, in this type of energy representation the addition of the carbene moiety in either a syn or anti manner would result in the same product mixture.

The difference between the types of products isolated during the decomposition of diazo compound I in polysubstituted aromatic substrates can be explained by either the energetics profile represented by Case III, Figure 2, or by a reversal in the carbene selectivity from anti to syn based on steric arguments. Both seem to represent an accurate description of the problem. However, the results from 4-tert-butyltoluene tend to support the interpretation involving a change in the carbene selectivity from anti in simple monosubstituted benzenes to syn in sterically hindered and polysubstituted benzenes. As demonstrated by models, anti addition of diphenyltriazol-5-ylcarbene next to the tert-butyl group of 4-tert-butyltoluene insures substantial steric repulsions and thus makes the addition highly suspect. No such repulsive factors are encountered during a syn addition of the diphenyltriazol-5-ylcarbene and it is therefore considered to be the reaction pathway followed by the attacking carbene moiety. The energy profile represented by case III, Figure 2, would still represent the product obtained by syn selectivity. However, the observed equilibrium would result because of an increased ground state free-energy of the equatorial tropilidene, due to non-bonded interactions between the diphenyltriazole group and the

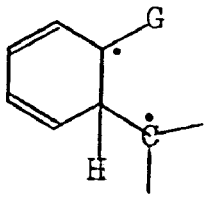
1-substituent. Mesitylene and 4-tert-butyltoluene were not unique cases. Durene, p-ethyltoluene, p-cymene and p-diisopropylbenzene all showed similar behavior.

A significant mechanistic conclusion emerges from this detailed analysis of the substituent effects in aromatic cycloadditions. The directive ability of a substituent is the composite of two distinct interactions. Strict steric repulsions between the groups attached to the attacking divalent carbon and the substituents on the substrate are effective in lowering the probability for addition to the bonds containing the substituents. This interaction is responsible for the selectivity displayed by diphenyltriazol-5-ylcarbene in aromatic cycloadditions. This steric interaction is, however, under the strong influence of the electronic factors present in the substrate moiety. A combination of the electronic and steric demands between substrate and carbene result in the remarkable discriminative ability displayed by 1,4-diphenyl-1,2,3-triazol-5-ylcarbene towards aromatic cycloaddition reactions as compared to all other known carbene and nitrene systems studied to date. The second and considerably more effective component of the directive impact of a substituent is exerted by selective stabilization of the transition states of competing reaction modes. This interaction is operative only if the transition state involves either ionic or diradical character, as implied in formulas A and B. As a consequence of the appreciable energy

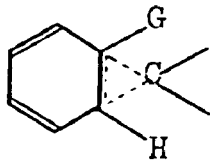
differences of the competing transitions, this component of the substituent effect imposes large reactivity differences on the various reactive sites of the benzene nucleus. The remarkable selectivity demonstrated by the addition of diphenyl-triazol-5-ylcarbene to disubstituted benzene substrates and the hypothesized change in carbene addition from an anti to syn selectivity can only be possible through intermediates such as A or B, represented in Figure 1. This evidence mitigates against the involvement of the simultaneous formation of two new C-C bonds as illustrated by formula C.



A



B



C

4. Experimental

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Grating Spectrophotometer, Model 237B. A Varian T-60, T60A or a Joel 100 MHz Nuclear Magnetic Resonance Spectrometer were used for the scanning of NMR spectra. In general, thin-layer chromatography was effected by the use of Eastman Chromagram Sheets, Type 6060 (silica gel with fluorescent indicator). Preparative pre-coated silica gel plates by Brinkman (2 mm) were used for preparative thin-layer chromatography. Column chromatographies were done on Woelm neutral alumina or silica gel with fluorescent indicator, "dry-column chromatography grade," or with J. T. Baker florisil (60-100 mesh).

Elemental analysis were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

A) Preparation of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole.

5-Bromomethyl-1,4-diphenyl-1,2,3-triazole: In a 500-ml flask was placed 10 g (0.046 mole) of 1,4-diphenyl-5-methyl-1,2,3-triazole,[41] 8.8 g of recrystallized N-bromosuccinimide, 2.0 g of benzoyl peroxide and 400 ml of carbon tetrachloride. The solution was refluxed for 24 hours and was then filtered hot into ca. 1 ℓ of water. The carbon tetrachloride layer was washed with five 500-ml portions of water and was then dried over anhydrous Na_2SO_4; removing the carbon tetrachloride under aspirator vacuum at room temperature left a reddish, viscous oil, which crystallized on cooling. Recrystallization from absolute ethanol gave 10.9 g (80%) of fine, off-white needles, mp 95-97°C; NMR ($CDCl_3$) δ 7.49 (m, 10H aromatic) and 4.48 ppm (s, 2H methylene), m/e = 314. Three subsequent recrystallizations from absolute ethanol gave an analytically pure sample, mp 97-98°C.

Anal. Calcd for $C_{15}H_{12}BrN_3$:
C, 57.41; H, 3.85; N, 13.37.
Found: C, 57.46; H, 3.85; N, 13.33.

1,4-Diphenyl-1,2,3-triazole-5-carboxaldehyde:

(A) By Moffatt reaction. To 10 g (0.038 mole) of 5-bromomethyl-1,4-diphenyl-1,2,3-triazole and 15 g of anhydrous $NaHCO_3$ was added 100 ml of anhydrous dimethyl sulfoxide under nitrogen. The resulting mixture was heated under a positive pressure of nitrogen at 60 to 100°C for 45 min to 2 hours, and was then poured into 500 ml of ice-water. The crude product mixture (93% material balance based on 100% conversion to aldehyde) was then dissolved in a minimal amount of benzene and chromatographed on a column packed with 100-200 g of alumina (100-200 mesh). The column was eluted with benzene and each fraction was examined by tlc after concentration, and ones of similar composition were combined.

The crude product mixture showed three components by tlc, which were easily separated by column chromatography (elution with benzene). The first fractions amounted to 5.5 g (58.5%) of white needle-like crystals, mp 169-171°C (lit. 169-172°C[31]). The infrared and PMR spectra and tlc behavior were identical with those of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde.[31] The second fraction consisted of 1.3 g (13.8%) of white crystals, mp 184-185°C (lit. 184-185°C[31]) and was identical with 1,4-diphenyl-1,2,3-triazole (IR and PMR spectra identical with authentic sample[31]). This product arises by decarbonylation of the carboxaldehyde under the reaction conditions. Prolonged heating or higher temperatures resulted in the formation

of larger amounts of 1,4-diphenyl-1,2,3-triazole. The final fraction, 2.2 g (25%) of yellowish crystals, proved to be 1,4-diphenyl-5-hydroxymethyl-1,2,3-triazole, mp 168-169°C (lit. 169-170°C[38]). Its IR and PMR spectra and tlc behavior were identical with the known compound.[38] The overall yield of aldehyde from 1,4-diphenyl-5-methyl-1,2,3-triazole was 45%.

1,4-Diphenyl-5-styryl-1,2,3-triazole: A solution of 6 g of benzyl styryl ketone[39] (0.027 mole), 3.6 g of phenyl azide[29] (0.03 mole) and 2.7 g of sodium methoxide in 100 ml of absolute ethanol was stirred at room temperature for 48 hr, poured into 500 ml of water and extracted with three 50-ml portions of dichloromethane. The dichloromethane extract was dried over anhydrous Na_2SO_4 and the solvent was removed under aspirator vacuum, yielding a reddish oil, from which 2.2 g (25%) of 1,4-diphenyl-5-styryl-1,2,3-triazole crystallized out as an off reddish-yellow solid, mp 188-194°C. Recrystallization from absolute ethanol gave 1.75 g (20%) of yellow needle-like crystals of 1,4-diphenyl-5-styryl-1,2,3-triazole, mp 193-195°C; PMR ($CDCl_3$) δ 7.40 (m, 10H aromatic) and 6.87 ppm (d, 2H vinyl). Four recrystallizations from absolute ethanol gave an analytically pure sample, mp 197-198°C.

Anal. Calcd for $C_{22}H_{17}N_3$:

C, 81.70; H, 5.30; N, 13.00.

Found: C, 81.79; H, 5.34; N, 12.97.

1,4-Diphenyl-1,2,3-triazole-5-carboxaldehyde:

(B) By ozonolysis of 1,4-diphenyl-5-styryl-1,2,3-triazole. In a 100-ml three-necked round bottom flask was placed 2 g (0.006 mole) of 1,4-diphenyl-5-styryl-1,2,3-triazole and 50 ml of chloroform. The solution was then ozonized at room temperature using a 0.02 M potassium iodide solution as an indicator. To the ozonide solution was added 200 mg of zinc dust and 1 ml of acetic acid, and this mixture was stirred for one hour at room temperature, filtered and steam-distilled to remove benzaldehyde. The resulting solution was extracted with three 50-ml portions of diethyl ether, and the combined extracts were neutralized by washing with two 100-ml portions of sodium bicarbonate followed by two 100-ml portions of water, and dried over anhydrous Na_2SO_4. Evaporation of the diethyl ether left 1.45 g (97%) of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde, mp 169-171°C (lit. 169-172°C[31]). The IR, PMR and tlc behavior was identical with authentic sample.

B) Preparation of 5-(1-Diazoethyl)-1,4-diphenyl-1,2,3-triazole:

5-Acetyl-1,4-diphenyl-1,2,3-triazole: To 5 g (0.02 mole) of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde in 30 ml of tetrahydrofuran and 150 ml of diethyl ether cooled by an isopropyl alcohol/Dry-Ice bath and under a nitrogen atmosphere was added dropwise 15 ml

(0.021 mole) of 1.4 M methyllithium with stirring. After 30 min at -78°C, the solution was allowed to warm to room temperature slowly. The excess methyllithium was destroyed by the dropwise addition of water. The resulting solution was washed with four 100-ml portions of saturated sodium chloride and dried over anhydrous Na_2SO_4; the solvent was removed under aspirator vacuum. The crude, oily 5-(1-hydroxyethyl)-1,4-diphenyl-1,2,3-triazole; PMR ($CDCl_3$) δ 7.40 (m, 10H aromatic), 5.00 (br. q, 1H) and 1.22 ppm (d, 3H methyl), was taken up into 20 ml of dry acetone to which was added an excess of Jones reagent. The mixture was stirred for one hour at room temperature. The acetone layer was then decanted and the residue was washed by decantation with two 20-ml portions of acetone. The acetone was removed under aspirator vacuum and the crude residue was taken up in 75 ml of diethyl ether. This solution was washed twice with 100-ml portions of saturated sodium chloride, dried over anhydrous Na_2SO_4 and the diethyl ether removed under aspirator vacuum, yielding 2.5 g (49%) of white, crystalline 5-acetyl-1,4-diphenyl-1,2,3-triazole, mp 119-121°C; PMR ($CDCl_3$) δ 7.38 (m, 10H aromatic) and 2.20 ppm (s, 3H methyl). Three recrystallizations from absolute ethanol gave an analytically pure sample, mp 121-121.5°C.

Anal. Calcd for $C_{16}H_{13}N_3O$:
C, 72.98; H, 4.97; N, 15.96.
Found: C, 73.02; H, 4.86; N, 15.89.

5-Acetyl-1,4-diphenyl-1,2,3-triazole Hydrazone: To 1 g (0.0038 mole) of 5-acetyl-1,4-diphenyl-1,2,3-triazole in 100 ml of warm absolute ethanol was added 5 ml of acetic acid and 5 ml of 97% hydrazine. The resulting mixture was gently refluxed for 2 hr and then concentrated on the rotary evaporator. The concentrated solution was poured into 500 ml of water and extracted with two 250-ml portions of diethyl ether. The combined extracts were washed four times with 250-ml portions of water and dried over anhydrous Na_2SO_4; the diethyl ether was removed under aspirator vacuum, yielding 860 mg (81%) of a yellowish oil. Thin-layer chromatography of the crude oil showed that two new products, in about equal portions, were formed under the reaction conditions; they were separated by column chromatography. A column packed with 50 g of alumina (100-200 mesh) was eluted with benzene and fractions were combined after concentration and examination by tlc. The first fraction amounted to 380 mg (45%) of the syn-methyl hydrazone, mp 182-185°C; PMR ($CDCl_3$) δ 7.55 (m, 10H aromatic), 5.46 (br. s, 2H hydrazone NH_2) and 1.98 ppm (s, 3H methyl); m/e 277; IR ($CDCl_3$ solution cells) 3405 (hydrazone NH_2) 1601 and 1500 (aromatic C=C) and 995, 1072 and 1145 cm^{-1} (triazole). Two additional recrystallizations from a diethyl ether/petroleum ether (30-60°) mixture gave analytically pure material, mp 190.5-192°C.

Anal. Calcd for $C_{16}H_{15}N_5$:

C, 69.30; H, 5.45; N, 25.24.

Found: C, 69.34; H, 5.32; N, 25.18.

The second fraction amounted to 480 mg (55%) of the anti-methyl hydrazone, mp 159-164°C; PMR ($CDCl_3$) δ 7.50 (m, 10H aromatic), 5.59 (s, 2H hydrazone NH_2) and 1.72 ppm (s, 3H methyl); m/e 277; IR ($CDCl_3$ solution cells) 3420 and 3300 (hydrazone NH_2), 1603 and 1502 (aromatic C=C) and 999, 1075 and 1137 cm^{-1} (triazole).

5-(1-Diazomethyl)-1,4-diphenyl-1,2,3-triazole:

The oily hydrazone from 1 g (0.0038 mole) of 5-acetyl-1,4-diphenyl-1,2,3-triazole (vide supra) was dissolved in 20 ml of methylene chloride, and 1 ml (0.79 g = 0.008 mole) of cyclohexylamine was added. This solution was cooled to -10°C in an ice-salt bath with magnetic stirring. To this a solution of 1.28 g (0.0038 mole) of phenyliodose acetate[26] in 20 ml of dichloromethane was added at a rate such that the temperature was maintained at -5°C. After addition was complete, the mixture was stirred for one hour at about 0°C and then cooled to -40°C. The insoluble cyclohexylammonium acetate was removed by suction filtration. The filtrate was extracted with four 100-ml portions of ice-water, and the extracts were dried over anhydrous K_2CO_3. The methylene chloride was removed by aspirator vacuum without external warming, leaving a dark reddish-brown oil. This was titrated with 40 ml of ether, precipitating 580 mg (67.5%) of a reddish-orange solid, mp

103-105°C with decomposition and gas evolution; PMR ($CDCl_3$) δ 7.45 (m, 10H aromatic) and 1.89 ppm (s, 3H methyl); IR ($CDCl_3$ solution cell) 2050 cm^{-1}, the strongest band in the spectrum, characteristic of the diazo function, 1600 and 1501 cm^{-1} (aromatic C=C) and 997, 1076 and 1140 cm^{-1} (triazole). The overall yield from the ketone was 55%. This material was recrystallized twice by dissolving it at room temperature in a minimum amount of anhydrous ether, adding an equal volume of petroleum ether (bp 30-60°) and allowing crystallization to proceed at Dry-Ice/acetone temperature. Bright orange crystals were obtained, mp 114-115°C with decomposition.

Anal. Calcd for $C_{16}H_{13}N_5$:
C, 69.98; H, 4.76; N, 25.44.
Found: C, 70.47; H, 4.83; N, 25.14.

C) Decomposition of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole in Aromatic Solvents:

Solutions of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole ranging in concentration from 0.01 to 0.02 M, were prepared in carefully dried equipment by dissolving the diazo compound in the appropriate amount of neat aromatic substrate. In cases where the aromatic substrate was a solid, methylene chloride was used as a solvent; it did not appear to interfere with the carbene reaction. The resulting bright-red solutions were then flushed with a stream of dry nitro-

gen gas for a minimum of one hour, agitated by magnetic stirring, and then immersed in an oil bath preheated to 45-55°C. A positive pressure of nitrogen was maintained in the flask throughout the decomposition period. The decompositions were completed after four to five hours, at which time the oil bath was removed and the mixture was allowed to cool to room temperature. The workup procedures are described separately for the individual substrates.

(1) Decomposition in Ortho-Xylene:

Thermolysis of 0.572 g (0.002 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in 70 ml of dry o-xylene gave a yellow solution, which was filtered to remove a very small amount of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde azine.[24] The excess o-xylene was removed by vacuum distillation (0.1 mm) at room temperature, leaving a viscous, yellow oil, which was triturated with four 25-ml portions of petroleum ether (bp 30-60°). The combined petroleum ether extracts were refrigerated, whereupon 310 mg (46%) of a white, crystalline material, mp 156-159°C, precipitated. The mother liquor was then concentrated, and the resulting clear oil chromatographed on a column of 50 g of 100-200 mesh alumina (activity III). The column was eluted with benzene and each fraction was examined by tlc after concentration; fractions of similar composition were combined. An additional 185 mg (27%) of material, the tlc behavior of which was identical to that

of the precipitated compound, was isolated. The PMR spectrum clearly indicated that only one of the four possible positional isomers was formed. The PMR spectrum displayed two multiplets, one centered at δ 7.70 (2H, aromatic) and one at 7.32 (8H, aromatic), four vinylic hydrogens, two centered at 5.81 (d, $J_{5,6} = J_{1,2} = 9$ Hz; 2H C=C-CH=C) and two centered 4.61 (doublet of doublets, $J_{1,2} = J_{5,6} = 9$ Hz and $J_{1,7} = J_{7,6} = 5.5$ Hz; 2H C=CH-C), a triplet methine hydrogen at 2.82 ($J_{7,1} = J_{7,6} = 5.5$ Hz; 1H triazolic methine H) and a singlet at 1.82 ppm (s, 6H methyls). On the basis of these characteristics, the adduct was identified as 3,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XVIId). The total isolated yield of compound XVIId was 73%. Three recrystallizations from absolute ethanol gave an analytically pure sample, mp 160-161°C, m/e - 339.

Anal. Calcd for $C_{23}H_{21}N_3$:
C, 81.36; H, 6.23.
Found: C, 81.29; H, 6.16.

(2) Decomposition in m-Xylene:

Thermolysis of 0.522 g (0.002 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in 70 ml of freshly distilled reagent-grade m-xylene gave a brownish-yellow solution. A workup procedure identical to that described for the o-xylene system yielded 395 mg (58%) of a white solid, mp 169-171°C. On the basis of the following PMR spectrum, it

was identified as 2,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XVIIIc): δ 7.71 (m, 2H aromatic), 7.39 (m, 8H aromatic), 6.13 (s, 1H C=CH-C=C), 5.80 (d, 1H C=C-CH=C), 4.67 (m, 1H C=CH-C), 4.37 (m, 1H C=CH-C), 2.96 (t, 1H triazolic methine H), 1.93 (s, 3H methyl) and 1.75 ppm (s, 3H methyl). A portion of this material was purified on a 2-mm preparative silica tlc plate by elution with a benzene ethyl acetate (20:1) mixture. The cycloheptatriene (XVIIIc) was removed from the silica by extraction with 100% ethyl acetate, and the ethyl acetate was removed under aspirator vacuum at room temperature, whereupon 200 mg compound XVIIIc crystallized, mp 170-171°C. Two recrystallizations from absolute ethanol gave an analytically pure sample, mp 171-173°C, m/e = 339.

Anal. Calcd for $C_{23}H_{21}N_3$: C, 81.36; H, 6.23.
Found: C, 81.22; H, 6.20.

(3) Decomposition in p-Xylene (a) Thermolysis:

Decomposition in the standard fashion of 0.522 g (0.002 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in 70 ml of reagent grade p-xylene resulted in a yellow solution, from which the p-xylene was removed by vacuum distillation (0.1 mm) at room temperature. The workup, identical to those previously described, yielded 450 mg (67%) of a white crystalline material, mp 168-171°C. The residual material, after concentration of the mother liquor, showed the same compound to be present as had been

previously isolated. On the basis of the PMR spectrum, compound XIXb was identified as 1,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene: δ 7.75 (m, 2H aromatic), 7.40 (m, 8H aromatic), 6.05 (d, $J_{5,6}$ = 6 Hz; 1 H C=C-CH=C), 5.91 (d, $J_{2,3}$ = 9 Hz; 1H C=CH-C=C), 5.64 (d, $J_{2,3}$ = 9 Hz; 1H C=C-CH=C), 4.81 (doublet of doublets, $J_{5,6}$ = 6 Hz and $J_{6,7}$ = 6 Hz; 1H C=CH-C), 3.17 (d, $J_{6,7}$ = 6 Hz; 1H triazolic methine H), 1.83 (s, 3H methyl) and 1.78 ppm (s, 3H methyl). Two recrystallizations from absolute ethanol gave an analytically pure sample, mp 171-173°C, m/e = 339.

Anal. Calcd for $C_{23}H_{21}N_3$:
C, 81.36; H, 6.23; N, 12.38.
Found: C, 81.55; H, 6.30; N, 12.14.

(b) Photolysis:

In a 70-ml test tube was placed 0.522 g of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole and 50 ml of reagent p-xylene. The resulting solution was purged with dry nitrogen for one hour and cooled to 15°C with an internal cold-finger apparatus. The test tube solution and cold finger were then placed in a Rayonett photolysis chamber and irradiated with a bank of 3500Å lights for five hours. During this time the solution was continually flushed with dry nitrogen gas while an internal temperature of 15°C was maintained. The resulting yellow solution was vacuum-distilled (0.1 mm) at room temperature to remove the

excess p-xylene, and the residual yellow oil was treated in a manner identical to that described for the thermolysis experiments, yielding 485 mg (72%) of compound XIXb. This material proved to be identical to that isolated in the thermal decomposition of diazo compound XIXb in p-xylene, mp 170-171°C, m/e = 339.

(4) Decomposition in Mesitylene:

A solution of 0.522 g of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in 70 ml of reagent-grade mesitylene was thermolyzed at 50°C as usual. The excess mesitylene was removed at room temperature by vacuum distillation at 0.1 mm pressure, and the resulting yellowish oil was triturated with petroleum ether (bp 30-60°) to induce crystallization. The PMR spectrum of the crystallized adduct displayed two multiplets, one centered at δ 7.83 (2H, aromatic) and one at 7.40 (8H, aromatic), two broad singlets at 5.73 (1H, vinylic) and 5.26 (1H, vinylic), two doublets centered at 3.71 (1H, cyclopropyl C_6-H; $J_{1,7}$ = 6.5 Hz) and 2.88 (1H, cyclopropyl C_7-H; $J_{1,7}$ = 6.5 Hz) and these three-proton singlets at 1.69, 1.50 and 1.40 ppm (methyl groups). The structural assignment of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (XXII), the initial product expected from the addition of the carbene to mesitylene, agrees well with all the features of the PMR spectrum. Two recrystallizations from slightly warmed (about 35°) absolute ethanol gave glossy

white leaflets of analytical purity, mp 137-139°C, m/e = 353.

Anal. Calcd for $C_{24}H_{23}N_3$:
C, 81.54; H, 6.57; N, 11.90.
Found: C, 81.57; H, 6.59; N, 12.02.

(5) Decomposition in Durene:

In a 250-ml three-necked flask equipped with nitrogen inlet and condenser was placed 50 g of recrystallized durene and 100 ml of dry dichloromethane. This solution was stirred magnetically and flushed with dry nitrogen for one hour. To this solution was added 0.522 g (0.002 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole, and the resulting red mixture was immersed in an oil bath and thermolyzed in the usual way. After five hours, the durene was removed from the reaction mixture by steam distillation. The residue was exhaustively extracted with chloroform, the organic layers were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated under aspirator vacuum to leave 720 mg of white crystalline material, mp 133-179°C. Sublimation of the residue removed the remaining durene impurity. The residue was then triturated with three 30-ml portions of petroleum ether (bp 30-60°), which were combined and then cooled in an ice bath. A white solid (320 mg, 45%) formed and was isolated by filtration; mp 187-193°C. On the basis of the following PMR

spectrum, the adduct was identified as 1,3,4,6-tetramethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (XXIIIa): δ 7.51 (m, 10H aromatic), 4.72 (s, 2H C=CH-C), 2.87 (s, 1H cyclopropyl C_7-H), 1.46 (s, 6H methyls) and 1.38 ppm (s, 6H methyls). Four recrystallizations from absolute ethanol gave an analytically pure sample, mp 201-202.5°C, m/e = 367.

Anal. Calcd for $C_{25}H_{25}N_3$:
C, 81.59; H, 6.86; N, 11.43.
Found: C, 81.52; H, 7.01; N, 11.39.

The mother liquor was concentrated, giving an additional 82 mg (11%) of a clear oil. The PMR spectrum of this oil showed the following features: δ 7.80 (m, 2H aromatic), 7.50 (m, 8H aromatic), 5.57 (s, 1H C=CH-C=C), 2.49 (d, $J_{6,7}$ = 6.0 Hz, cyclopropyl C_6-H), 2.10 (d, $J_{7,6}$ = 6.0 Hz, cyclopropyl C_7-H), 1.63 (s, 3H methyl), 1.36 (s, 3H methyl), 1.30 (s, 3H methyl) and 0.99 ppm (s, 3H methyl), plus about 25% of the corresponding isomeric compound XXIIIa. The PMR spectrum agrees well with a structural assignment of 1,2,4,5-tetramethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (XXIIIb), the other possible adduct from the carbene addition to durene.

(6) Decomposition in Naphthalene:

In a 250-ml three-necked flask equipped with nitrogen inlet and condenser was placed 50 g of recrystallized naphthalene and 150 ml of dry dichloromethane. This solu-

tion was stirred magnetically and flushed with dry nitrogen for one hour. To this solution was added 0.522 g (0.002 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole, and the resulting red mixture was immersed in an oil bath and thermolyzed at 55°C for 5.5 hr. The excess naphthalene was removed from the reaction mixture by steam distillation. The residue was exhaustively extracted with chloroform, the organic layers were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated under aspirator vacuum to leave 1.26 g of white crystalline material. This crude product mixture showed three components by tlc, which were easily separated by column chromatography (elution with benzene).

The crude mixture was dissolved in a minimal amount of benzene and chromatographed on a column packed with 50 g of alumina (100-200 mesh). The column was eluted with benzene and each fraction was examined by tlc after concentration, and ones of similar composition were combined. The first fractions amounted to 600 mg of naphthalene which had not been removed by steam-distillation. The second fraction amounted to 420 mg (58.5%), mp 195-198°C. On the basis of the following PMR spectrum, the adduct was identified as 7-(1,4-diphenyl-1,2,3-triazol-5-yl)-2,3-benzonorcaradiene (XXVIIa): δ 7.83 (m, 2H aromatic), 7.50 (m, 8H aromatic), 7.06 (m, 4H aromatic), 6.29 (d, $J_{3,4}$ = 9.5 Hz; 1H vinylic), 5.90 (doublet of doublets, $J_{4,3}$ = 9.5 Hz and $J_{3,2}$ = 5.5 Hz; 1 H vinylic), 2.26 (m, 1H cyclo-

propyl C_1-H), 1.75 (m, 1H cyclopropyl C_2-H) and 1.35 ppm (t, 1H cyclopropyl C_7-H). Two recrystallizations from absolute ethanol gave an analytically pure sample, mp 203-204.5°C; m/e 361.

Anal. Calcd for $C_{25}H_{19}N_3$:
C, 83.11; H, 5.30; N, 11.63.
Found: C, 83.06; H, 5.36; N, 11.60.

The third fraction 240 mg (41%), mp 192-196°C, was assigned the structure 7-(1,4-diphenyl-1,2,3-triazol-5-yl)-3,4-benzocycloheptatriene (XXVIIb), based on the following PMR spectrum: δ 7.40 (m, 14H aromatic), 5.75 (d, 2H vinylic), 4.85 (doublet of doublets, 2H vinylic) and 2.87 ppm (t, 1H triazolic methine H); m/e 361. A portion of this material was purified on a 2-mm preparative silica tlc plate by elution with a benzene/ethyl acetate (20:1) mixture. The benzocycloheptatriene (XXVIIb) was removed from the silica by extraction with 100% ethyl acetate, and the ethyl acetate was removed under aspirator vacuum at room temperature, whereupon compound XXVIIb crystallized, mp 196-201°C. Two recrystallizations from absolute ethanol gave an analytically pure sample, mp 201-202°C.

Anal. Calcd for $C_{25}H_{19}N_3$:
C, 83.11; H, 5.30; N, 11.63.
Found: C, 82.94; H, 5.21; N, 11.59.

(7) Decomposition in p-Ethyltoluene:

Thermolysis of 0.400 g (0.0015 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in 25 ml of 98% p-ethyltoluene gave a yellowish solution. A workup procedure identical to that described for the o-xylene system yielded 365 mg (68%) of a white solid, mp 121-126°C. The PMR of this material indicates two isomers were present in approximately a 50:50 ratio, however, all attempts to separate these isomers failed. Structural assignments were made on the basis of relative intensities and with the aid of decoupled spectra. On the basis of the following PMR spectrum the adduct was identified as 1-methyl-4-ethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XXIVb): δ 7.55 (m, 10H aromatic, 5.90 (d, $J_{3,2}$ = 8 Hz; 1H C=CH-C=C), 5.62 (d, $J_{2,3}$ = 8 Hz; 1H C=C-CH=C), 5.72 (d, $J_{5,6}$ = 7 Hz; 1H C=C-CH=C), 4.75 (doublet of doublets, $J_{6,5}$ = 7 Hz and $J_{6,7}$ = 6 Hz; 1H C=CH-C), 3.07 (d, $J_{7,6}$ = 6 Hz; 1H triazolic methine H), 2.12 (br. q, 2H ethyl), 1.71 (s, 3H methyl) and 0.92 ppm (br. t, 3H ethyl). The other isomeric tropilidene was identified as 1-ethyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XXIVc): δ 7.55 (m, 10H aromatic), 6.05 (d, $J_{3,2}$ = 7 Hz; 1H C=CH-C=C), 5.82 (d, $J_{2,3}$ = 7 Hz; 1H C=C-CH=C), 5.40 (d, $J_{5,6}$ = 8 Hz; 1H C=C-CH=C), 3.91 (t, $J_{6,5}$ = 8 Hz and $J_{6,7}$ = 7 Hz; 1H C=CH-C), 2.86 (d, $J_{7,6}$ = 7 Hz; 1H triazolic methine H), 2.12 (br. q, 2H ethyl), 1.71 (s, 3H methyl) and 0.92 ppm (br. t, 3H ethyl). An analytical sample of these isomers

was prepared by two recrystallizations from absolute ethanol, mp 129-130°C; m/e 353.

Anal. Calcd for $C_{24}H_{23}N_3$:
C, 81.54; H, 6.56; N, 11.89.
Found: C, 81.48; H, 6.56; N, 11.93.

(8) Decomposition in 4-tert-Butyltoluene:

Thermolysis of 0.400 g (0.0015 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in 50 ml of reagent-grade 4-tert-butyltoluene gave a yellowish solution. The excess 4-tert-butyltoluene was removed by vacuum distillation (0.1 mm) at 45°C. The brownish-yellow residue was triturated with petroleum ether (bp 30-60°), yielding 435 mg (75%) of a white crystalline material, mp 151-153°C. On the basis of the PMR spectrum, the compound was identified as 4-methyl-1-tert-butyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XXVc): δ 7.60 (m, 10H aromatic), 5.98 (d, $J_{3,2}$ = 8 Hz; 1H C=CH-C=C), 5.66 (d, $J_{5,6}$ = 8.5 Hz; 1H C=C-CH=C), 5.46 (d, $J_{2,3}$ = 8 Hz; 1H C=C-CH=C), 4.07 (t, $J_{6,5}$ = 8.5 Hz and $J_{6,7}$ = 7 Hz; 1H C=CH-C), 2.87 (d, $J_{7,6}$ = 7 Hz; 1H triazolic methine H), 1.55 (s, 3H methyl) and 0.92 ppm (s, 9H tert-butyl). Two recrystallizations from absolute ethanol gave an analytically pure sample, mp 154-155.5°C; m/e 381.

Anal. Calcd for $C_{26}H_{27}N_3$:
C, 81.85; H, 7.13; N, 11.01.
Found: C, 81.74; H, 6.93; N, 11.03.

(9) Decomposition in p-Cymene:

Thermolysis of 0.500 g (0.002 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in 75 ml of freshly distilled p-cymene gave a yellowish solution. The excess p-cymene was removed by vacuum distillation (0.1 mm) at 40°C and the resulting yellowish oil was triturated with petroleum ether (bp 30-60°) to induce crystallization. However, the crude product mixture, 87% yield, would only oil under the conditions used for these attempted crystallizations. The crude material was then purified on a 2-mm preparative silica tlc plate by elution with a benzene/ethyl acetate (20:1) mixture. Two major bands were removed from the silica by extraction with 100% ethyl acetate, and the ethyl acetate was removed under aspirator vacuum at room temperature. The first fraction 275 mg (39%), a clear oil, was identified as 1-methyl-4-isopropyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XXVIb), on the basis of the following PMR spectrum: ($CDCl_3$) δ 7.57 (m, 10H aromatic), 6.00 (d, $J_{3,2}$ = 8 Hz; 1H C=CH-C=C), 5.68 (d, $J_{2,3}$ = 8 Hz and $J_{5,6}$ = 8 Hz; 2H C=C-CH=C and C=C-CH=C), 4.63 (m, 1H C=CH-C), 3.05 (d, $J_{7,6}$ = 7 Hz; 1H triazolic methine H), 2.25 (m, 1H isopropyl methine hydrogen) 1.70 (s, 3H methyl) and 0.92 ppm (q, 6H isopropyl methyls). Two recrystallizations from a diethyl ether/petroleum ether (bp 30-60°) mixture gave an analytically pure sample, mp 162.5-163.5°C.

Anal. Calcd for $C_{25}H_{25}N_3$:

C, 81.77; H. 6.87; N, 11.44.

Found: C, 81.86; H, 6.83; N, 11.40.

The second fraction 325 mg (48%), a clear oil, was identified as 1-isopropyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XXVIc), on the basis of the following PMR spectrum: ($CDCl_3$) δ 7.68 (m, 2H aromatic), 7.45 (m, 8H aromatic), 5.77 (d, $J_{3,2}$ = 8.4 Hz; 1H C=C<u>H</u>-C=C), 5.33 (d, $J_{2,3}$ = 8.4 Hz; 1H C=C-<u>CH</u>=C), 5.12 (d, $J_{5,6}$ = 6.5 Hz; 1H C=C-<u>CH</u>=C), 3.59 (t, $J_{6,5}$ = 6.5 Hz and $J_{6,7}$ = 8.0 Hz; 1H C=<u>CH</u>-C), 3.13 (d, $J_{7,6}$ = 8.0 Hz; 1H triazolic methine hydrogen), 1.62 (s, 3H methyl), 1.77 (m, 1H isopropyl methine hydrogen) and 0.75 ppm (q, 6H isopropyl methyls). All attempts to crystallize compound XXVIIc failed. Column chromatography (25 g florisil, elution with benzene) afforded an analytically pure oil.

Anal. Calcd for $C_{25}H_{25}N_3$:

C, 81.77; H, 6.87; N, 11.44.

Found: C, 81.81; H, 6.87; N, 11.31.

(10) Decomposition in Thiophene:

Thermolysis of 0.522 g (0.002 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in 70 ml of freshly distilled thiophene gave a yellow solution, which was filtered to remove a small amount of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde azine. The excess thiophene was removed

by vacuum distillation (0.1 mm) at room temperature, leaving a viscous, yellow oil, which was triturated with three 25-ml portions of petroleum ether (bp 30-60°). The combined petroleum ether extracts were refrigerated, whereupon 405 mg (60%) of a white, crystalline material, mp 171-185°C, precipitated. On the basis of the following PMR spectrum, the adduct was identified as 6-(1,4-diphenyl-1,2,3-triazol-5-yl)-2-thiabicyclo[3.1.0]-hex-3-ene (XXVIII): ($CDCl_3$), δ 7.75 (m, 2H aromatic), 7.43 (m, 8H aromatic), 6.00 (d, $J_{3,4}$ = 6.0 Hz; 1H S-CH=C), 5.58 (doublet of doublets, $J_{4,3}$ = 6.0 Hz and $J_{4,5}$ = 3.0 Hz; 1H S-C=CH-C), 2.70 (doublet of doublets, $J_{1,5}$ = 8.0 Hz and $J_{1,6}$ = 3.0 Hz; 1H cyclopropane C_2-hydrogen), 2.34 (m, 1H cyclopropane C_3-hydrogen) and 1.62 ppm (t, $J_{6,1} = J_{6,5}$ = 3.0 Hz; 1H cyclopropane C_6-hydrogen. Two recrystallizations from an ethanol/petroleum ether (bp 30-60°) mixture yielded analytically pure material, mp 191-192°C.

Anal. Calcd for $C_{19}H_{15}N_3S$:
C, 71.66; H, 4.75 ; N, 13.20.
Found: C, 71.68; H, 4.87 ; N, 13.29.

(11) Decomposition in Indan:

Decomposition in the standard fashion of 0.522 g (0.002 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in 70 ml of freshly distilled indan resulted in a yellow solution, from which the excess indan was removed by

vacuum distillation (0.1 mm) at room temperature. The residual oil was triturated with three 25-ml portions of petroleum ether (bp 30-60°). The combined petroleum ether extracts were refrigerated, whereupon 122 mg (17.4%) of a white, crystalline material, mp 157-165°C, precipitated. The crude precipitate was dissolved in a minimal amount of benzene and chromatographed on a column of 25 g of 60-100 mesh florisil. The column was eluted with a 10:1 mixture of benzene/diethyl ether and each fraction was examined by tlc after concentration; fractions of similar composition were combined. Removal of solvent by aspirator distillation yielded 93 mg of white needle-like crystals, mp 169-171°C. The PMR spectrum clearly indicated that only one of the four possible positional isomers was formed. The PMR spectrum displayed two multiplets, one centered at δ 7.80 (2H, aromatic) and one at 7.45 (8H, aromatic), four vinylic hydrogens, two centered at 6.21 (d, $J_{1,2} = J_{5,6} = 9.0$ Hz; 2H C=CH-C=C) and two centered at 5.27 (doublet of doublets, $J_{1,2} = J_{6,5} = 9.0$ Hz and $J_{1,7} = J_{6,7} = 5.0$ Hz; 2H C=CH-C), a triplet methine hydrogen at 3.38 ($J_{7,1} = J_{7,6} = 5.0$ Hz; 1H triazolic methine H) and a triplet (4H) and quartet (2H) at 2.65 and 2.00 ppm, respectively, assigned to the methylene bridge. On the basis of these characteristics, the adduct was identified as 3,4-trimethylene-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene (XXd). Two recrystallizations from a diethyl ether/petroleum ether (bp 30-60°) mixture gave an

analytically pure sample, mp 170-171°C, m/e = 351.

Anal. Calcd for $C_{24}H_{21}N_3$:
C, 82.02; H, 6.02; N, 11.95.
Found: C, 81.98; H, 6.02; N, 11.86.

(12) Decomposition in p-Diisopropylbenzene:

Thermolysis of 0.522 g (0.002 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in 70 ml of reagent-grade p-diisopropylbenzene gave a yellow solution, which was filtered to remove a very small amount of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde azine. The excess p-diisopropylbenzene was removed by vacuum distillation (0.1 mm) at 50°, leaving a viscous, yellow oil. The oily residue was chromatographed on a column of 50 g of 60-100 mesh florisil. The column was eluted with a benzene/diethyl ether (10:1) mixture and each fraction was examined by tlc after concentration; fractions of similar composition were combined. The clear oil obtained after column chromatography was dissolved in a diethyl ether/petroleum ether (bp 30-60°) mixture and cooled, whereupon 632 mg (80%) of a white, crystalline material, mp 145-150°C, precipitated. The PMR spectrum clearly indicated that two 1:1 adducts, one the result of C-C addition of the carbene to the aromatic nucleus, and the other resulting from C-H insertion into methine C-H bond of an isopropyl group, were formed. The PMR spectrum displayed two multiplets, one centered at δ 7.70 (2H aromatic) and one at 7.50 (8H aromatic), three

vinylic hydrogens, one centered at 5.69 (d, $J_{3,2}$ = 9.0 Hz; 1H CH=C-C) one centered at 5.18 (d, $J_{2,3}$ = 9.0 Hz; 1H C=CH-C) and one centered at 5.13 (d, $J_{5,6}$ = 7.0 Hz; 1H C=CH-C), 3.34 (t, 1H cyclopropyl C_6-H), 3.07 (d, 1H cyclopropyl C_7-H), 2.06 (m, 2H isopropyl methine hydrogens), 0.74 (d, 6H C_4-isopropyl methyls), 0.77 and 0.79 ppm (doublet of doublets, 6H C_1-isopropyl methyls). On the basis of these characteristics, the adduct was identified as 1,4-diisopropyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-norcaradiene (XXIXa). The other isomer present was assigned the structure 1,1-dimethyl-1-p-isopropylbenzene-2-(1,4-diphenyl-1,2,3-triazol-5-yl)ethane XXX, based on the following PMR spectrum; δ 7.65 (m, 2H aromatic), 7.50 (m, 8H aromatic), 7.00 (m, 4H aromatic), 3.34 (s, 2H methylene), 2.80 (m, 1H isopropyl methine hydrogen), 1.19 (d, 6H isopropyl methyls) and 0.922 ppm (s, 6H methyls). The mixture of isomers was taken up in a small volume of ethanol and the solution was allowed to crystallize. Recrystallization twice from ethanol gave an analytically pure mixture of isomeric adducts, mp 151-153°C; m/e = 395.

Anal. Calcd for $C_{27}H_{29}N_3$:
C, 81.99; H, 7.39; N, 10.62.
Found: C, 81.93; H, 7.36; N, 10.60.

(13) Decomposition in p-di-tert-Butylbenzene:

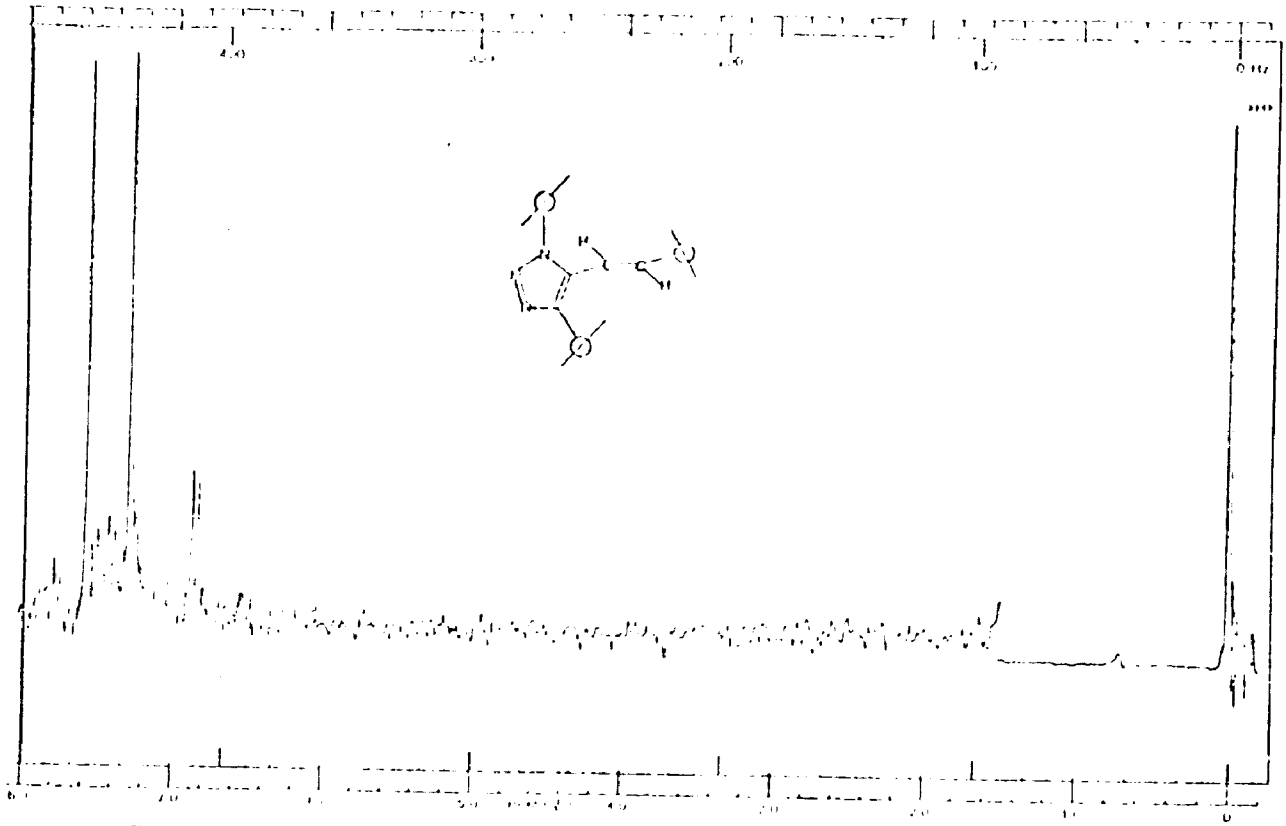
Thermolysis of 0.522 g (0.002 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I) in 25 g of p-di-tert-

butylbenzene dissolved in 50 ml of dichloromethane gave a reddish-brown solution, which was freed from p-di-tert-butylbenzene by steam distillation. The residue was extracted with chloroform, and the extracts were combined, dried (Na_2SO_4), and evaporated to leave a dark brown oil, which on tlc examination revealed the presence of at least seven components. Separation by preparative tlc on silica gel furnished only the component of highest R_f in reasonably pure form. Recrystallization of this fraction from acetone afforded 55.0 mg (16%) of a white solid, mp 171-173°, identified as 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde (NMR, IR, mixture melting point). All fractions were examined by PMR spectroscopy, however, none displayed olefinic absorptions. It was concluded that no products derived from the addition of 1,4-diphenyl-1,2,3-triazol-5-ylcarbene across the C-C bond of the aromatic substrate were formed during the thermolysis.

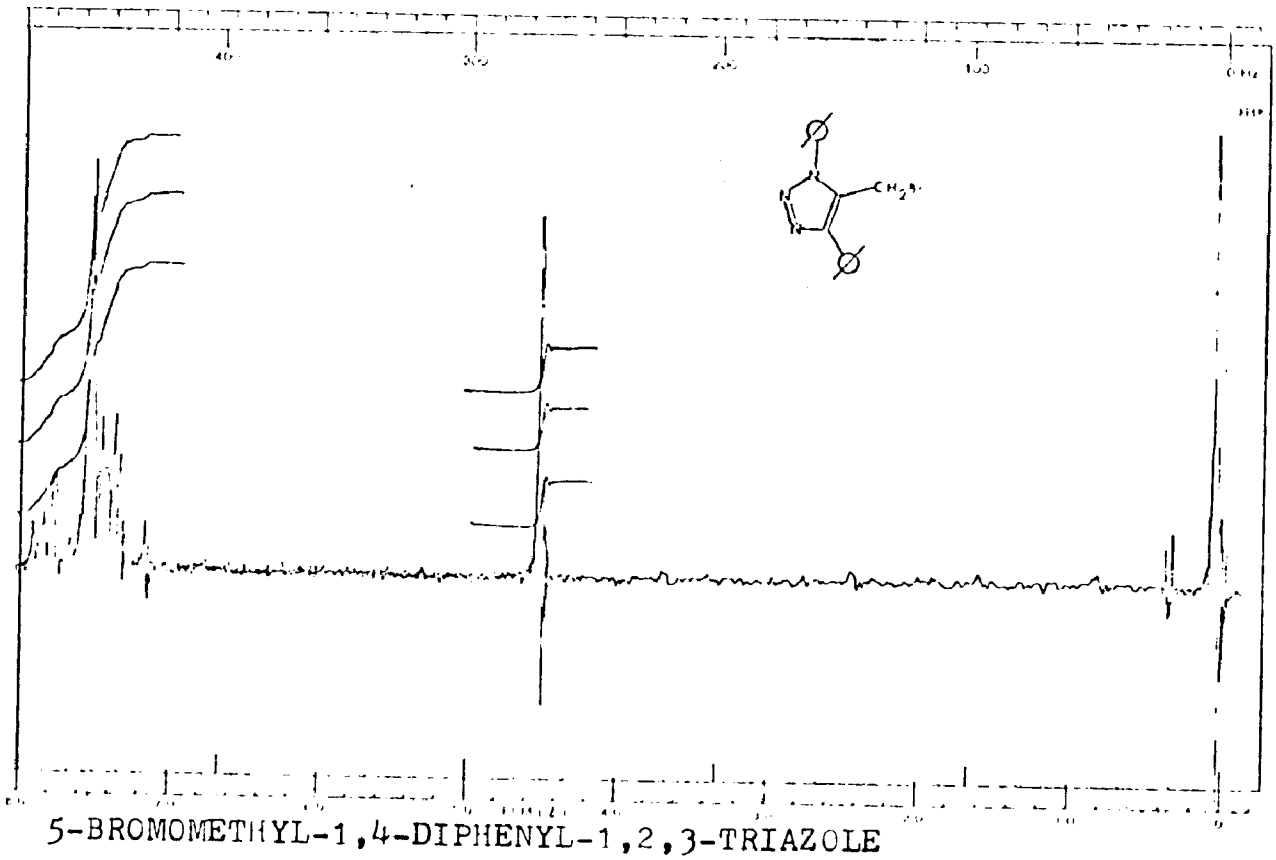
5. Spectra:

On the following pages are reproduced the infrared, PMR, ^{13}CMR and mass spectra of the novel compounds encountered in this study. Their special features and diagnostic value have been discussed in the previous pages.

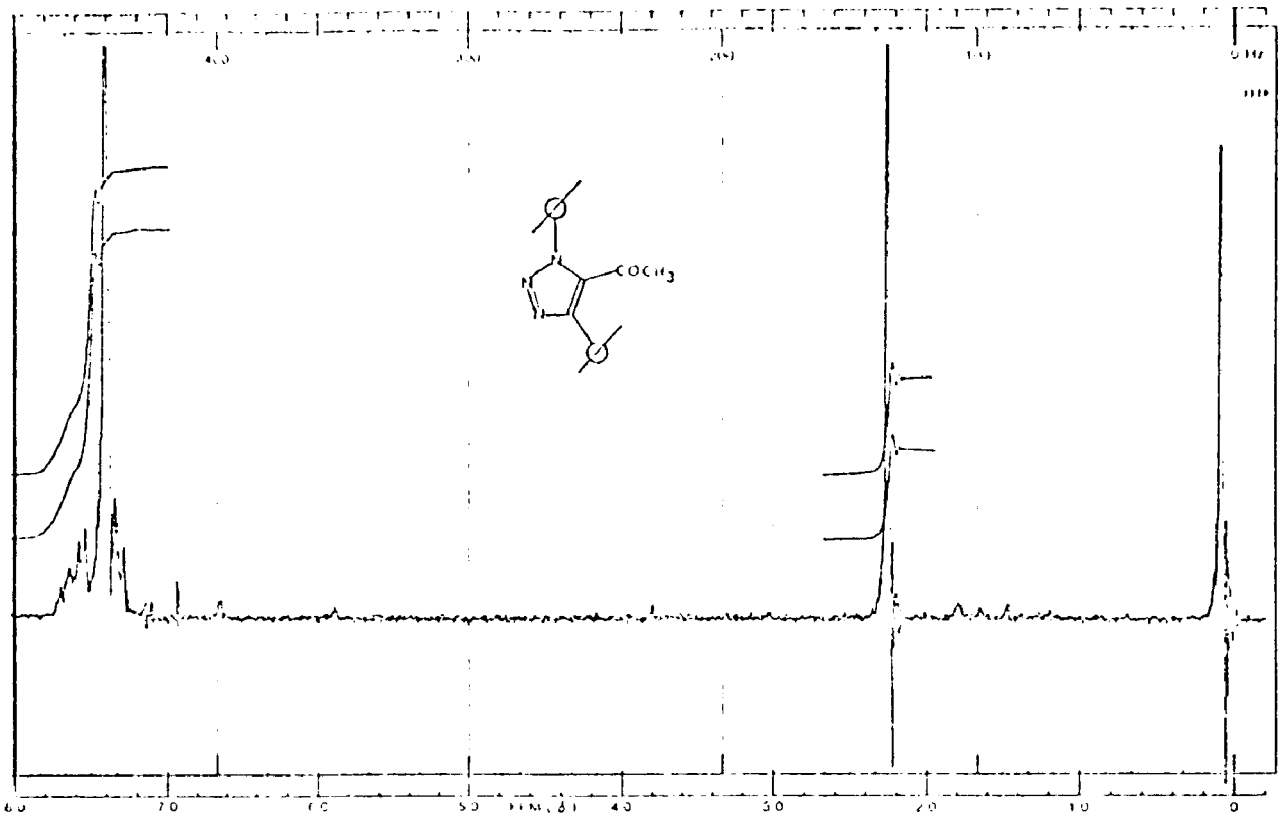
All PMR and ^{13}CMR spectra were determined on solutions in $CDCl_3$ with TMS as internal standard.



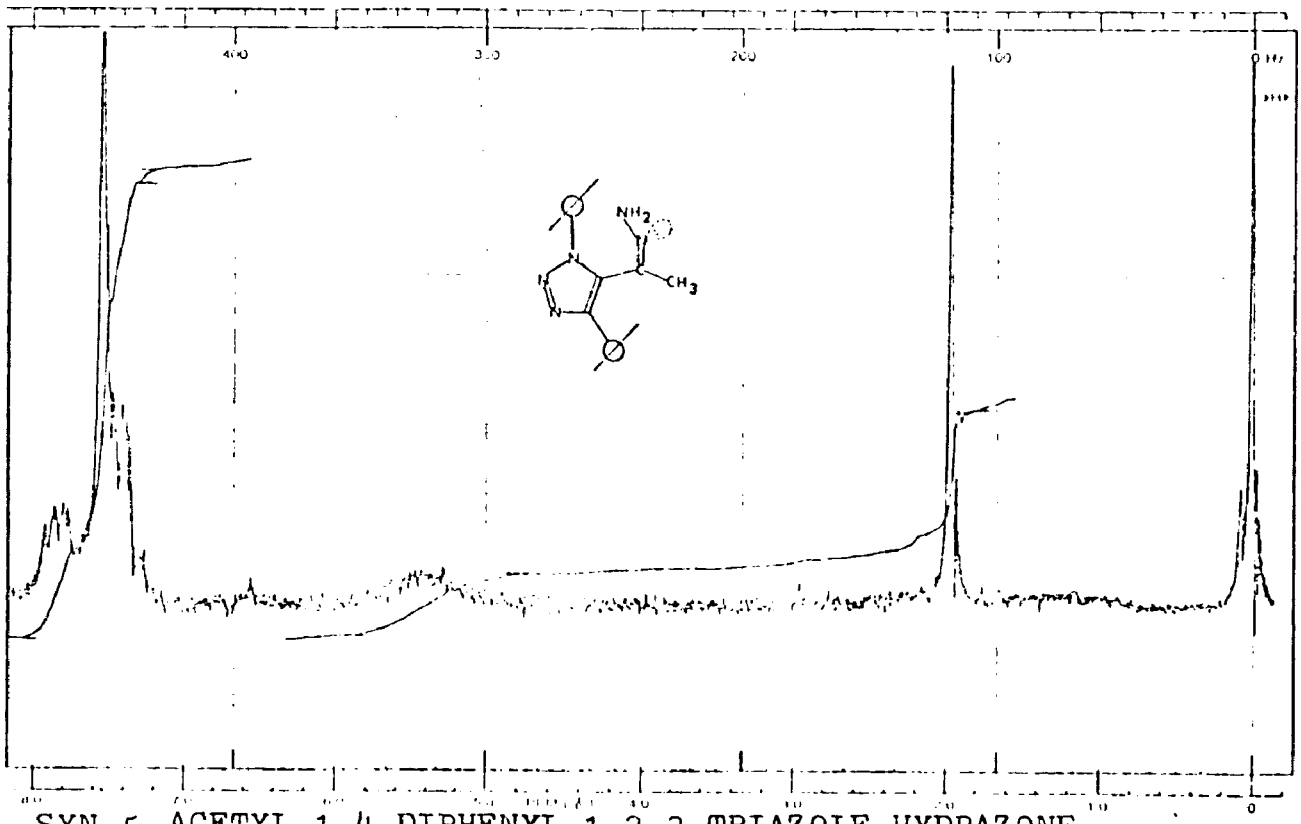
5-STYRYL-1,4-DIPHENYL-1,2,3-TRIAZOLE



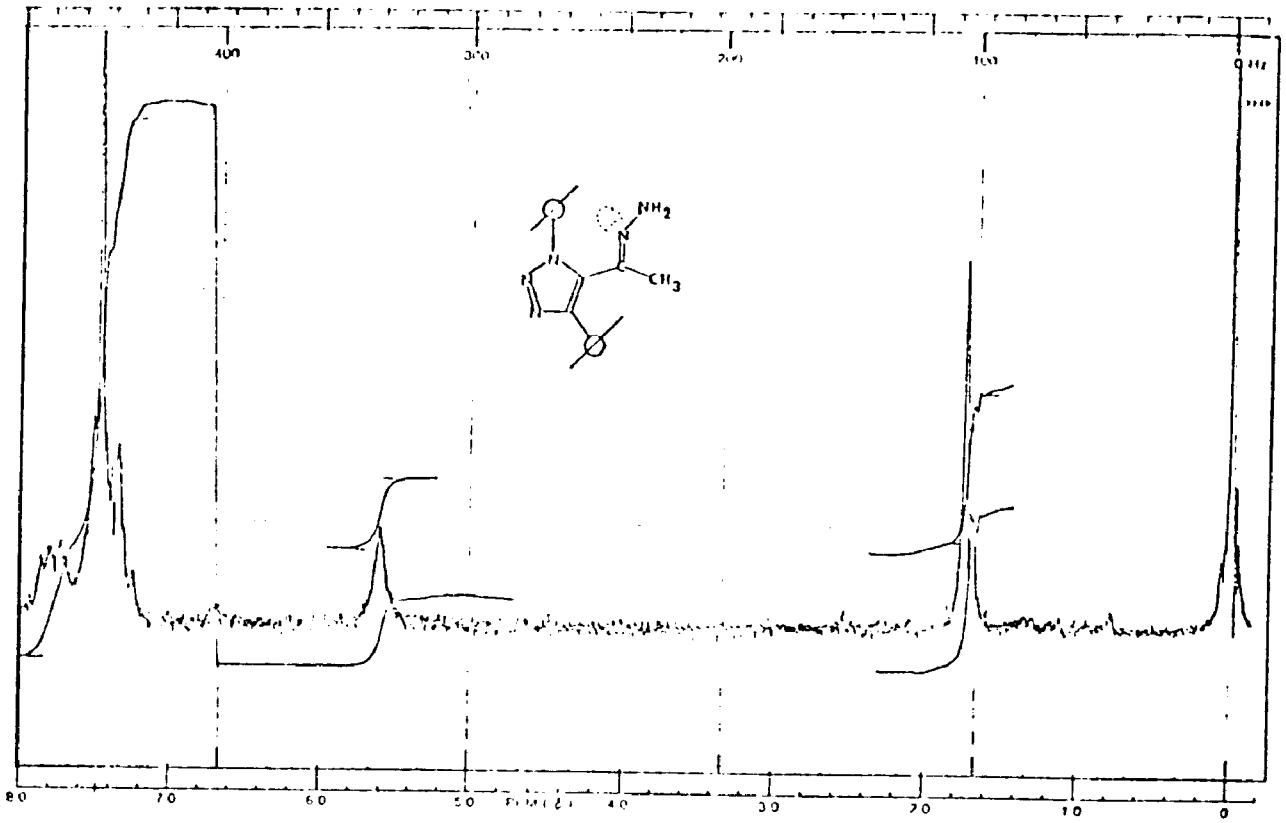
5-BROMOMETHYL-1,4-DIPHENYL-1,2,3-TRIAZOLE



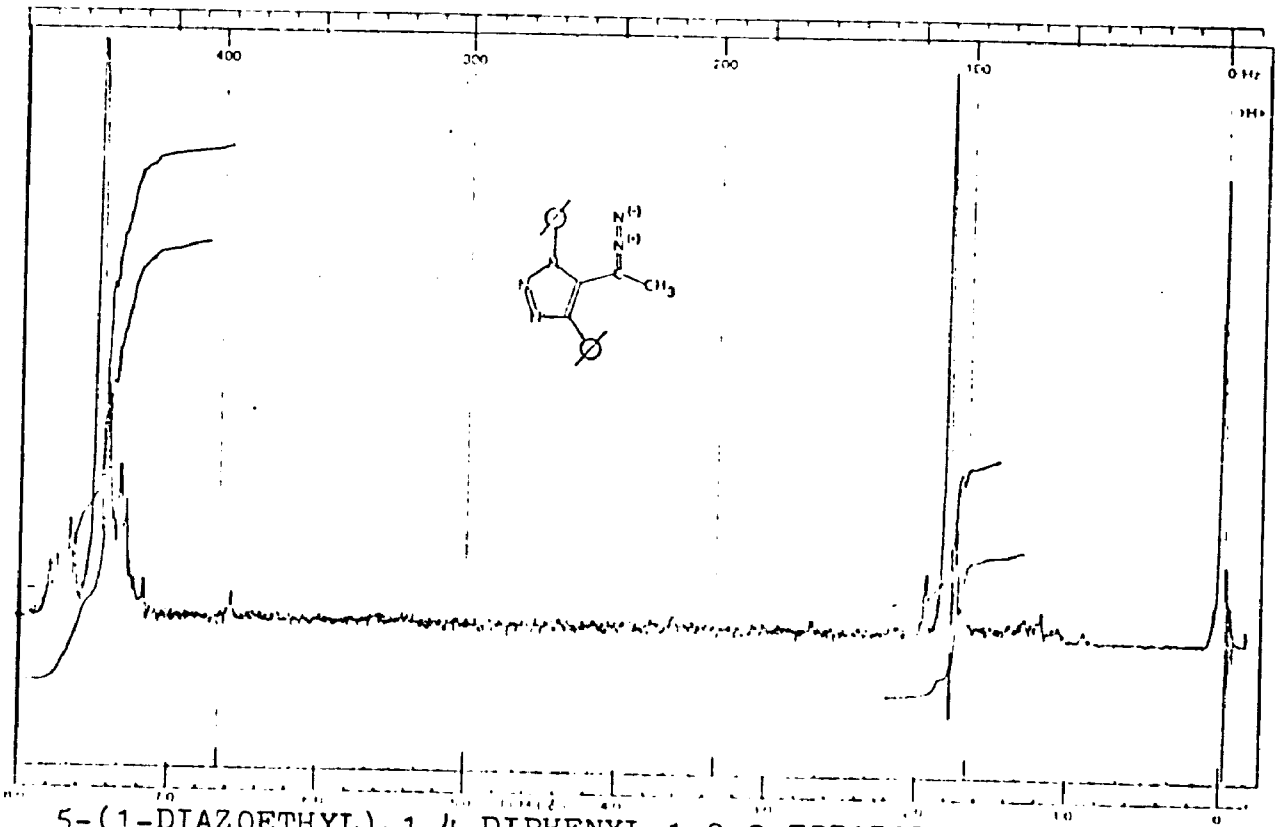
5-ACETYL-1,4-DIPHENYL-1,2,3-TRIAZOLE



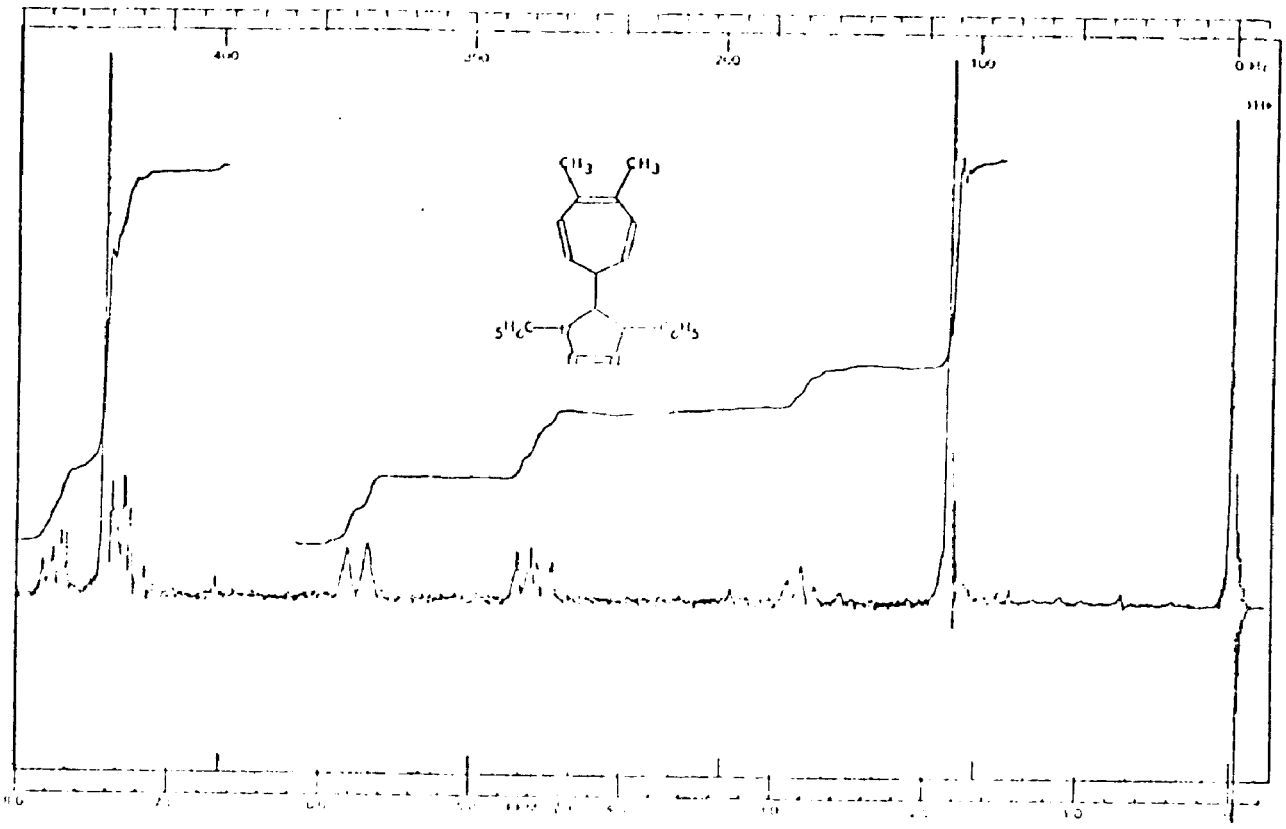
SYN-5-ACETYL-1,4-DIPHENYL-1,2,3-TRIAZOLE HYDRAZONE



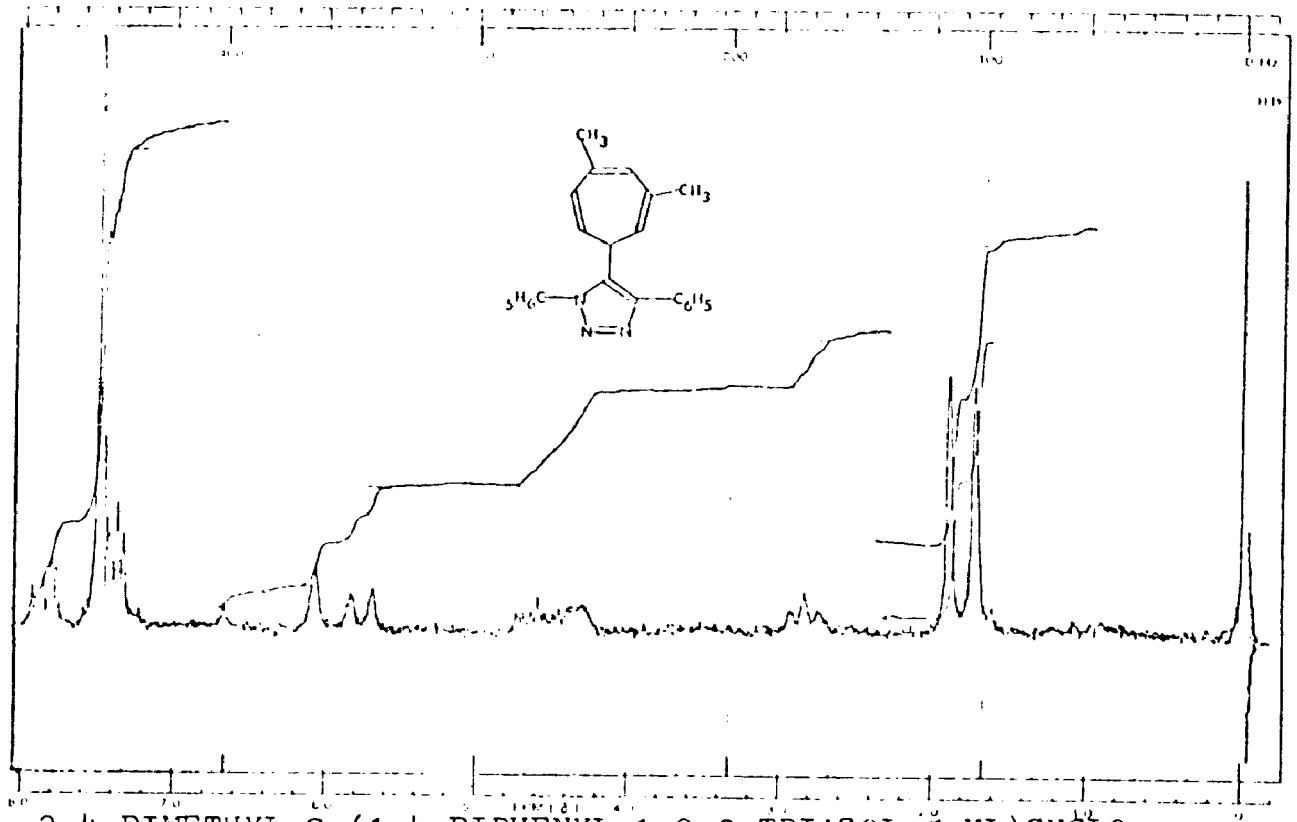
ANTI-5-ACETYL-1,4-DIPHENYL-1,2,3-TRIAZOLE HYDRAZONE



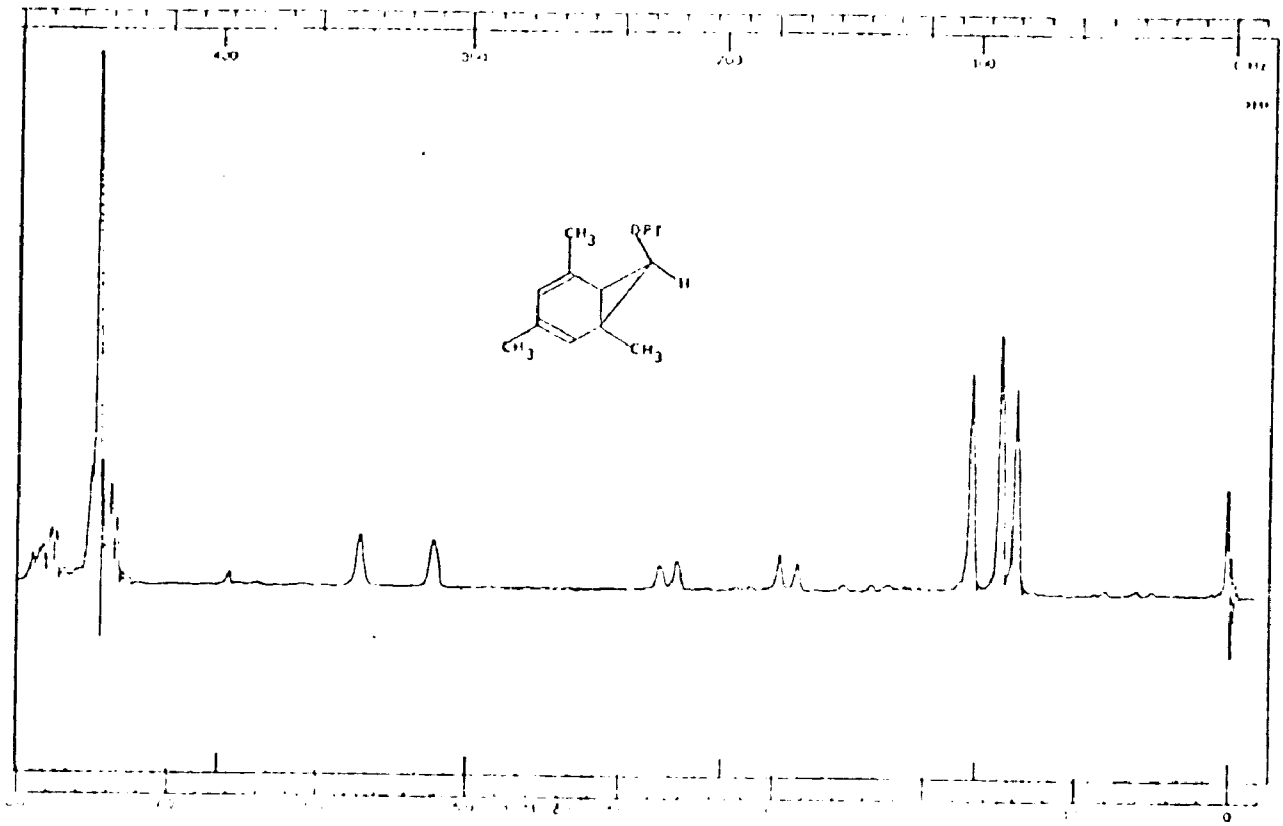
5-(1-DIAZOETHYL)-1,4-DIPHENYL-1,2,3-TRIAZOLE



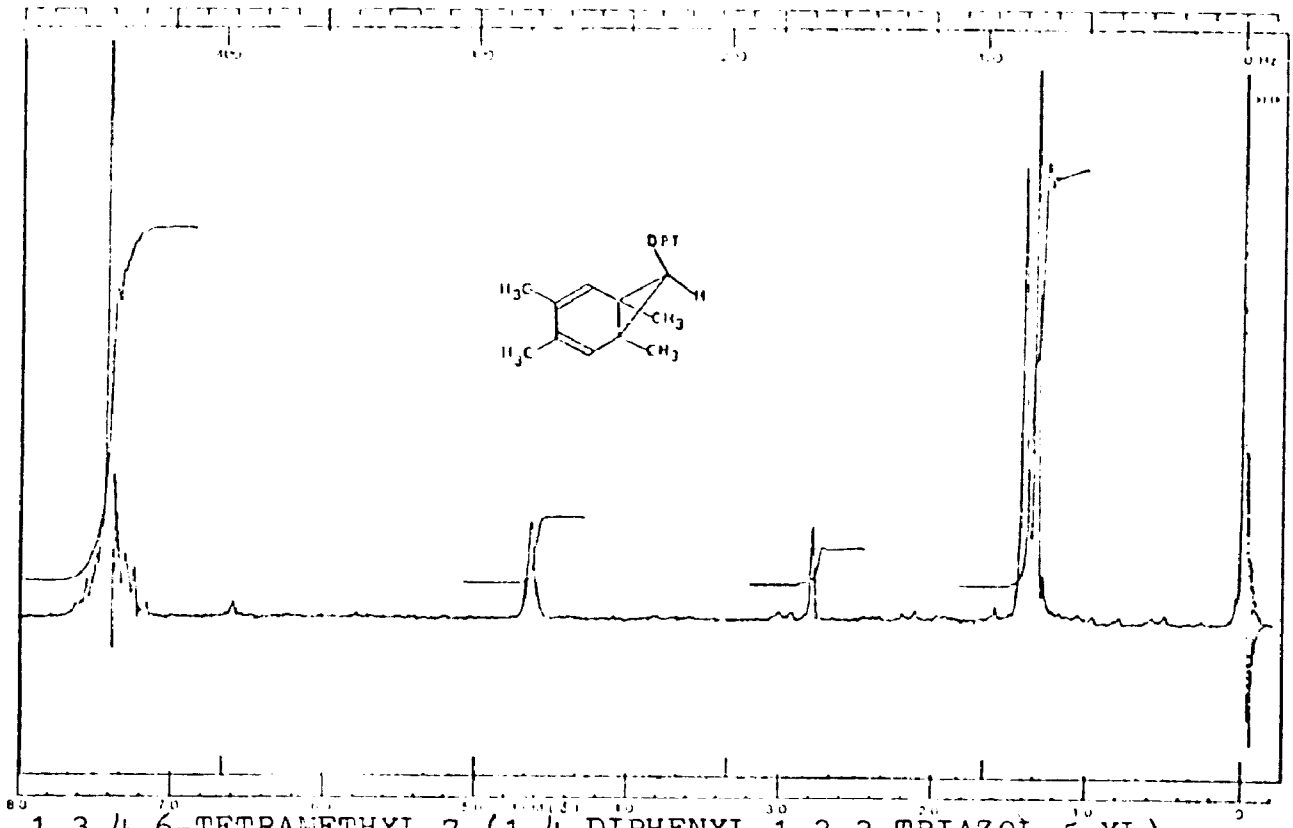
3,4-DIMETHYL-2-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)CYCLO-HEPTATRIENE



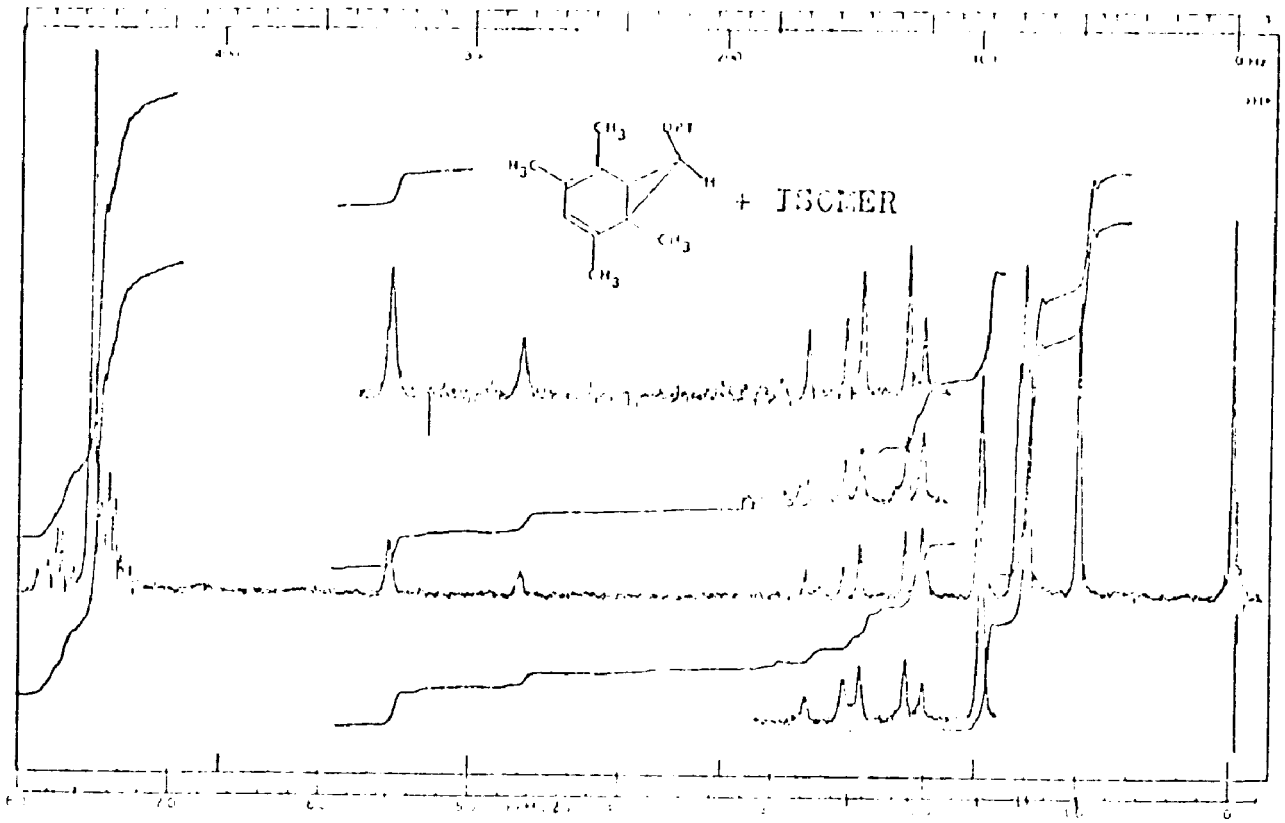
2,4-DIMETHYL-2-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)CYCLO-HEPTATRIENE



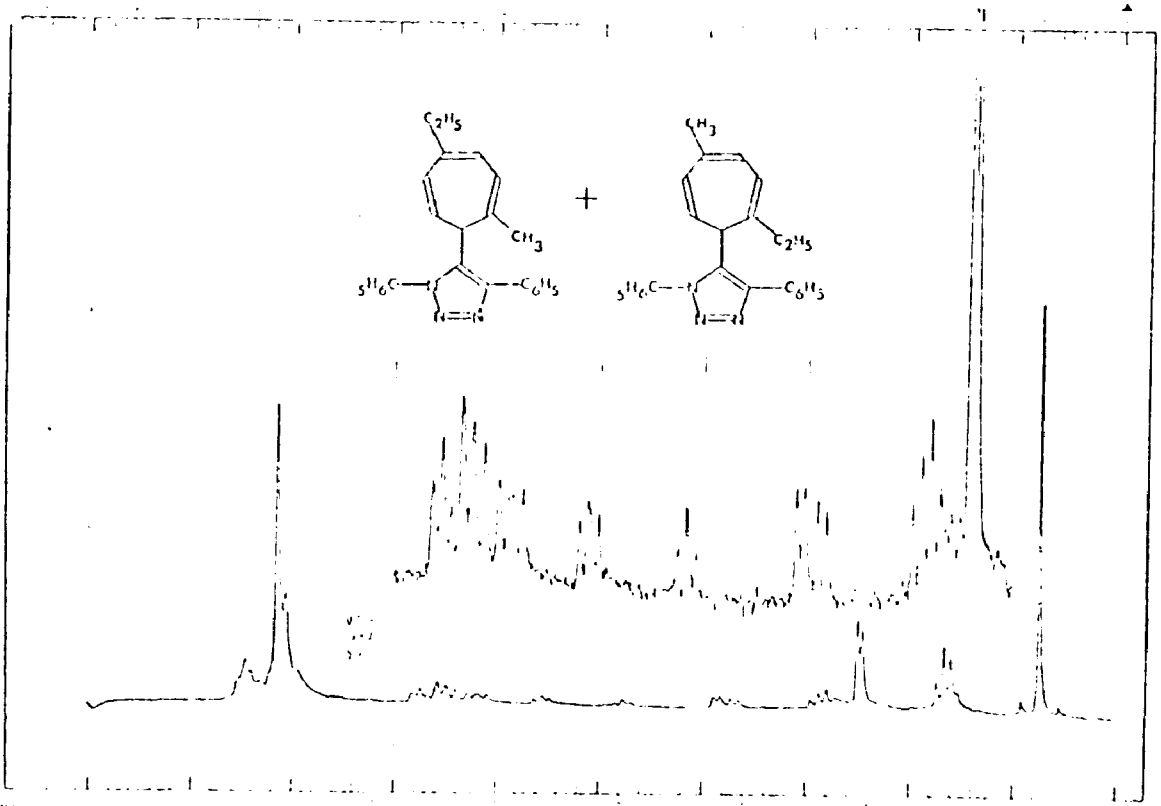
1,3,5-TRIMETHYL-7-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)-NORCARADIENE



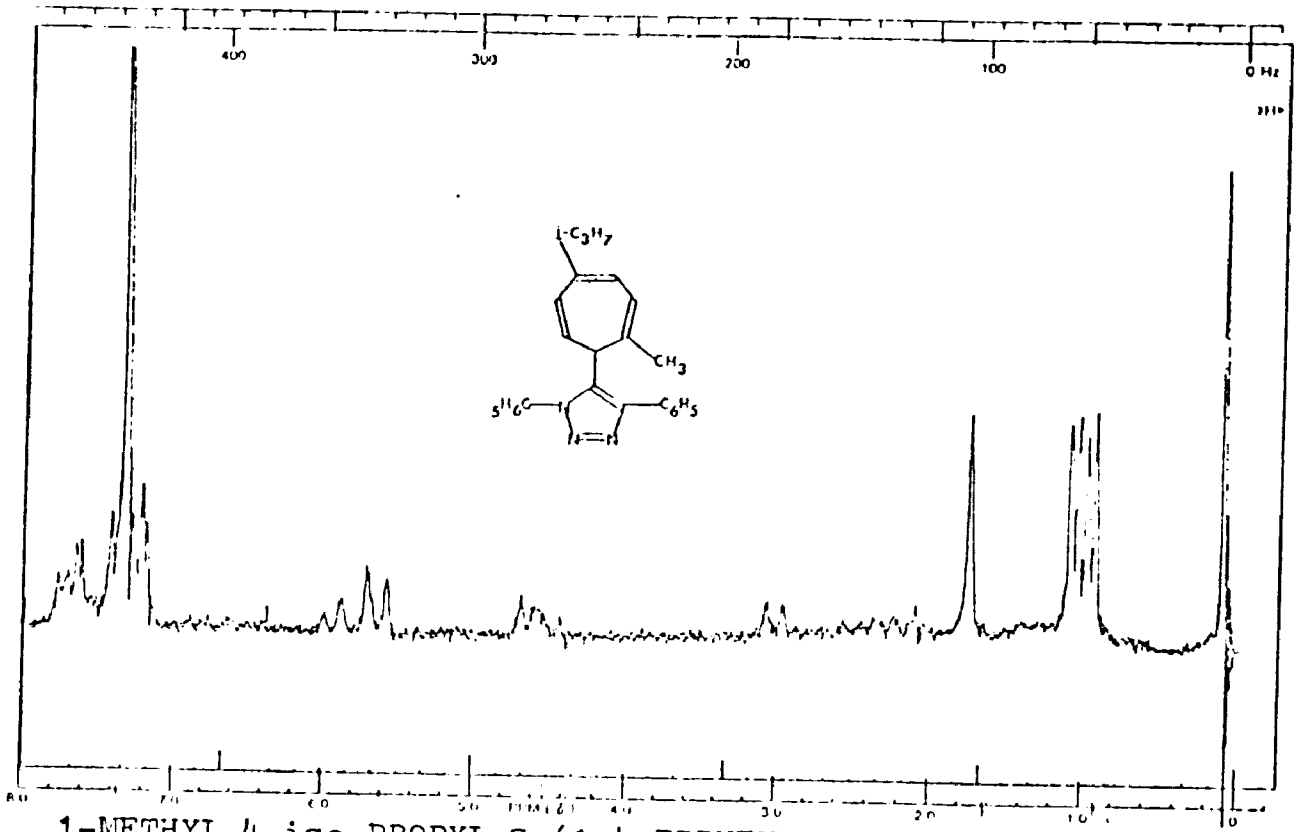
1,3,4,6-TETRAMETHYL-7-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)-NORCARADIENE



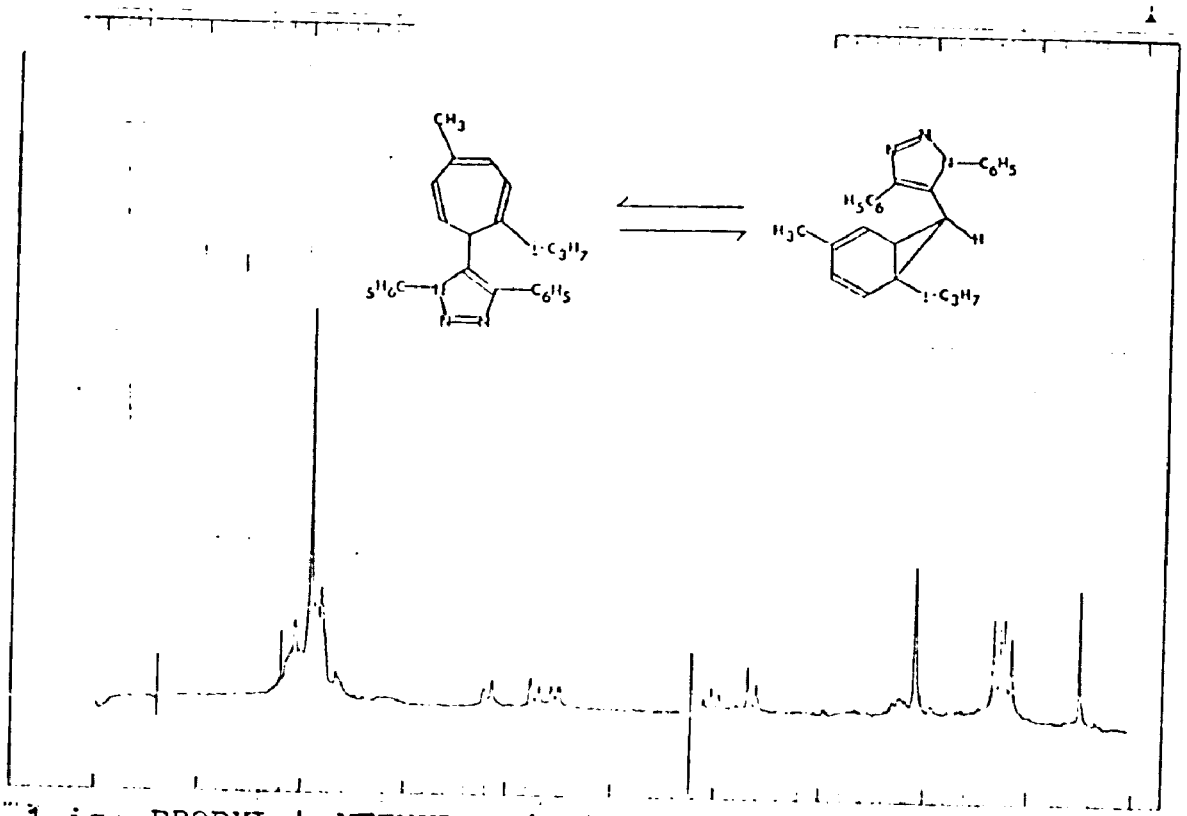
1,2,4,5-TETRAMETHYL-7-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)-NORCARADIENE



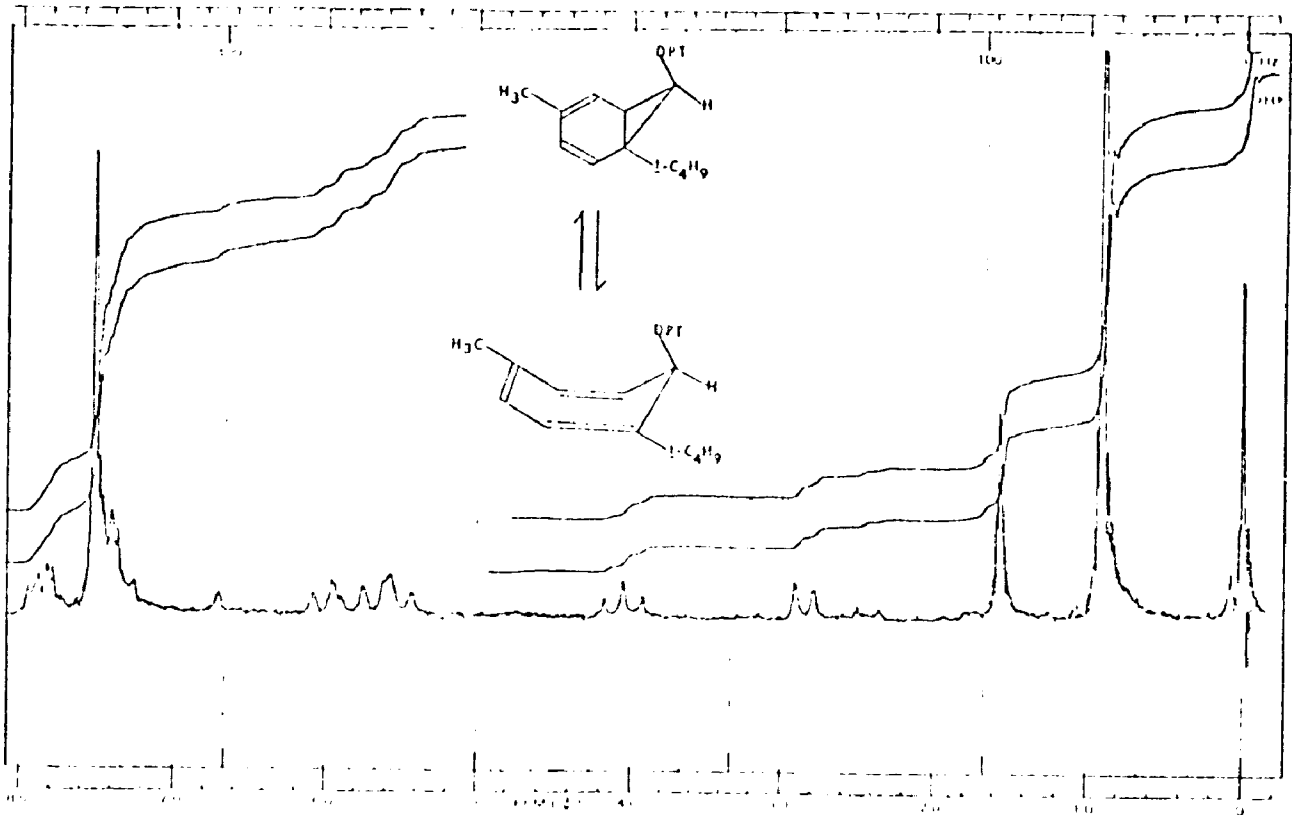
1-METHYL-4-ETHYL- & 1-ETHYL-4-METHYL- 7-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)CYCLOHEPTATRIENE



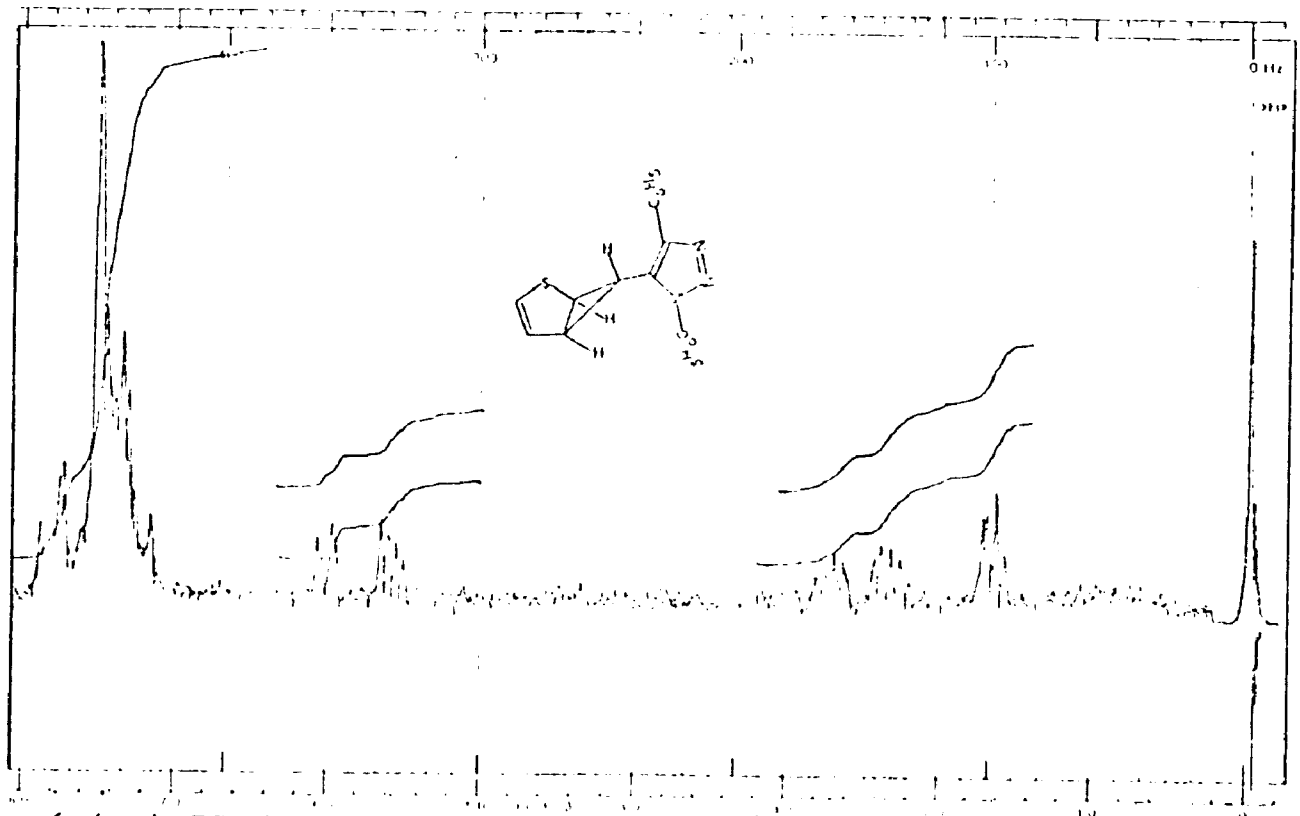
1-METHYL-4-<u>iso</u>-PROPYL-7-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)-CYCLOHEPTATRIENE



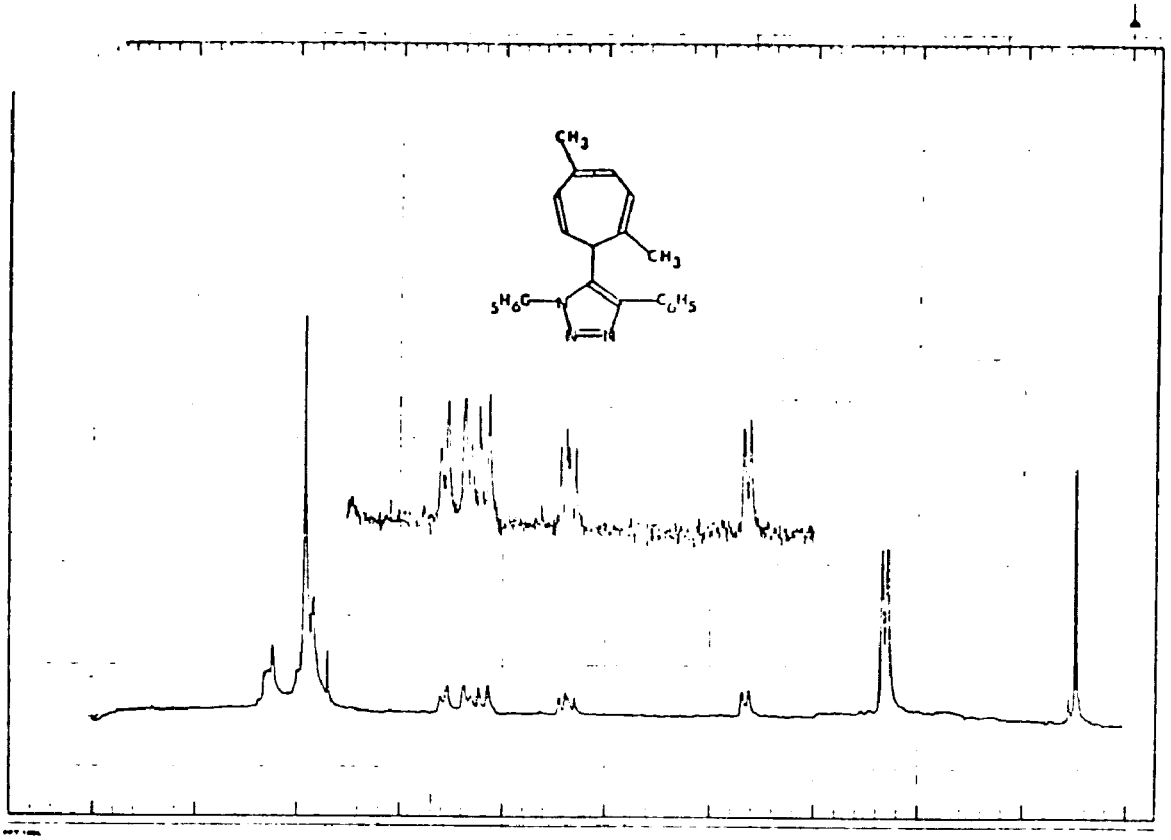
1-<u>iso</u>-PROPYL-4-METHYL-7-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)-CYCLOHEPTATRIENE



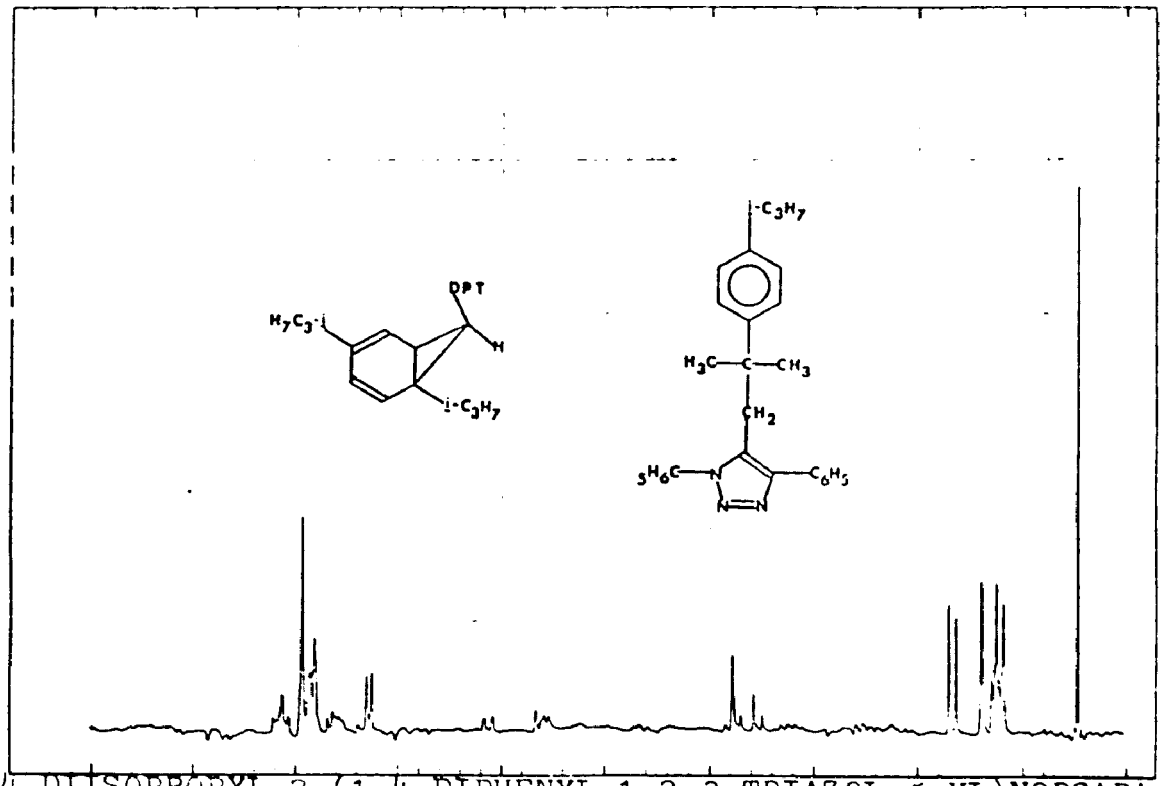
1-<u>tert</u>-BUTYL-4-METHYL-2-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)-CYCLOHEPTATRIENE



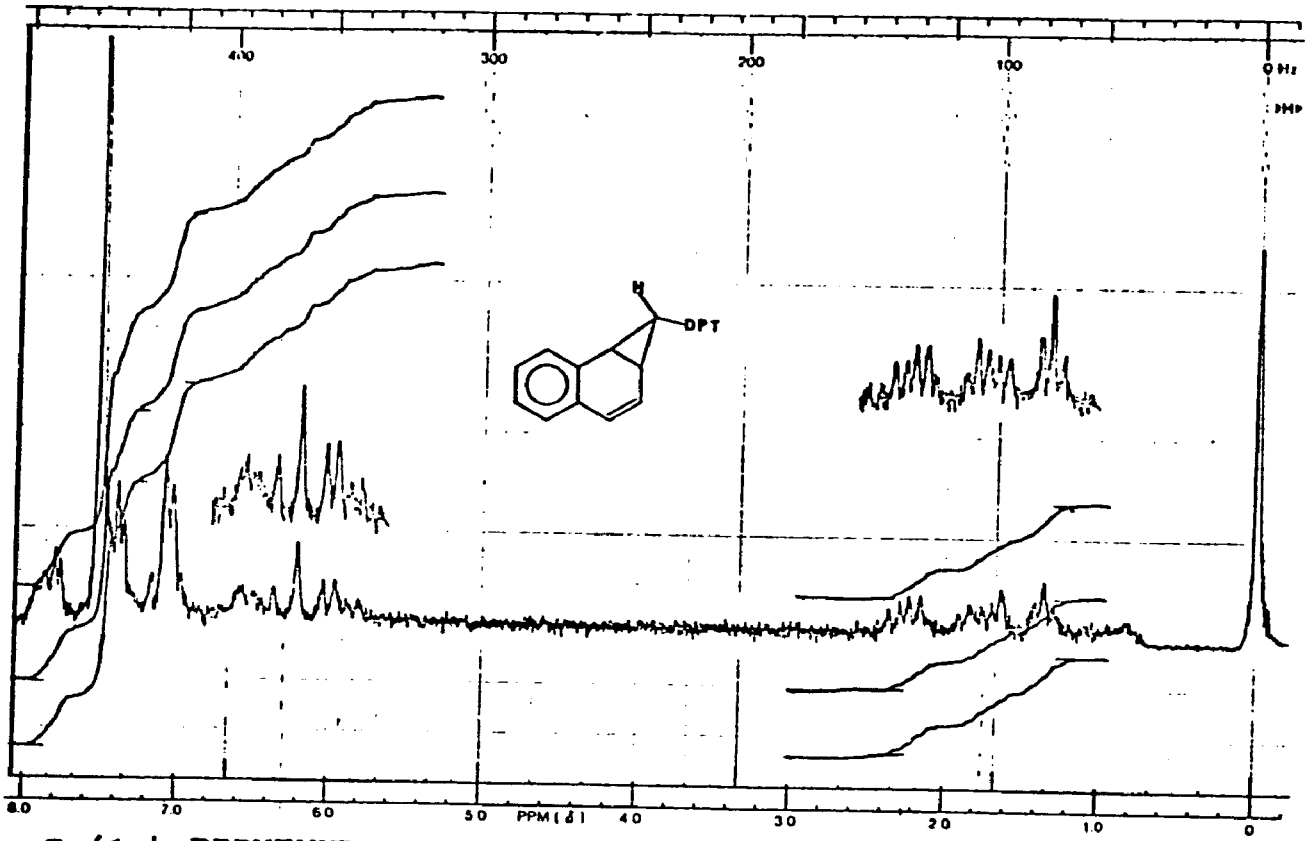
6-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)-2-THIABICYCLO(3.1.0)-HEX-3-ENE



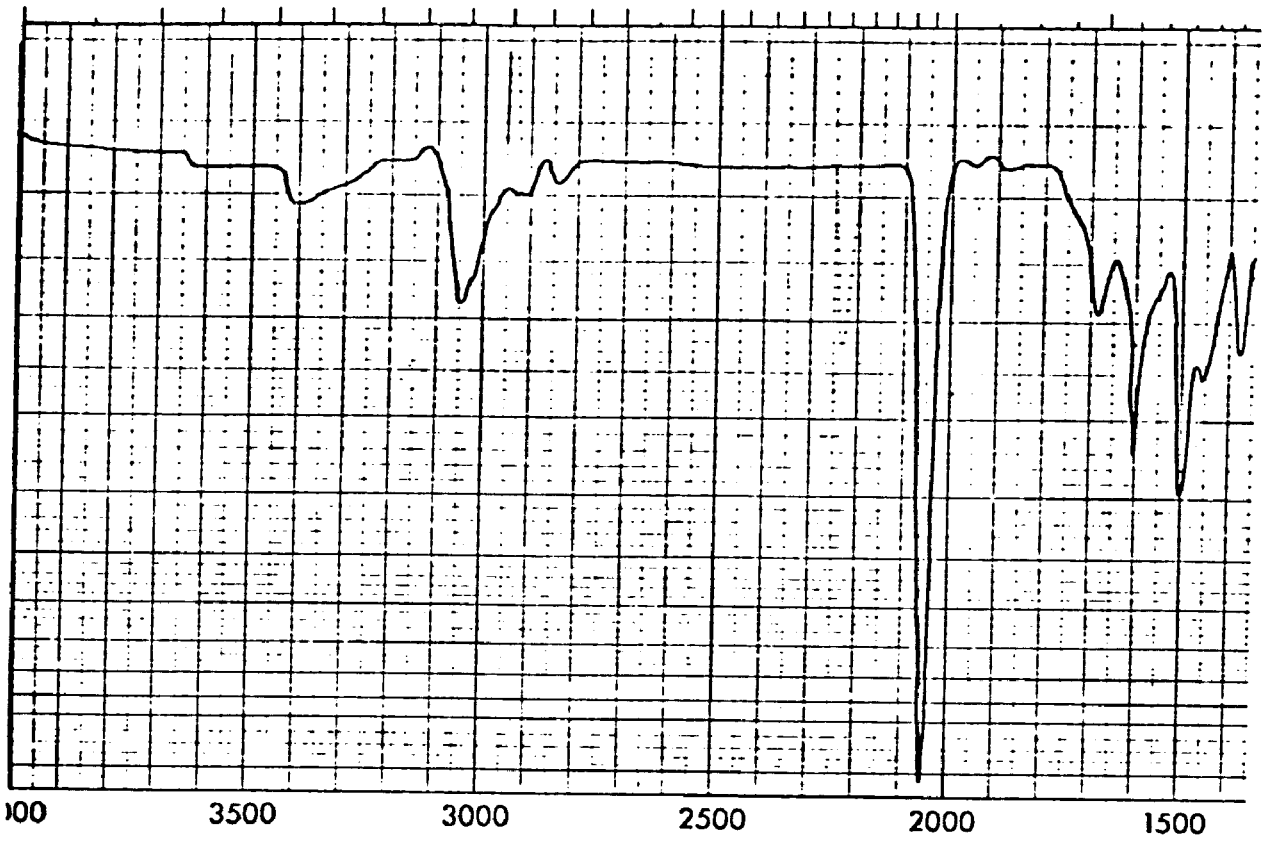
1,4-DIMETHYL-7-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)CYCLO-HEPTATRIENE

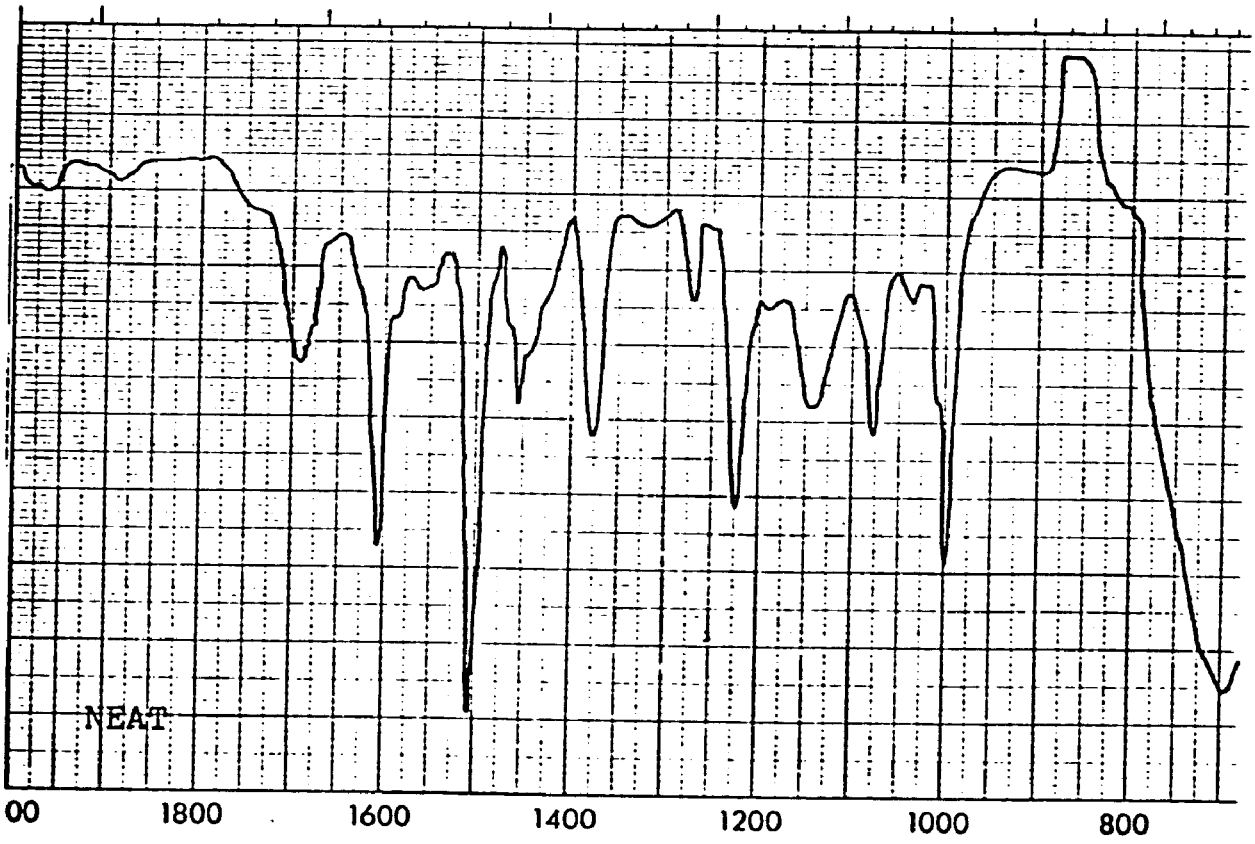


1,4-DIISOPROPYL-7-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)NORCARA-DIENE & 5-(2-METHYL-2-p-CUMYLPROPYL)-1,4-DIPHENYL-1,2,3-TRIAZOLE

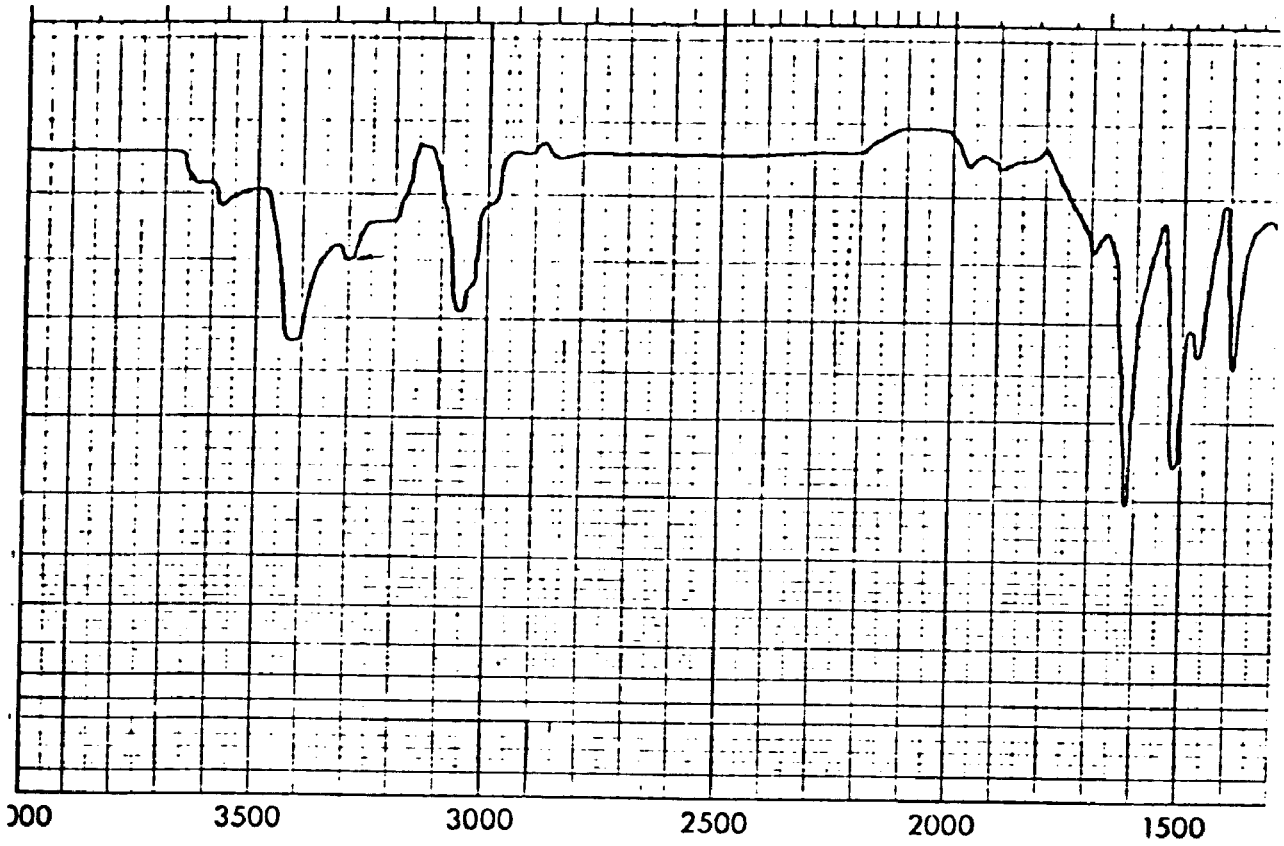


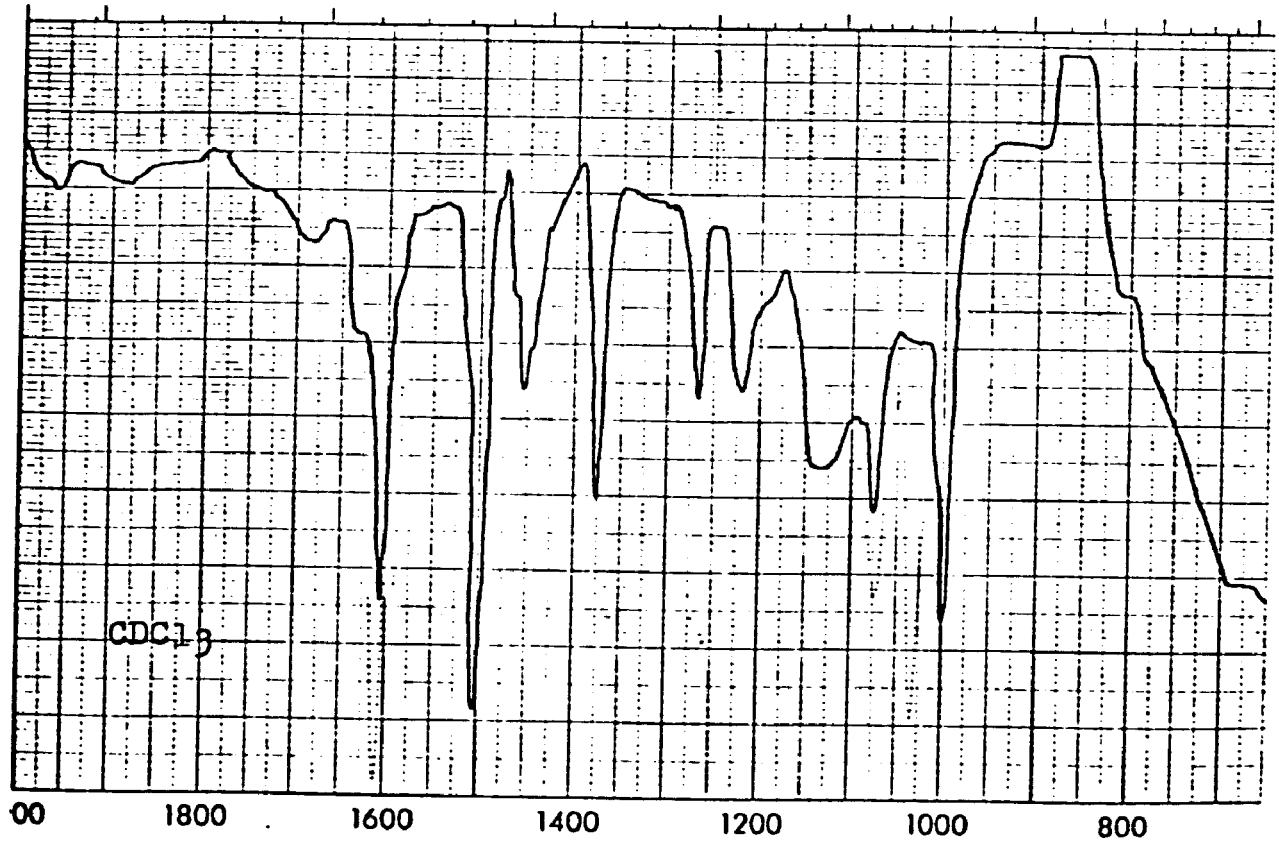
7-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)-2,3-BENZONORCARADIENE



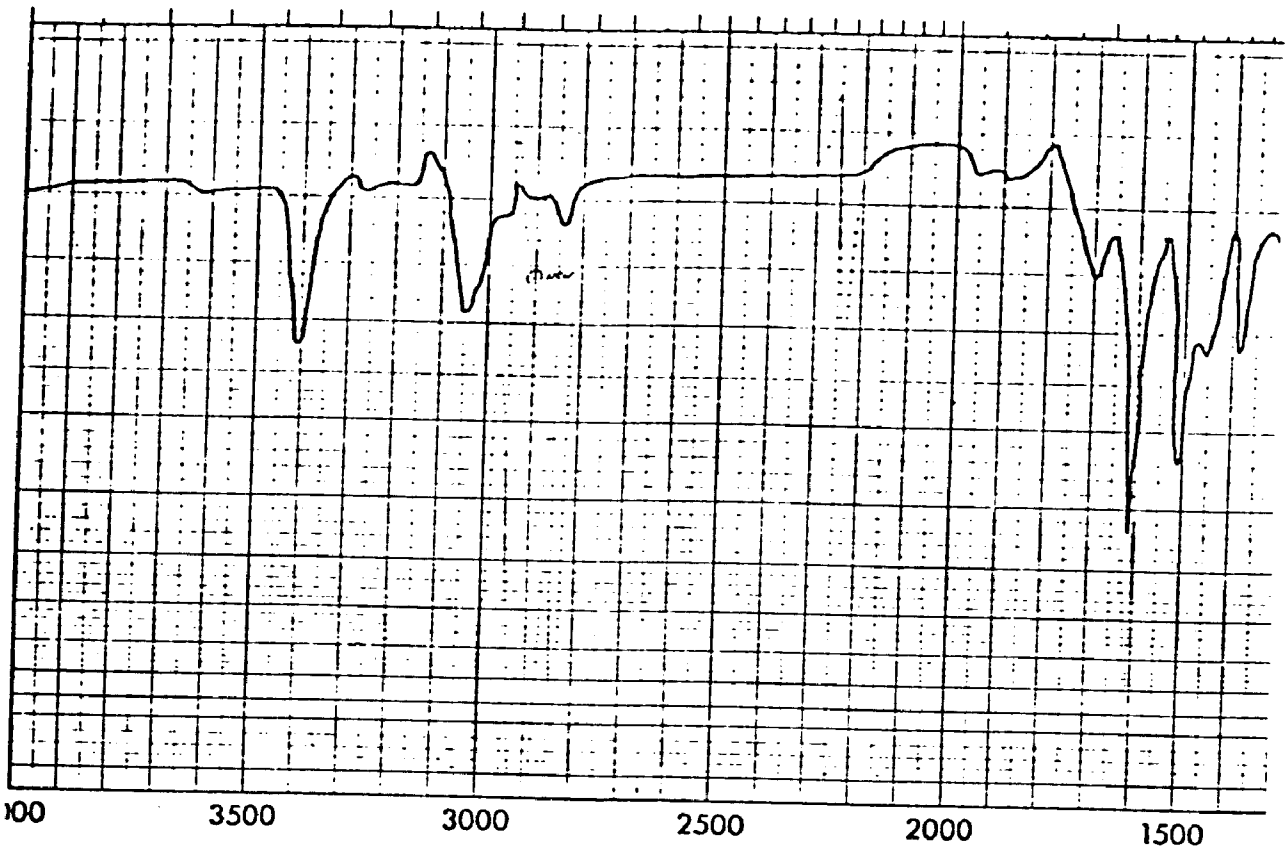


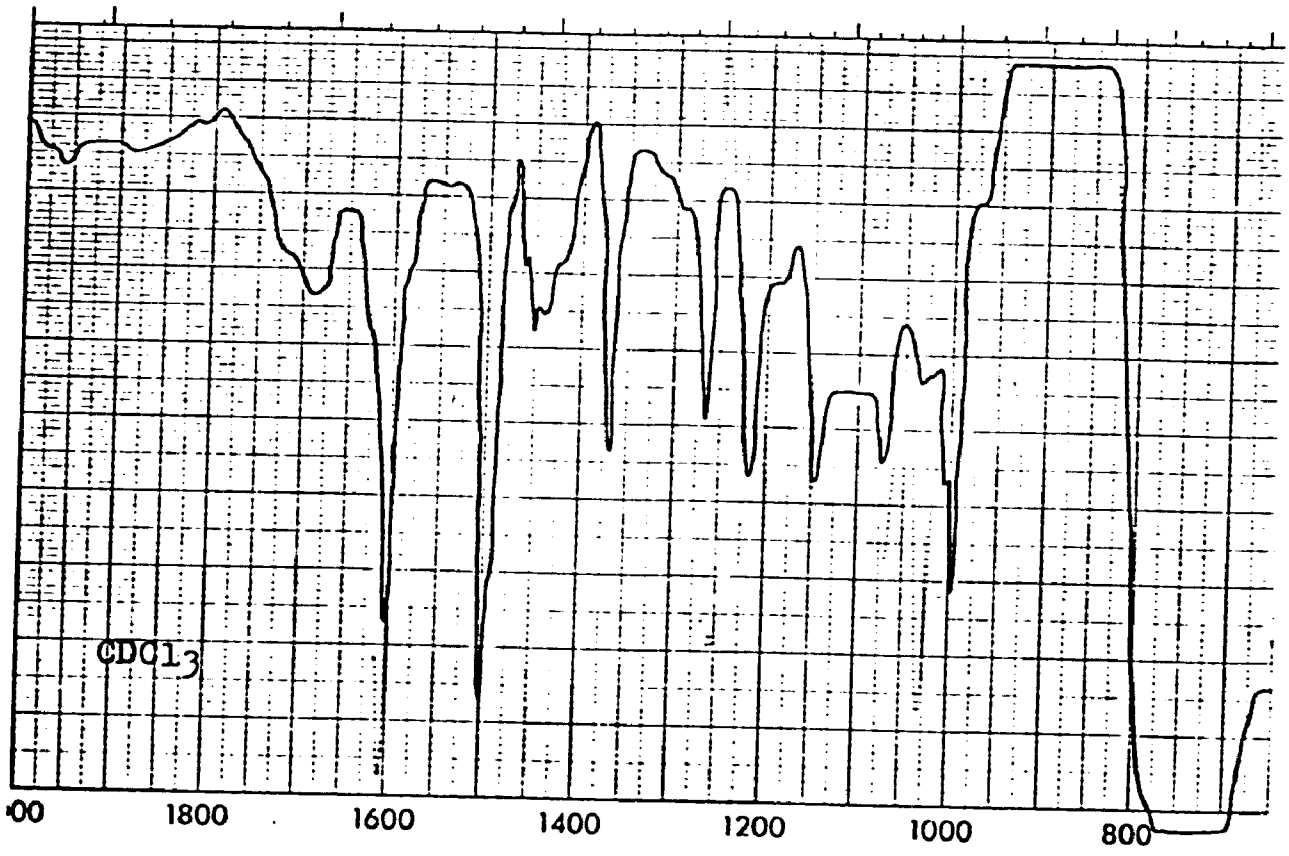
5-(1-DIAZOETHYL)-1,4-DIPHENYL-1,2,3-TRIAZOLE





ANTI-5-ACETYL-1,4-DIPHENYL-1,2,3-TRIAZOLE HYDRAZONE





SYN-5-ACETYL-1,4-DIPHENYL-1,2,3-TRIAZOLE HYDRAZONE

REFERENCES

1. J. De Boer and H. J. Backer, Org. Syn., Coll. Vol., 4, p. 250.

2. a) W. D. McPhee and E. Klingsberg, Org. Syn., Coll. Vol., 3, p. 119; b) F. Arndt, Org. Syn., Coll. Vol., 2, p. 165.

3. J. Hine, "Divalent Carbon," Ronald Press, New York, N.Y., 1964.

4. Reference 3, Chapter I.

5. a) W. Kirmse, Angew. Chem., 71, 537 (1959); b) E. Chinoporos, Chem. Rev., 63, 235 (1963); c) R. Huisgen, Angew. Chem., 67, 439 (1955); d) H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, 1961; e) R.A. Moss and M. Jones, Jr., "Carbenes," Vol. I, II, John Wiley and Sons, Inc., New York, N.Y., 1975.

6. W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1971.

7. a) L. Friedman and J. G. Berger, J. Amer. Chem. Soc., 82, 5728 (1960); b) W. von E. Doering and A. K. Hoffmann, ibid., 76, 6162 (1954).

8. a) D. Seyferth, M. E. Gordon, J. Yick-Pui Mui, and J. M. Burlitch, ibid., 89, 959 (1967); b) D. Seyferth and R. L. Lambert, Jr., J. Organometal. Chem., 16, 21 (1969).

9. a) G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Schechter, J. Amer. Chem. Soc., 89, 5736 (1967); b) Reference 5e, Vol. I, Chapter 1.

10. a) G. Wittig and K. Schwarzenback, Justus Liebigs Ann. Chem., 650, 1 (1962); b) E. Muller, H. Fricke, and W. Rundel, ibid., 661, 38 (1963); c) A. G. Davis, D. G. Hare, O. R. Khan, and J. Sikora, Proc. Chem. Soc., 172 (1961); d) G. D. Buckley, L. H. Cross, and N. H. Ray, J. Chem. Soc., 2714 (1950); e) C. E. H. Brown and A. Ledwith, Chem. and Ind., (London), 1180 (1957).

11. a) M. Schlosser and L. V. Chan, Angew. Chem., Intl. Ed., 10, 138 (1971); b) W. Kirmse and B. Graf von Wedel, ibid., 2, 481 (1963); c) U. Burger and R. Huisgen, Tetrahedron Lett., 3049 (1970).

12. a) H. M. Frey and M. T. H. Liw, J. Chem. Soc., A, 1916 (1970); b) G. A. Bottomley and G. L. Nyberg, Aust. J. Chem., 17, 406 (1964).

13. a) G. Wittig and K. Schwarzenback, Angew. Chem., 71, 652 (1959); b) H. E. Simmons and R. D. Smith, J. Amer. Chem. Soc., 80, 5323 (1958); c) R. S. Shank and H. Schechter, J. Org. Chem., 24, 1825 (1959).

14. a) W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc., 72, 2305 (1950); ibid., 75, 297 (1953); b) H. Meerwein, H. Dissenlnkötter, F. Rappen, H. von Rintelen, and H. von DeVloed, Justus Liebigs Ann. Chem., 604, 151 (1957); c) R. M. Lemmon and W. Strohmeier, J. Amer. Chem. Soc., 81, 106 (1959); d) G. A. Russell and D. G. Hendry, J. Org. Chem., 28, 1933 (1963).

15. E. von Müller, H. Kessler, H. Fricke and W. Kiedwisch, Justus Liebigs Ann. Chem., 675, 63 (1964).

16. P. S. Skell and R. M. Elter, Proc. Chem. Soc., 443 (1961).

17. a) G. L. Closs and R. A. Moss, J. Amer. Chem. Soc., 86, 4042 (1964); b) G. L. Closs, R. A. Moss, and J. J. Coyle, ibid., 84, 4985 (1962); c) G. L. Closs, L. E. Closs, and S. H. Goh, J. Org. Chem., 34, 25 (1969).

18. D. S. Crumrine and H. H. B. Yen, J. Amer. Chem. Soc., 98, 297 (1976).

19. R. A. Moss, J. Org. Chem., 30, 3261 (1965).

20. a) A. M. Trozzolo and E. Wasserman in Ref. 5e, Vol. 11, 1975, p. 193; b) E. Easserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, J. Chem. Phys., 40, 2408 (1964); c) R. W. Brandon, G. L. Closs, C. A. Hutchinson, Jr., B. E. Kohler, and R. Silber, ibid., 43, 2006 (1965).

21. W. J. Baron, M. E. Hendrick and M. Jones, Jr., J. Amer. Chem. Soc., 95, 6286 (1973).

22. I. Moritani, Y. Yamamoto, and S. I. Murahashi, Tetrahedron Lett., 5697 (1968), ibid., 5755 (1968).

23. Reference 6, Chapter 6.

24. P. A. S. Smith and J. G. Wirth, J. Org. Chem., 33, 1145 (1968).

25. J. G. Wirth, Ph.D. Thesis, University of Michigan, 1965.

26. P. A. S. Smith and E. M. Bruckmann, J. Org. Chem., 39, 1047 (1974).

27. E. M. Bruckmann, Ph.D. Thesis, University of Michigan, 1971.

28. E. Buchner and T. Curtius, Chem. Ber., 18, 2377 (1885).

29. R. O. Lindsay and C. F. H. Allen, Org. Syn., Coll. Vol., 3, p. 710.

30. a) C. F. H. Allen and C. O. Edens, Org. Syn., 25, p. 92; b) B. W. Howk and J. C. Sauer, J. Amer. Chem. Soc., 80, 4607 (1958).

31. J. C. Sheehan and C. A. Robinson, ibid., 73, 1207 (1951).

32. B. Staskun and O. G. Backeberg, J. Chem. Soc., Suppl. No. 1, 5880 (1964).

33. a) W. Kirmse and L. Horner, Justus Liebigs Ann. Chem., 614, 1 (1958); b) R. Huisgen, R. Knorr, L. Mobius, and G. Szeimies, Chem. Ber., 98, 4014 (1965); c) G. Wittig and A. Krebs, ibid., 94, 3260 (1961); d) F. Moulin, Helv. Chim. Acta., 35, 167 (1952).

34. a) A. Dornow and J. Helberg, Chem. Ber., 93, 2001 (1960); b) E. Lieber, T. S. Chao, and C. N. R. Rao, J. Org. Chem., 22, 654 (1957); c) E. Lieber, C. N. R. Rao and T. V. Rajbumar, ibid., 24, 134 (1959); d) G.R. Harvey, ibid., 31, 1587 (1966).

35. E. Lieber, T. S. Chao, and C. N. R. Rao, J. Org. Chem., 22, 654 (1957).

36. R. D. Rieke and S. E. Bales, J. Amer. Chem. Soc., 96, 1775 (1974).

37. J. Mathieu and J. Weill-Raymal, "Formation of C-C Bonds," Vol. I, Georg Thieme Publishers, Stuttgart, 1973, p. 160.

38. A. E. Senear, J. Wirth, and R. G. Neville, J. Org. Chem., 25, 807 (1960).

39. a) H. Plant and J. J. Ritter, J. Amer. Chem. Soc., 73, 4076 (1951); b) A. Knopfer, Monatsh., 18, 438 (1897).

40. a) K. Torssell, Tetrahedron Lett., 4445 (1966); b) A. Kalir, Org. Syn., 46, p. 81; c) F. Kröhnke, Angew. Chem., Intl. Ed., 2, 380 (1963).

41. O. Dinroth, E. Fusoni, and S. Marshall, Chem. Ber., 37, 3920 (1906).

42. P. A. S. Smith, "Open Chain Nitrogen Compounds," W. A. Benjamin, Inc., New York, N.Y., Vol. II, p. 152, 1966.

43. a) H. Nozaki, R. Noyori, and K. Sisido, Tetrahedron, 20, 1125 (1964); b) C. G. Gutsche, G. L. Bachmann, and R. S. Coffey, ibid., 18, 617 (1962); c) G. L. Closs and L. E. Closs, Tetrahedron Lett., 26 (1960).

44. K. R. Kopecki, G. S. Hammond, and P. H. Leermakers, J. Amer. Chem. Soc., 84, 1015 (1962).

45. J. E. Baldwin and R. A. Smith, ibid., 89, 1886 (1967).

46. a) E. Buchner and T. Curtius, Chem. Ber., 18, 2377 (1885); b) E. Buchner and L. Feldman, ibid., 36, 3509 (1903), and intermediate publications.

47. a) W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc., 72, 2305 (1950); b) ibid., 75, 257 (1953); c) T. Nozoe, Progr. Org. Chem., 5, 132 (1961).

48. K. Alder, R. Muders, W. Krane, and P. Wirtz, Justus Liebigs Ann. Chem., 627, 59 (1959).

49. J. E. Baldwin and R. A. Smith, J. Org. Chem., 32, 3511 (1967).

50. a) R. A. Abramovitch, J. Roy, and V. Uma, Canda.J. Chem., 43, 3407 (1965); b) also see Reference 45.

51. K. Conrow, M. E. H. Howden, and D. Davis, J. Amer. Chem. Soc., 85, 1929 (1963).

52. G. Maier, Angew. Chem., Intl. Ed., 6, 402 (1967).

53. G. Wittig, H. Eggers, and P. Duffner, Justus Liebigs Ann. Chem., 619, 10 (1958).

54. a) E. Ciganek, J. Amer. Chem. Soc., 87, 652 (1965); b) ibid., 89, 1454, 1458 (1967).

55. a) R. Huisgen and G. Juppe, Chem. Ber., 94, 2332 (1961); b) V. Boekelheide and C. D. Smith, J. Amer. Chem. Soc., 88, 3950 (1966).

56. J. D. Graham and M. T. Rodgers, ibid., 84, 2249 (1962).

57. A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N.Y., 1961, Chapter 11.

58. a) G. L. Closs, R. A. Moss, and J. J. Coyle, J. Amer. Chem. Soc., 84, 4985 (1962); b) U. Schollkopf, Chem. Eng. News, Aug. 5, 1963, p. 42; c) R. A. Moss, in "Selective Organic Transformations," Vol. 1, B. S. Thyagarajan, Ed., John Wiley and Sons, Inc., New York, N.Y., 1970.

59. W. E. Heyd and C. A. Cupas, J. Amer. Chem. Soc., 93, 6068 (1971).

60. a) F. A. L. Anet, ibid., 86, 458 (1964); b) F. R. Heusen and L. A. Smith, ibid., 86, 956 (1964).

61. a) H. Günther and R. Wehner, ibid., 97, 923 (1975); b) H. Günther, W. Peters, and R. Wehner, Chem. Ber., 106, 3683 (1973).

62. G. E. Hall and J. D. Roberts, J. Amer. Chem. Soc., 93, 2203 (1971).

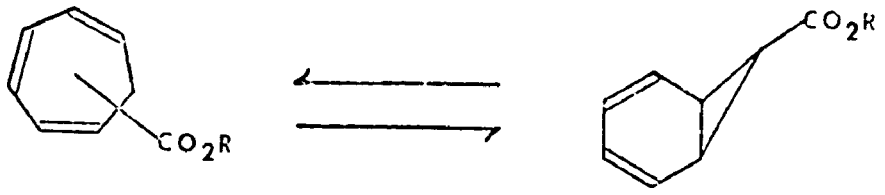
63. a) M. Görlitz and H. Günther, Tetrahedron, 25, 4467 (1969); b) H. Tsuruta, S. Mori, and T. Mukai, Chem. Lett., 1127 (1974); c) H. J. Reich, E. Ciganek, and J. D. Roberts, J. Amer. Chem. Soc., 92, 5166 (1970).

CHAPTER II

THE NORCARADIENE/CYCLOHEPTATRIENE PROBLEM

Introduction

The valence tautomerism of the norcaradiene/1,3,5-cycloheptatriene system has been deciphered only since the advent of high-resolution nuclear magnetic resonance spectroscopy.[1] Following a suggestion by his tutor, Curtius,[2] Buchner[3] attempted to identify the products formed in the thermal decomposition of diazoacetic ester in benzene. He found a mixture of esters ("Buchner esters or acids") that appeared to contain the ester of bicyclo[4,1,0]hepta-2,4-dienecarboxylic acid as well as three isomeric cycloheptatrienecarbonylic acids (R = CH_3, C_2H_5).



II I

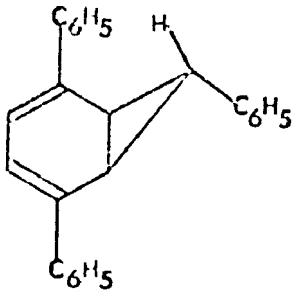
Doering,[4] in 1956, repeated Buchner's experiments and found that all Buchner esters have the same basic structure, and may be regarded as the four positionally isomeric cycloheptatriene esters. Thus it seemed that Buchner had not obtained a norcaradiene derivative. However, the controversy over the norcaradiene/cycloheptatriene structure of Buchner's esters did not remain buried for long. Günther and Wehner[5] elegantly demonstrated that Buchner's acid was

in a dynamic equilibrium between its norcaradiene and cycloheptatriene isomeric forms. They found that at -150°C, approximately 3% of the equilibrium mixture belonged to the norcaradiene structure. Thus, after almost a century of investigations on the Buchner esters and acids, the problem appears to have been solved.

Much interest has been focused on the cycloheptatriene/norcaradiene equilibrium,[6] and sustained efforts have been extended toward the preparation of stable, substituted norcaradienes, but only a handful of these have met with success. The most general entrance into the norcaradiene-cycloheptatriene valence-isomer system is by addition of carbenes to benzene and derivatives. The equilibrium for the valence isomerization I $\rightleftarrows$ II generally lies on the cycloheptatriene II side. However, briding the C_1 and C_6 positions with a three-atom bridge,[7] incorporation of one of the two double bonds into a condensed aromatic system,[8] or the introduction of strongly negative groups at the C_7 position[9] favor the norcaradiene isomer (I). Hoffmann[6] has postulated a net electron transfer from the cyclopropane to the π-system of the 7-substituent by mixing of unoccupied, low-lying molecular orbitals of the π-acceptor with the orbitals of cyclopropane. Such a transfer would weaken the C_1-C_6 antibonding and the 7-6 and 1-7 bonds, while strengthening the C_1-C_6 bond. Experimental evidence supports this interpretation; cyano, cyclopentadienyl, and cyclohexadienyl are good π-acceptors and all three form

stable norcaradienes.[9-11] These norcaradienes have been isolated pure, uncontaminated with the tropilidene isomer.

Whereas two cyano groups at the 7-position shift the equilibrium entirely to the norcaradiene, combinations of one cyano group or carbocthoxy group and one other substituent, such as CF_3, CO_2CH_3, C_6H_5, p-NO_2-C_6H_4, p-CH_3O-C_6H_4, CH_3, C_2H_5 and isopropyl group give rise to equilibrium mixtures of the norcaradiene and tropilidene forms.[12] One striking observation is the absence of norcaradiene systems with a hydrogen atom in the 7-position. However, T. Mukai and coworkers[13] prepared the norcaradiene III, the only known example of a non-bridged norcaradiene containing a



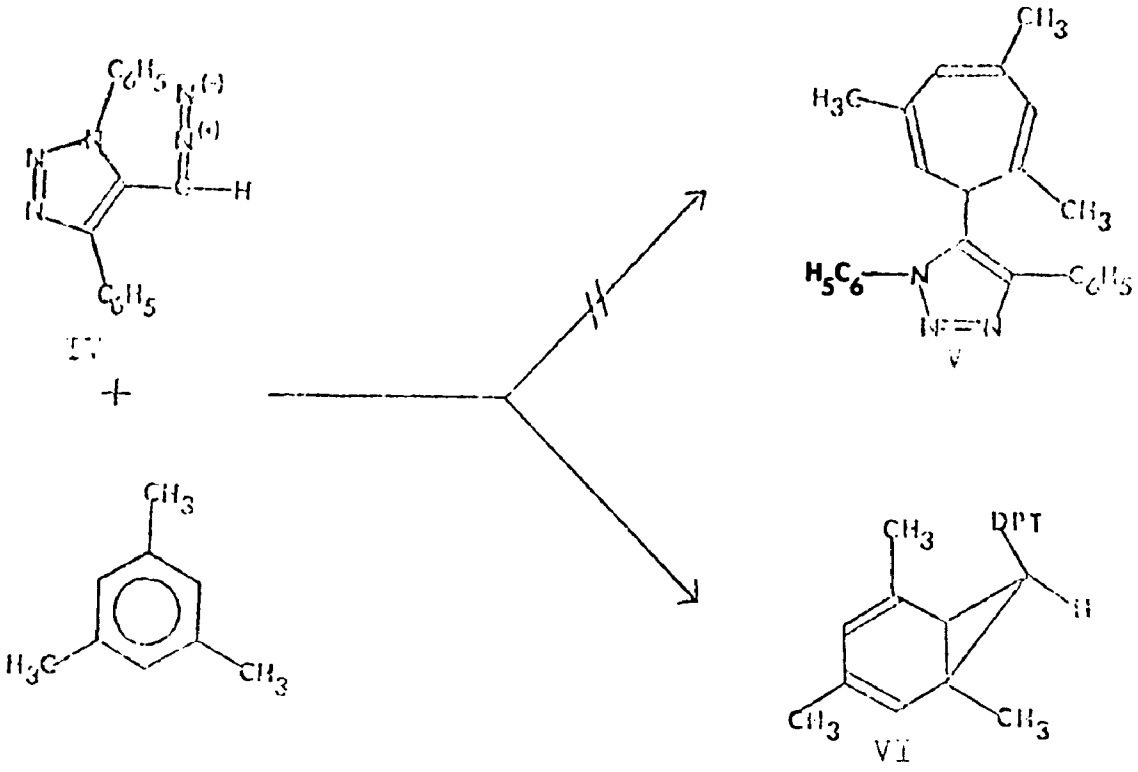
III

7-hydrogen, besides the 3% postulated by Günther and Wehner for Buchner's acid at -150°C.

The range generally observed for the olefinic hydrogens of 7,7-disubstituted norcaradienes is δ 5.8-6.7 for H_3 and H_4, and 6.0-6.2 for H_2 and H_5.[14] The olefinic protons in VI are shifted upfield to 5.26 and 5.73, presumably by the combined effects of electron-withdrawal and deshielding exerted by the 1,4-diphenyl-1,2,3-triazole.

These effects are also consistent with a syn orientation of the diene system and the diphenyltriazole moiety. This is also manifested in the chemical shift of the three methyl groups, which are slightly higher than those of the isomeric dimethyl-7,7-dicyanonorcaradienes.[10] Considerable variation in the chemical shifts of the 6-hydrogens had been observed for the available model compounds, namely 3.22, 3.12 for the dimethyl-7,7-dicyanonorcaradienes, 3.47 for 7,7-dicyanonorcaradiene,[10] 2.75 for the 7-cyano-7-amidinorcaradiene,[6] and 3.18 to 3.99 for 7-aryl-7-carbomethoxynorcaradienes.[14] In the spiro derivative H_1 and H_6 resonate at δ 3.60[11] and at 3.88 ppm in 2,5,7-triphenylnorcaradiene.[13] The value of 3.71 ppm observed for the adduct from diphenyltriazolylcarbene to mesitylene is thus within the expected range.[15]

The PMR spectrum of the material isolated from decomposition of diazo compound IV in mesitylene was quite unexpected; it clearly indicated that the cycloheptatriene V, which had been expected in analogy to the adducts with monosubstituted benzenes, had not been formed. However, the PMR spectrum was quite reasonable for the structural assignment of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazole-5-yl)norcaradiene (VI), the immediate product expected from addition of the carbene to mesitylene.[15] This change in isolated product prompted further investigations on the decomposition of IV in polysubstituted arene substrates.



2. Statement of Problem.

Two basic limiting cases may be discussed for the relationship between the norcaradiene and the cycloheptatriene ring systems: (a) Both compounds with norcaradiene structures and compounds with tropilidene structures can exist, and are to be regarded as independent entities with an energy barrier between the two systems so high that no interconversion takes place; (b) norcaradienes and tropilidenes are related by a valence-tautomeric equilibrium similar to that known for the bicyclo[4,2,0]octa-2,4-diene/cyclooctа-1,3,5-triene system.[16] As mentioned, the factors which govern the equilibrium are not fully understood. The decomposition of diazo compound IV in polysubstituted benzene substrates offered a unique opportunity to examine the dynamic equilibrium between norcaradiene and tropili-

dene isomers, especially in light of the dramatic differences obtained from decomposition of IV in monosubstituted benzene substrates as compared to mesitylene. To this end, the approach planned was to alter the size, position and number of alkyl substituents on the benzene nucleus, and to examine their subsequent effect on the norcaradiene/tropilidene dynamic equilibrium. The xylene series, p-ethyltoluene, p-cymene, 4-tert-butyltoluene, mesitylene and durene were chosen as substrate partners for diazo compound IV, with the hopes that a clearer picture of the factors which govern the norcaradiene/cycloheptatriene valence-bond isomerization could be obtained.

3. Discussion and Results.

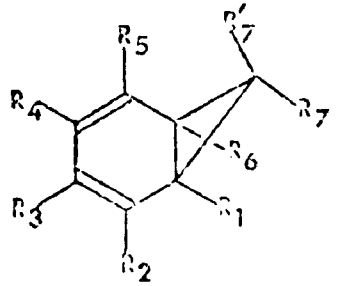
(1) The Mesitylene Case:

The thermal decomposition of diazo compound IV in mesitylene yielded the norcaradiene adduct VI.[16] The PMR spectrum (Table VI) clearly indicated that a one-to-one adduct of substrate and carbene was formed during the decomposition.

The ^{13}CMR spectrum of norcaradiene VI confirmed the structural assignment. Assignments were made on the basis of relative signal intensities and with the aid of coupled spectra. All of the possible tropilidene isomers would possess four alkyl carbon atoms; however, the ^{13}CMR spectrum clearly indicated that six alkyl-type carbon atoms

Table VI

PMR Spectrum of Norcaradiene Adduct VI. Comparison with Known Norcaradiene Adducts, Chemical Shifts in ppm, Relative to TMS



	Adduct VI			(a)		(b)		(c)		(d)		(e)
R_1	CH_3	1.40	H	3.22	CH_3	1.73	H	3.99	H	3.41	H	3.88
R_2	H	5.26	CH_3	2.13	H	6.04	H	6.26	H	6.27	ϕ	7.40
R_3	CH_3	1.69	H	6.19	H	6.27	H	5.95	H	5.83	H	6.75
R_4	H	5.73	H	6.19	CH_3	2.03	H	5.95	H	5.83	H	6.75
R_5	CH_3	1.50	CH_3	2.13	H	- -	H	6.26	H	6.27	ϕ	7.40
R_6	H	3.71	H	3.22	H	3.12	H	3.99	H	3.41	H	3.88
R_7	H	2.88	CN	- -	CN	- -	ϕ	- -	ϕNO_2	- -	H	1.08
R'_7	DPT[f]	7.50	CN	- -	CN	- -	CO_2CH_3	- -	CO_2CH_3	- -	ϕ	7.40

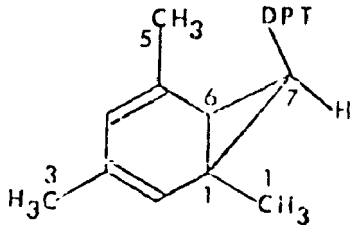
(a) 2,5-Dimethyl-7,7-dicyanonorcaradiene.[10] (b) 1,4-Dimethyl-7,7-dicyanonorcaradiene.[10] (c) 7-Phenyl-7-carbomethoxynorcaradiene.[14] (d) 7-(p-Nitrophenyl)-7-carbomethoxynorcaradiene.[14] (e) 2,5,7-Triphenylnorcaradiene.[13] (f) 1,4-Diphenyl-1,2,3-triazole.

were present (Table VII).

Table VII

^{13}CMR Spectrum of Norcaradiene Adduct VI:

Chemical Shifts in ppm, Relative to TMS

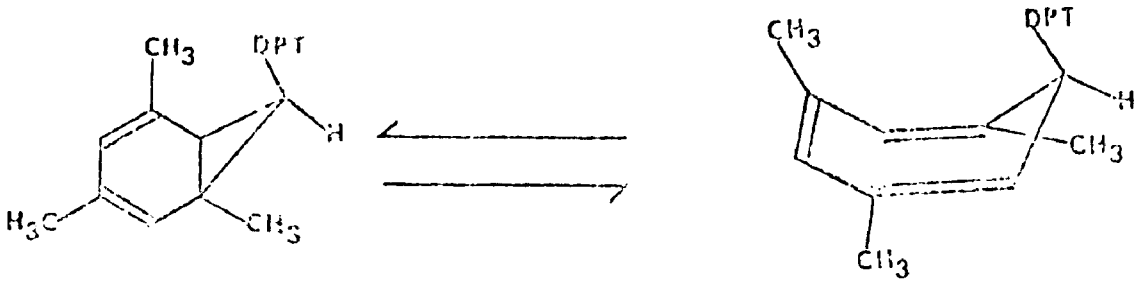


Adduct VI		Coupled spectra
CH_3-1	21.994	quartet
CH_3-3	23.555	quartet
CH_3-5	22.921	quartet
C-7	26.237	doublet
C-6	81.326	doublet
C-1	88.789	singlet
vinylic and aromatic carbons		123.492-146.425 (a)

(a) Due to the complexity of the vinyl and aromatic region, individual assignments were impossible.

The unusual ^{13}CMR chemical shifts observed for the C-1 and C-6 carbon atoms of compound VI could not simply be explained by distortions of the cyclopropane ring system, although a considerable amount of steric strain is believed to exist between the large diphenyltriazole group and the diene portion of the ring. These chemical shifts, however,

are consistent with a system in dynamic equilibrium between the norcaradiene VI and the valence-bond-isomeric tropilidene V.

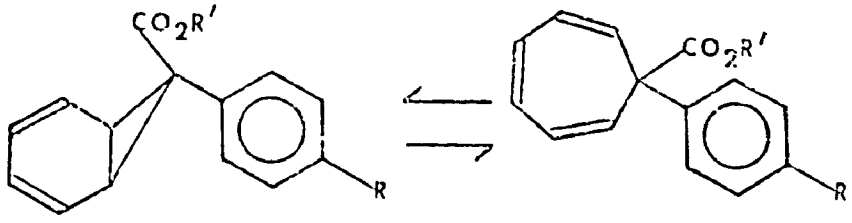


VI V

Cogent support was received by comparison with the $^{13}C_{MR}$ data of reported stable norcaradiene systems known to be in dynamic equilibrium (Table VIII).[17]

Table VIII

Chemical Shifts in ppm Relative to TMS



VII VII

	R	R'
a	H	CH_3
b	NO_2	CH_3
c	OCH_3	CH_3
d	H	C_2H_5

	VI	VIIa	VIIb	VIIc	VIId
C-1	88.789	74.8	64.0	71.4	80.2
C-6	81.326	74.8	64.0	71.4	80.2
C-7	26.237	38.4	34.3	36.4	40.4

The product from decomposition of diazo compound IV in mesitylene is the first example of a dynamic equilibrium between norcaradiene and tropilidene isomers possessing a hydrogen atom at the 7-position.

The variable temperature ^{13}CMR studies on 7-aryl-7-carbomethoxynorcaradiene by Günther and coworkers,[17] prompted the low-temperature spectroscopic investigations of adduct VI, represented in Figures 3 and 4. The PMR spectra show complete coalescence of the 6- and 2-hydrogens at -75 to -80°C, however identification of the two isomeric materials was impossible because of the temperature limitations of the T-60A NMR and the substantial line broadening observed at lower temperatures, Figure 3.

The ^{13}CMR spectra, Figure 4, demonstrate a dramatic change in the chemical shifts of the aliphatic carbon atoms corresponding to temperature variations. The three methyl signals and the C-7 carbon atom well defined at 0°C have completely collapsed by -50°C along with the disappearance of the C_1 and C_6 carbon atoms. At -100°C the aliphatic region supports seven new signals which may be attributed to pure norcaradiene VI and tropilidene V. Once again, a coalescence temperature of -75 to -85°C is indicated from the ^{13}CMR spectra. The relative intensities of new absorptions indicate that the tropilidene and norcaradiene isomers are present in approximately a 1:1 ratio. Though definitive assignment of the absorptions was impossible, the presence of both isomers was ascertained. A ratio of

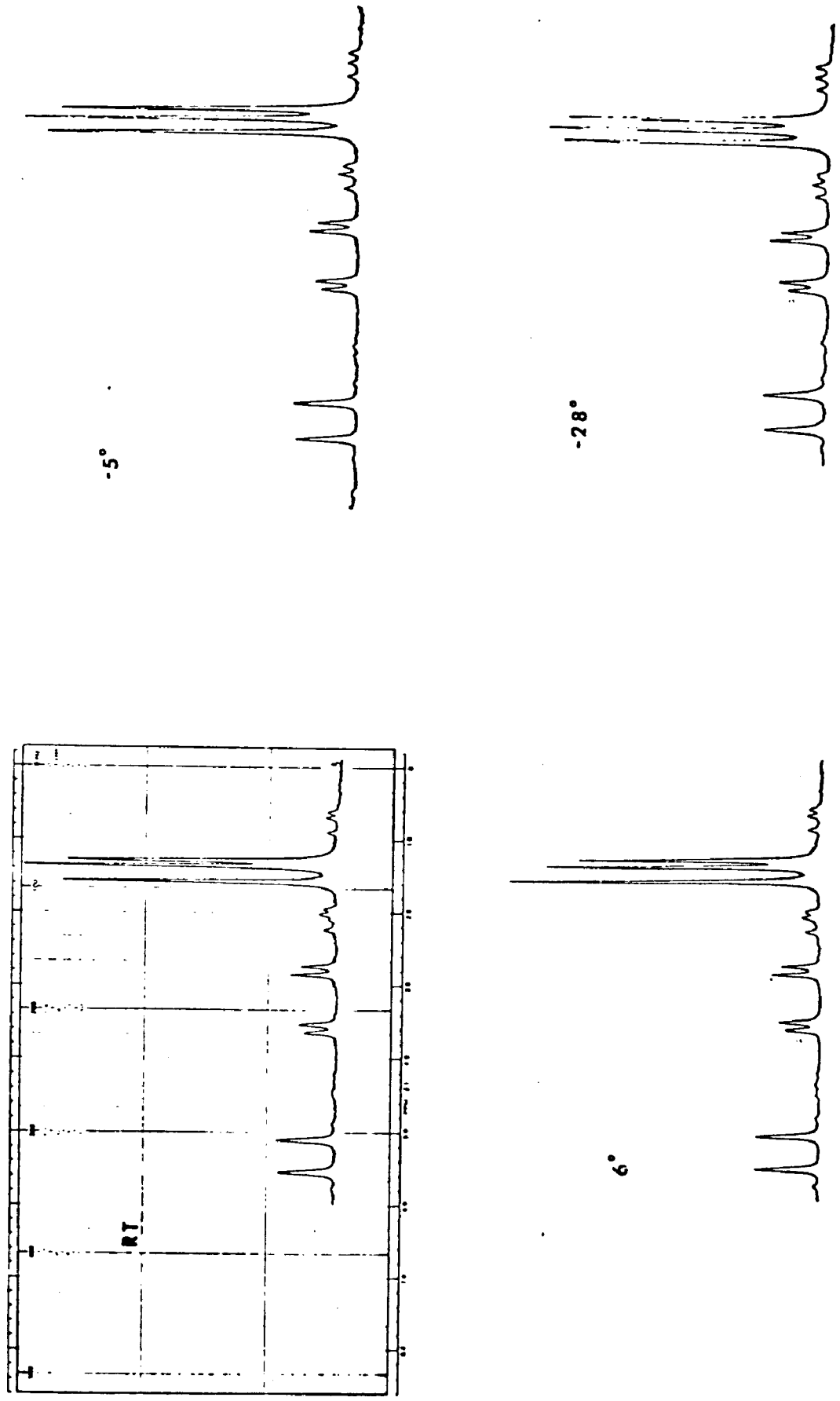


Figure 3. Variable temperature PMR spectra of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene. $CDCl_3/CS_2$ (50:50) locked on chloroform.

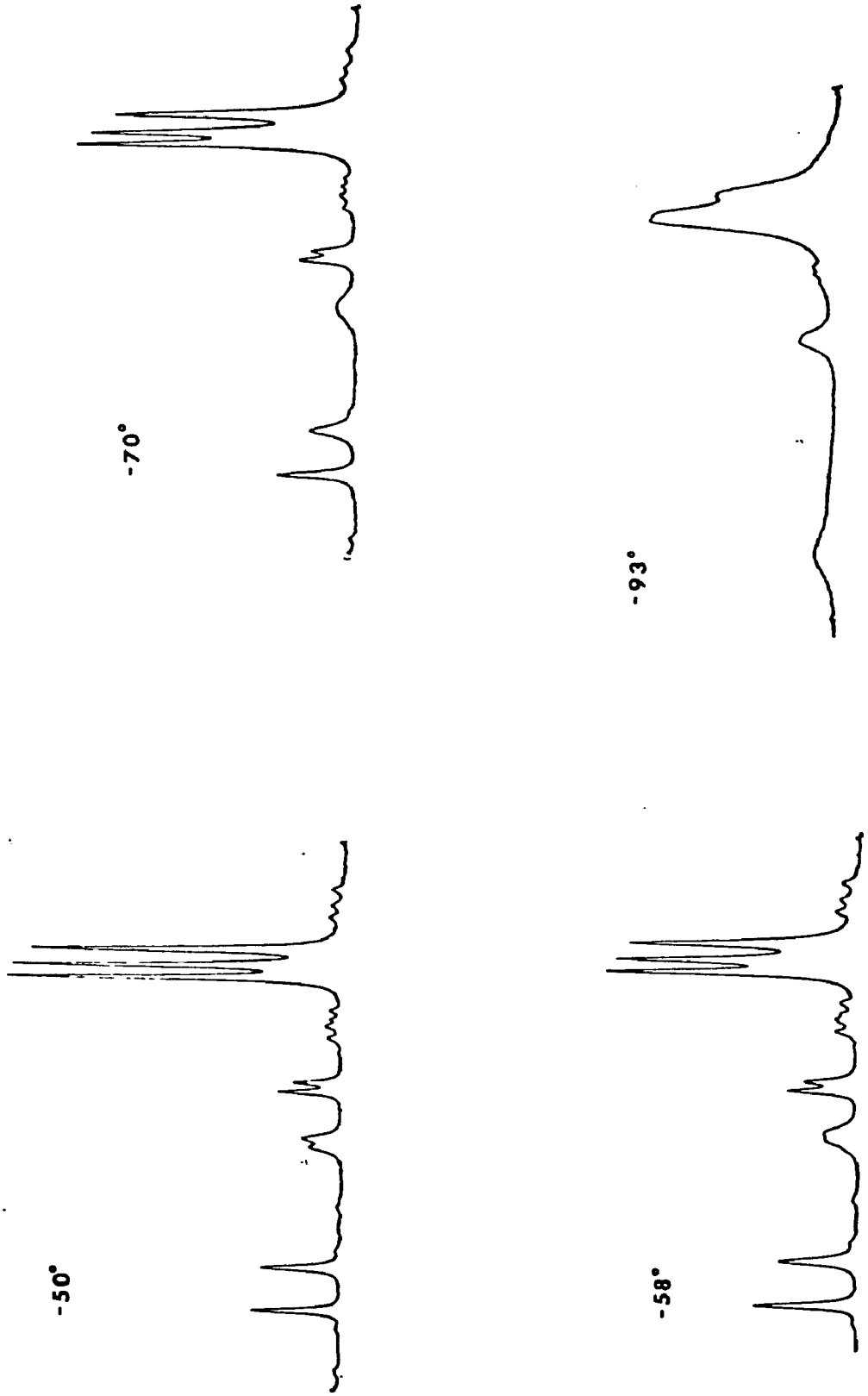
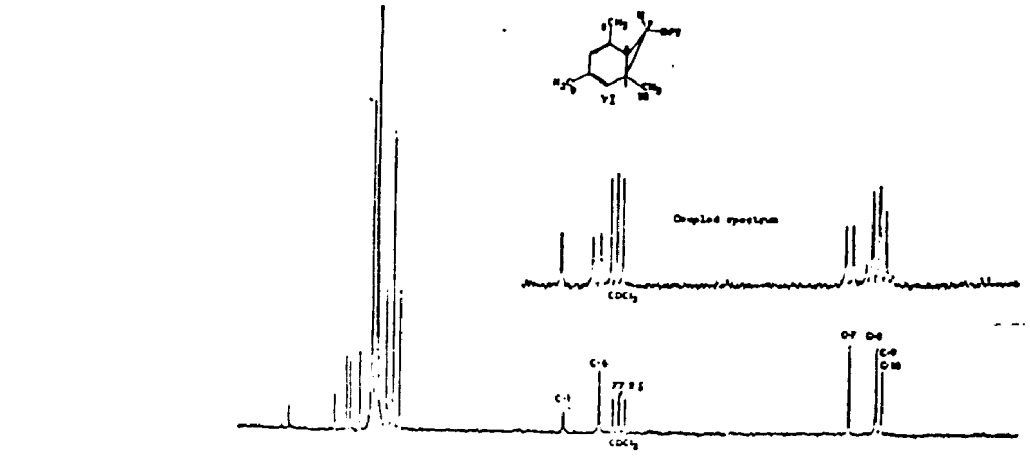


Figure 3 continued.



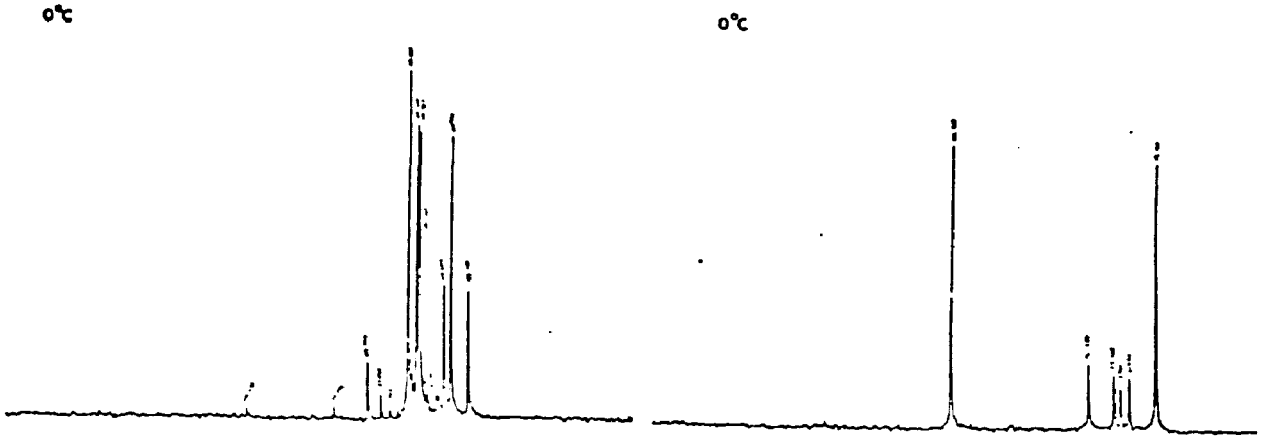




Figure 4. Variable temperature ^{13}CMR spectra of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-norcaradiene. CD_2Cl_2/CH_3CH_2Cl (80:20).

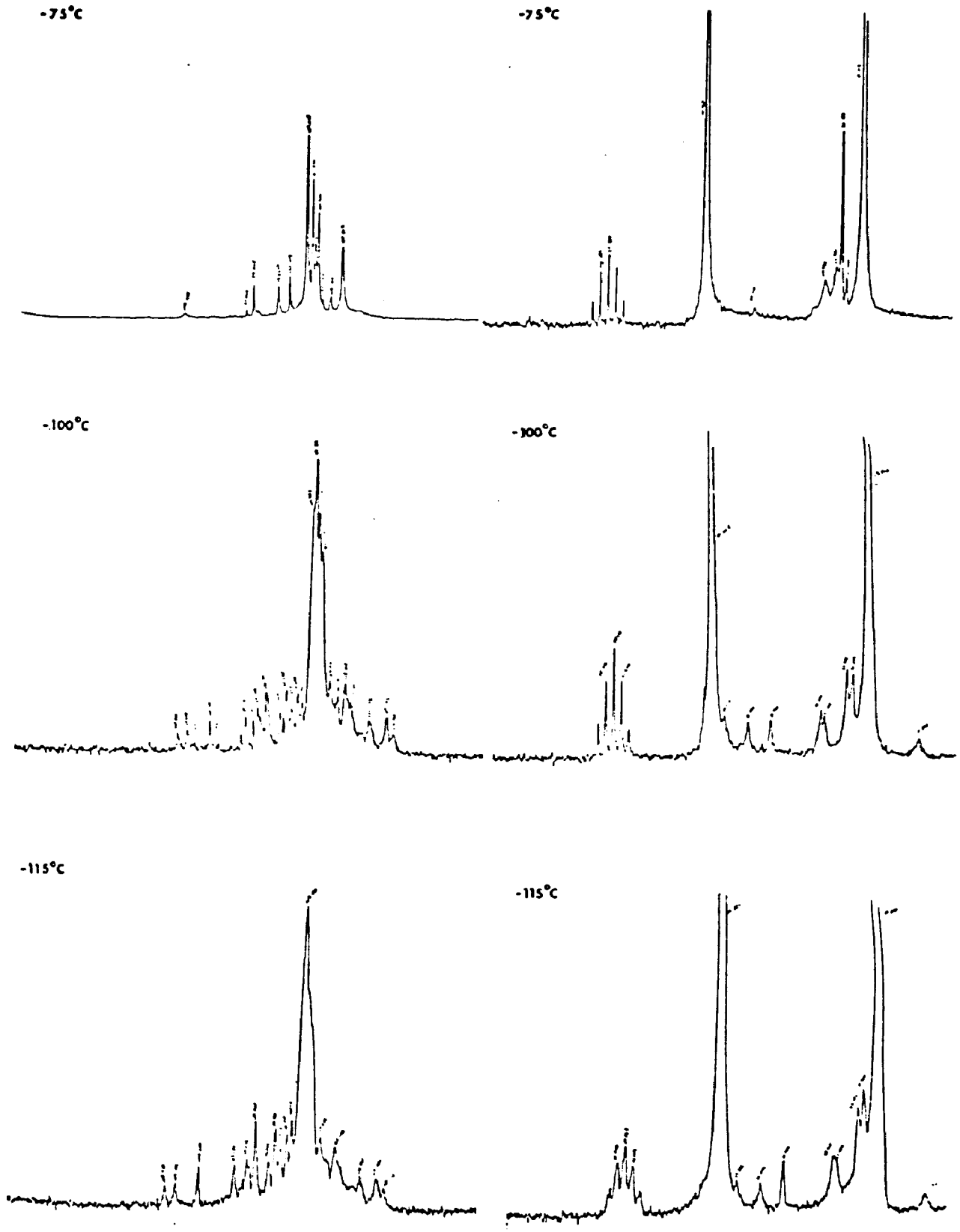


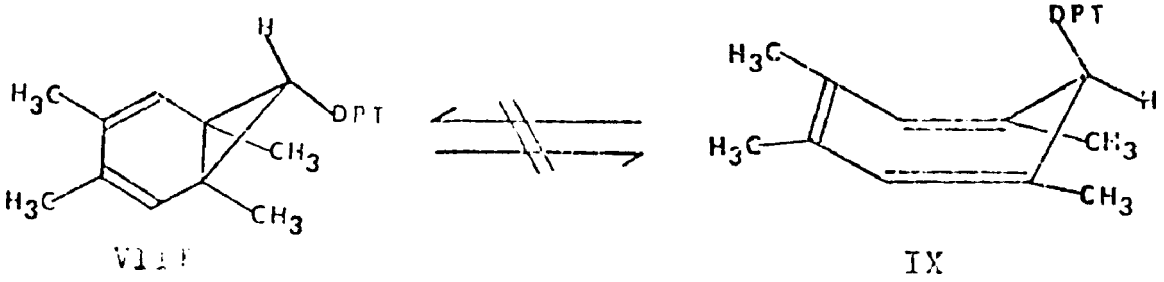
Figure 4 continued.

approximately 1:1 indicates a $\Delta G°$ of approximately ± 100 cal/mole, most likely in favor of norcaradiene side of the equilibrium. This conclusion is in accord with the observations of Hall and Roberts[14] on the 7-aryl-7-carbomethoxy-norcaradiene systems.

(2) The Durene Case.

The thermal decomposition of diazo compound IV in durene yielded the norcaradiene VIII as the major product. The PMR and ^{13}C NMR spectra (Tables IX and X, respectively) indicates that the norcaradiene structure assignment is correct especially in light of the results obtained from decomposition in mesitylene.

Unlike the mesitylene adduct VI, low-temperature PMR studies of norcaradiene VIII revealed that no equilibrium existed between VIII and the corresponding tropilidene isomer IX.



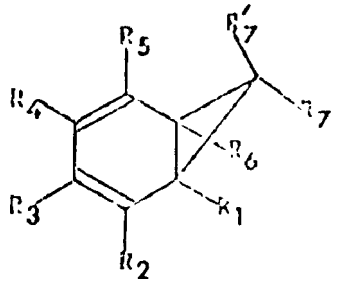
VIII IX

Even at -90°C, no coalescence or line broadening was observed. In light of the observations made on norcaradiene VI, one would expect that increased steric interactions

Table IX

PMR Spectrum of Norcaradiene VIII.

Chemical Shift in ppm Relative to TMS



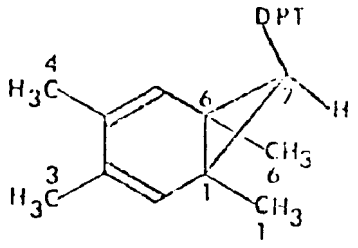
	Adduct VIII		Adduct VI	
R_1	CH_3	1.38	CH_3	1.40
R_2	H	4.72	H	5.26
R_3	CH_3	1.46	CH_3	1.69
R_4	CH_3	1.46	H	5.73
R_5	H	4.72	CH_3	1.50
R_6	CH_3	1.38	H	3.71
R_7	H	2.87	H	2.88
R'_7	DPT	7.51	DPT	7.50

introduced by the additional methyl substituent would increase the activation energy required for the valence-bond isomerization. Since this was not the case, the only conclusion to be drawn is that the tetramethyl-norcaradiene VIII exists solely in the norcaradiene form uncontaminated by its tropilidene isomer.

Table X

^{13}CMR Spectrum of Norcaradiene Adduct VIII:

Chemical Shifts in ppm Relative to TMS



Adduct VIII		Coupled Spectrum
CH_3-1 = CH_3-6	19.20	quartet
CH_3-3 = CH_3-4	22.72	quartet
C-7	27.27	doublet
C-1 = C-6	63.37	singlet
Vinylic and aromatic carbons	124-52-147.64 (a)	

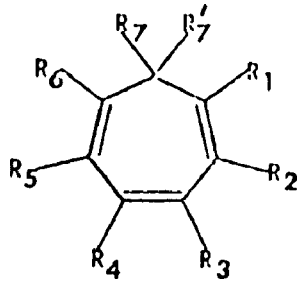
(a) Due to the complexity of the vinyl and aromatic region, individual assignments were impossible.

3. The Xylene Series.

As described in Chapter I, decomposition of diazo compound IV in o-, m- and p-xylene resulted in the isolation of one major tropilidene adduct in each case, XVII, XVI and X, respectively. The PMR spectrum (Table XI) clearly indicates that a one-to-one adduct of substrate and carbene was formed during the decomposition. The chemical shifts (Table XI) correlate well with those observed for cycloheptatriene,[18] which appear at 5.28, 6.12,

Table XI

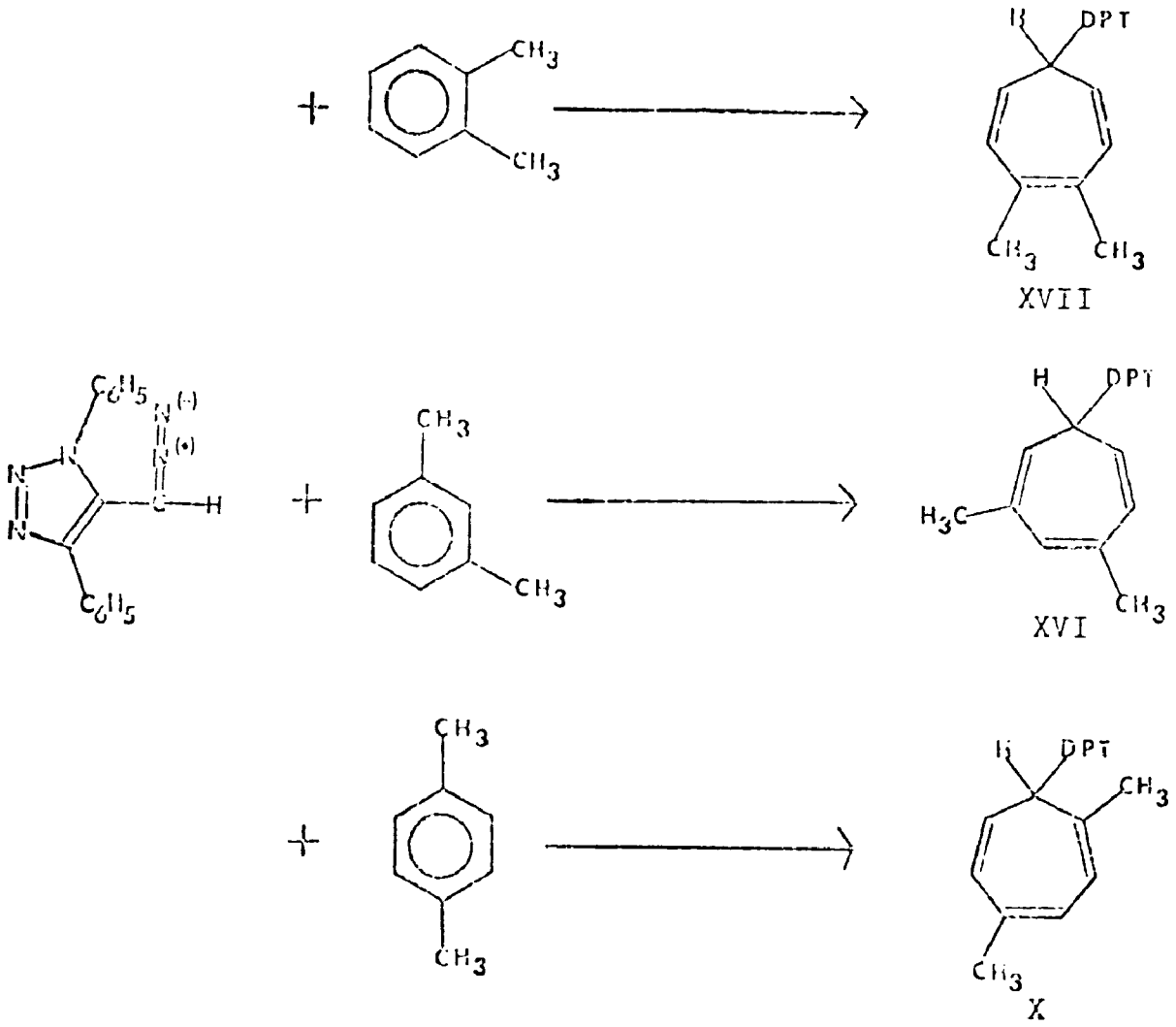
Chemical Shifts in ppm Relative to TMS



	Adduct X		Adduct XVI		Adduct XVII	
R_1	CH_3	1.81	H	4.37	H	4.61
R_2	H	5.88	CH_3	1.75	H	5.81
R_3	H	6.11	H	6.13	CH_3	1.82
R_4	CH_3	1.86	CH_3	1.93	CH_3	1.82
R_5	H	5.72	H	5.80	H	5.81
R_6	H	4.90	H	4.67	H	4.61
R_7	H	3.19	H	2.96	H	2.82
R'_7	DPT	7.47	DPT	7.50	DPT	7.45

6.55 and 2.20 ppm for the hydrogens in the 1-, 2-, 3-, and 7-positions, respectively.

Unlike the mesitylene adduct VI, low-temperature PMR studies of tropilidenes X, XVI, and XVII revealed that no equilibrium existed between the tropilidenes and their corresponding norcaradiene isomers. Even at -90 to -100°C, no coalescence or line broadening was observed. It is significant to note that adduct X derived from decomposition in p-xylene exists wholly as the tropilidene tautomer



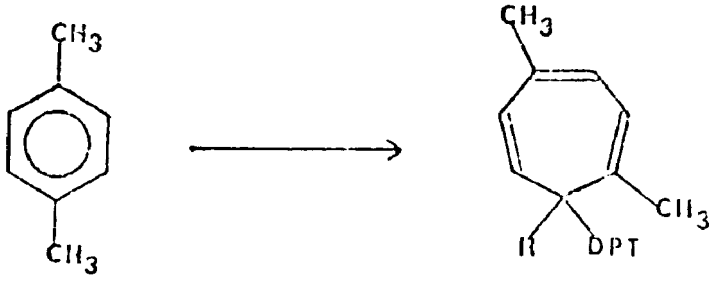
whereas adduct VI derived from decomposition in mesitylene exists as a tropilidene/norcaradiene mixture. The mere addition of one methyl group at a position remote from the crucial C_1-C_6-C_7 segment effects a transition from tropilidene to tropilidene/norcaradiene forms. The two compounds X and XI certainly constitute the most striking demonstration yet of a large effect exerted by a very subtle variation in substituents.

4. The p-Substituted Toluene Series.

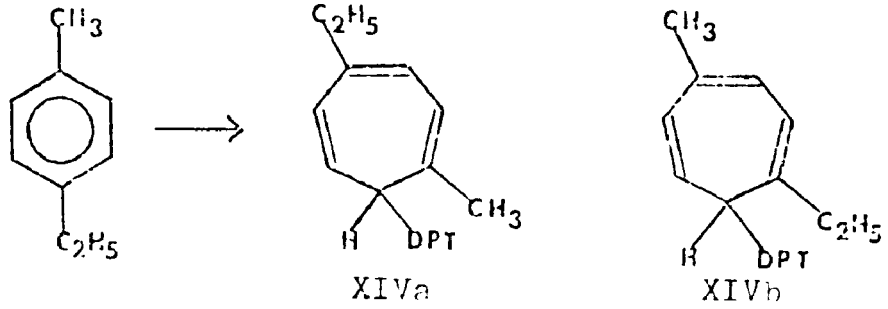
As described in Chapter I, decomposition of diazo

compound IV in p-ethyltoluene and p-cymene resulted in the isolation of two isomeric tropilidenes. The decomposition of IV in 4-tert-butyltoluene yielded only one product, assigned the 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene structure (XIII) based on the PMR and ^{13}CMR spectra. A comparison between the PMR spectra for tropilidene X (the adduct formed from decomposition of IV in p-xylene) and tropilidene XIII, Table XII, reinforced the structural assignments of the isomeric tropilidenes isolated from decompositions in p-ethyltoluene (XIVa and XIVb) and p-cymene (XVa and XVb). The similarity exhibited by adducts X, XIVa and IVa supported a structural assignment of 1-methyl-4-alkyl substituent. Likewise, the similarity exhibited by adducts XIII, XIVb and XVb confirmed the structural assignments of 1-alkyl substituent-4-methyl as the isolated tropilidene product.

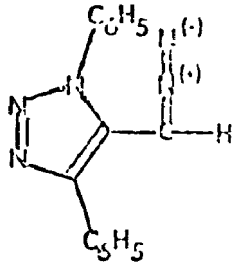
The chemical shifts observed for the 6- and 7-hydrogen atoms of adducts XIII, XIVb and XVb are very similar to those observed for the mesitylene, durene and other known norcaradiene systems (Table XIII). Therefore, their initial assignment was a norcaradiene structure. However, examination of the ^{13} CMR spectrum of adduct XIII revealed that only four-alkyl type carbon atoms were present at room temperature (Table XIV). From the ^{13}CMR spectrum adduct XIII, and by analogy XIVb and XVb, were assigned the cycloheptatriene structures.



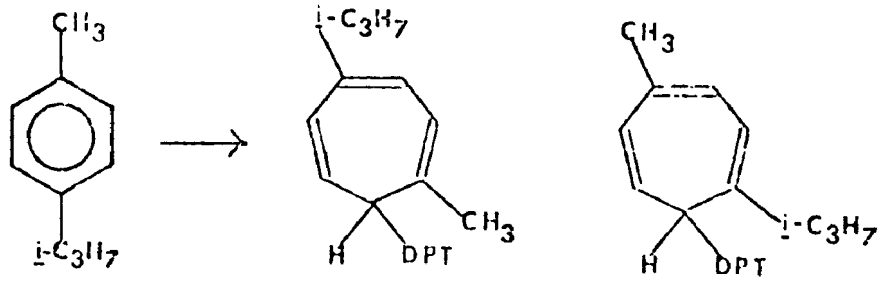
X



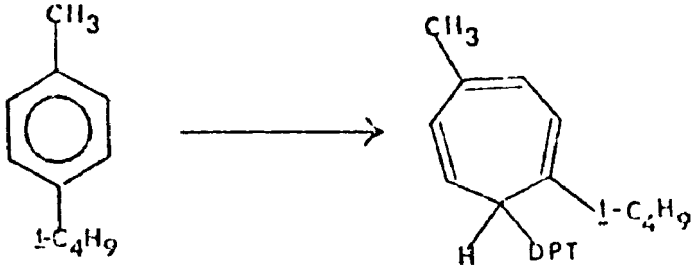
XIVa XIVb



IV



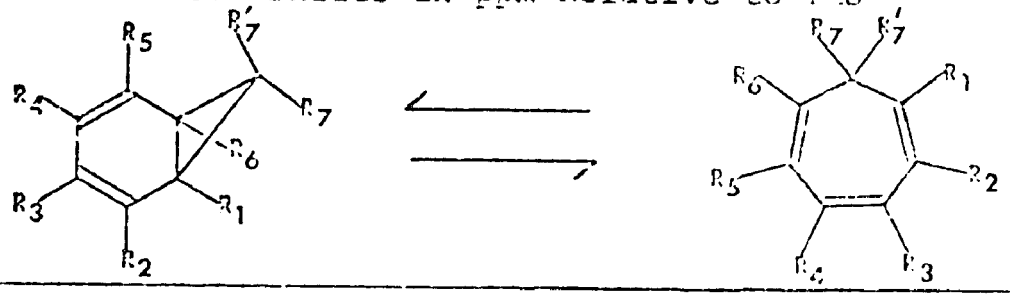
XVa XVb



XIII

Table XII

Chemical Shifts in ppm Relative to TMS



	Adduct V		Adduct XIVa		Adduct XVa		Adduct XIII		Adduct XIVb		Adduct XVb	
R_1	CH_3	1.81	CH_3	1.77	CH_3	1.70	C_4H_9	0.79	C_2H_5	2.12 0.92	i-C_3H_7	1.77 0.75
R_2	H	5.88	H	5.62	H	5.68	H	5.50	H	5.82	H	5.27
R_3	H	6.11	H	5.90	H	5.75	H	5.87	H	6.05	H	5.72
R_4	CH_3	1.86	C_2H_5	2.12 0.92	i-C_3H_7	2.25 0.91	CH_3	1.44	CH_3	1.73	CH_3	1.62
R_5	H	5.72	H	5.72	H	5.68	H	5.32	H	5.40	H	5.07
R_6	H	4.90	H	4.75	H	4.63	H	3.74	H	3.91	H	3.54
R_7	H	3.19	H	3.14	H	3.05	H	2.78	H	2.96	H	3.15
R'_7	DPT	7.47	DPT	7.55	DPT	7.56	DPT	7.45	DPT	7.55	DPT	7.45

Table XIII

Chemical Shifts in ppm Relative to TMS

	ADDUCT								
	XIII	XIVb	XVb	VI	VIII	VIa	VIb	VIc	III
H-6	3.74	3.91	3.54	3.71	- -	3.99	3.41	3.17	3.88
H-7	2.78	2.96	3.15	2.88	2.87	- -	- -	- -	1.08

Table XIV

^{13}CMR Spectrum of Adduct XIII.

Chemical Shifts in ppm Relative to TMS

		Coupled Spectra
CH_3-4	23.08	quartet
C-7	27.69	doublet
t-butyl-CH_3-1	34.18	quartet
t-butyl-C-1	34.73	singlet
C-6	120.40	doublet
Vinylic and aromatic carbons	122.95-147.34	(a)

(a) Due to the complexity of the vinyl and aromatic region, individual assignments were impossible.

This discrepancy between the PMR and ^{13}CMR assignments prompted low-temperature spectroscopic investigations of adduct XIII, represented in Figures 5 and 6. The results clearly indicate that adduct XIII is in a dynamic equili-

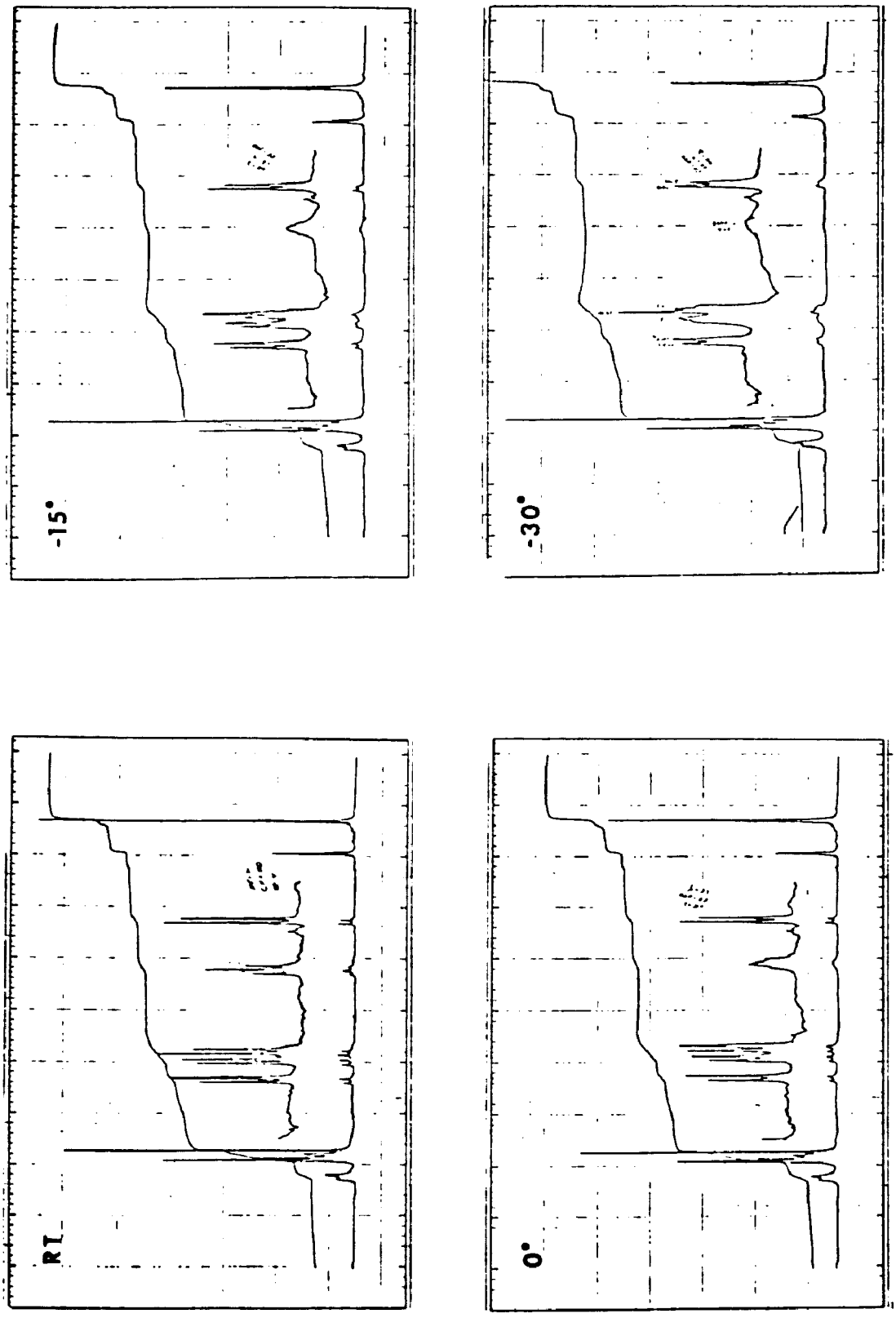


Figure 5. Variable temperature PMR spectra of 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene. CD_2Cl_2.

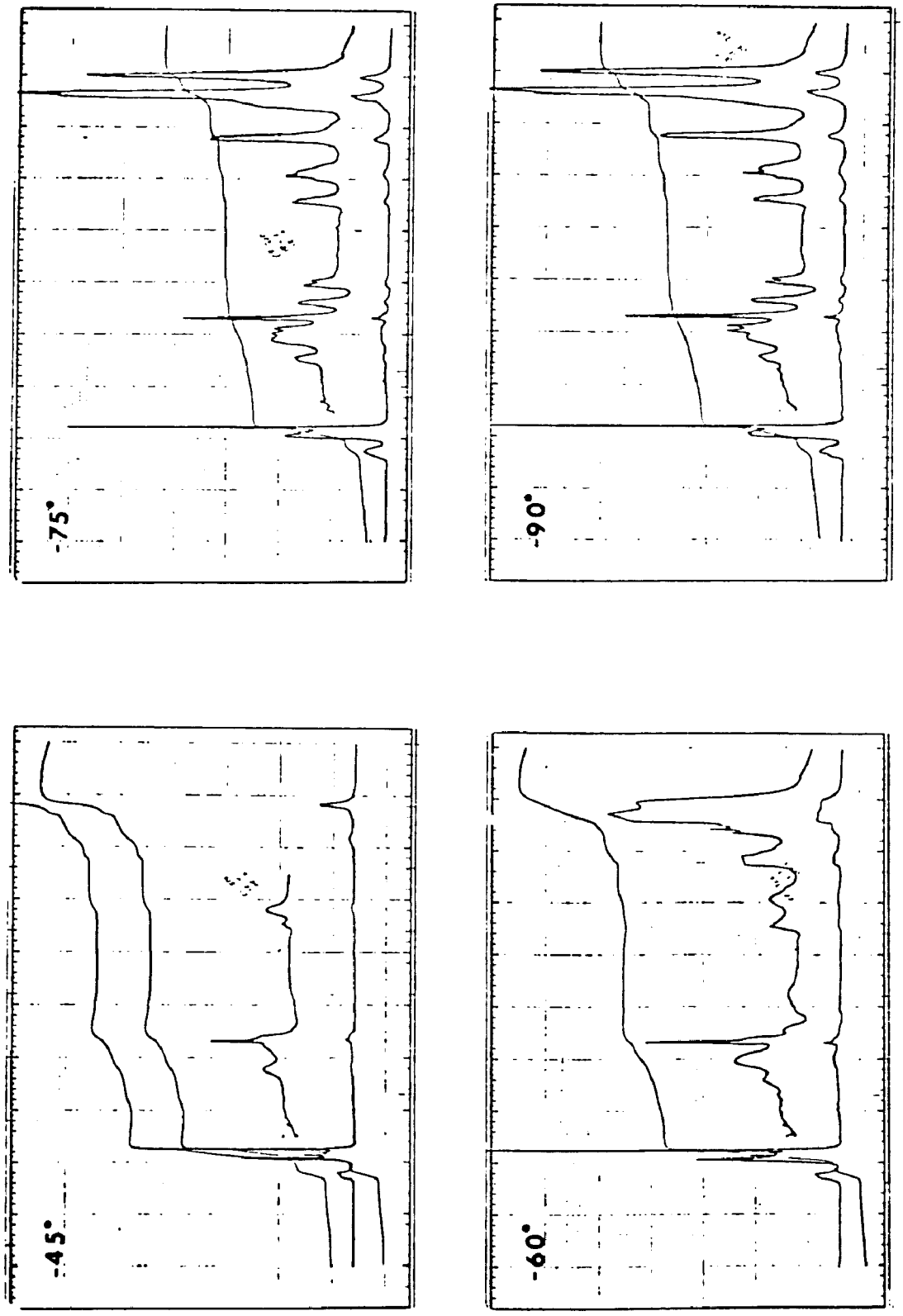


Figure 5 continued.

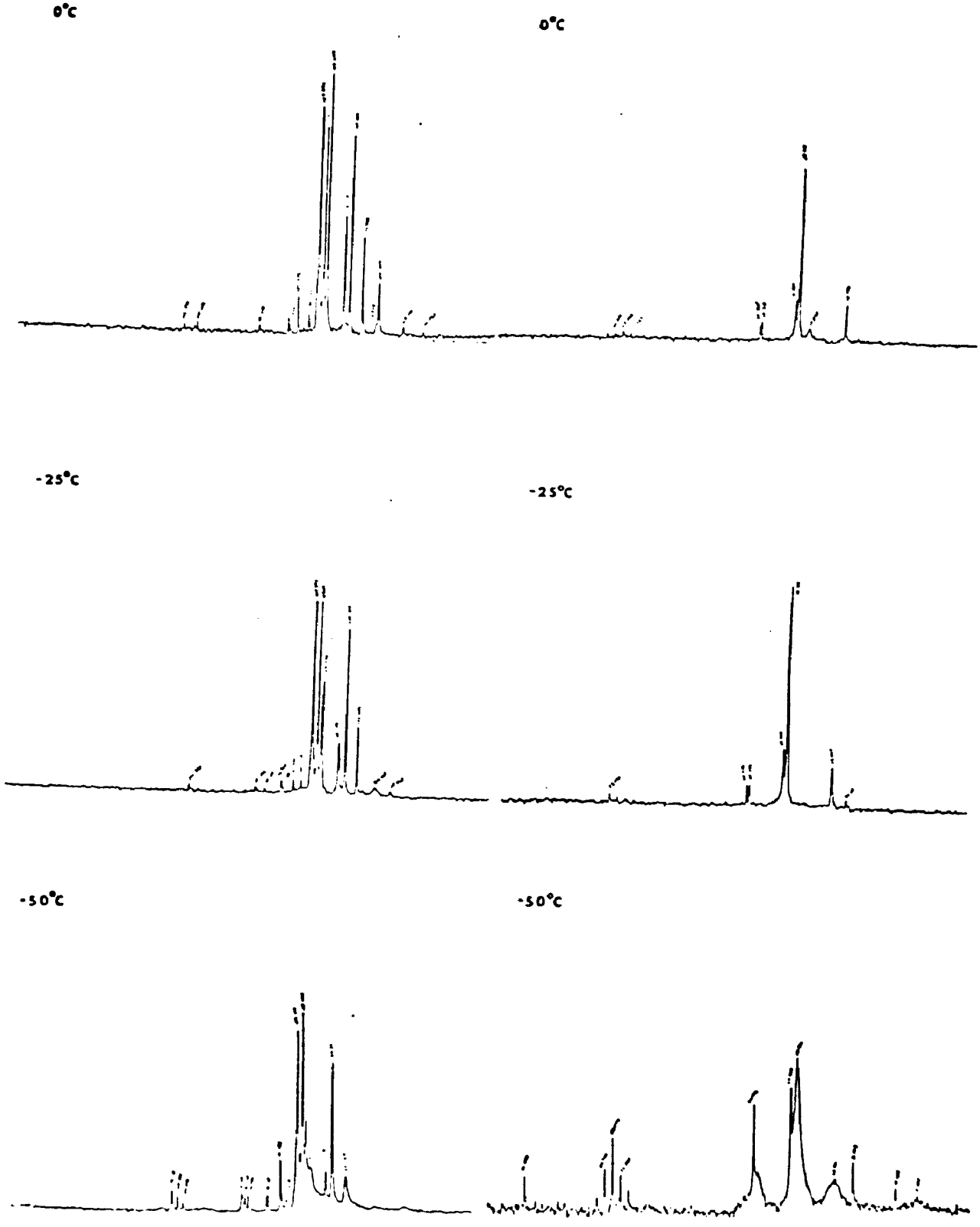


Figure 6. Variable temperature ^{13}CMR spectra of 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene. CD_2Cl_2.

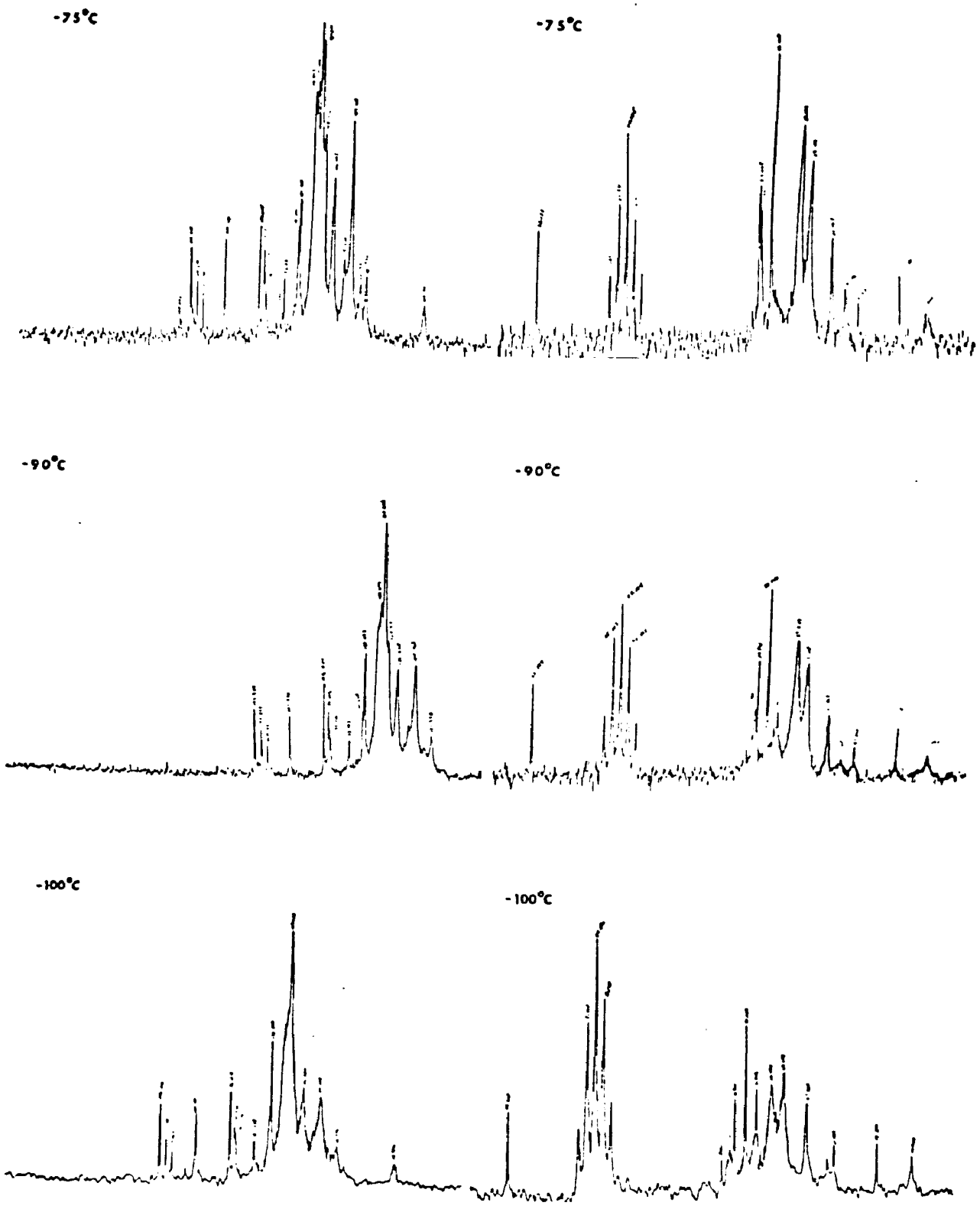


Figure 6 continued.

brium between its norcaradiene and tropilidene isomeric forms. The PMR spectra show complete coalescence of the 6-hydrogen at -35°C, followed by collapse and broadening of the t-butyl absorption at -50°C. At -84°C, the two isomeric forms are identifiable; however, the complexity of spectra does not allow the individual assignment of absorptions, Figure 5. A ratio of 4.86 (tropilidene isomer): 3.42 (norcaradiene isomer) indicates that a ΔG° of 132 cal/mole exists between the two forms, in favor of the tropilidene isomer.

The ^{13}CMR also revealed the dynamic equilibrium, Figure 4, demonstrated by the dramatic change in the chemical shifts of the aliphatic carbon atoms corresponding to temperature variations. Added evidence for the equilibrium is derived from the observations made by Günther and Wehner[5] on the Buchner's acid system, and the comparison with the 6-carbon atom of adduct XIII, which completely disappears between -25°C and -50°C. Again, a coalescence temperature of -35°C is obtained from the ^{13}CMR spectra. By -75°C the two isomeric tert-butyl groups had separated, allowing for a check on the ΔG° calculation obtained from the low-temperature PMR spectra. A ratio of 18.7 (tropilidene isomer): 16.1 (norcaradiene isomer) indicates that a ΔG° of 58.9 cal/mole exists between the two forms, in favor of the tropilidene isomer, and in excellent agreement with the results obtained from the PMR spectra. Though definitive assignment of the absorptions was impossible, the

presence of both isomers was ascertained; the tropilidene side of the equilibrium appeared to be favored.

5. Interpretive Discussion.

Although the factors mentioned in the Introduction such as, the π-acceptor ability of the 7-substituents, the incorporation of one of the double bonds of the diene system into a condensed aromatic system, or bridging the C_1 and C_6 position with a three-membered unit, may well be the most decisive controls on the relative stability of a norcaradiene, the isolation of the various norcaradienes, elucidated in the preceding pages, emphasizes that much more subtle forces can shift the delicate balance between tropilidene and norcaradiene. For, inasmuch as the 1,4-dimethyl isomer X, the sole product isolated in pure form from the decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in p-xylene exists wholly as the tropilidene tautomer, the addition of one methyl group at a position remote from the crucial C_1-C_6-C_7 segment effects a transition to a norcaradiene/cycloheptatriene valence-bond system. The incorporation of four methyl substituents on the arene substrate completely transforms the product isolated to the norcaradiene form, adduct VIII. Although the three compounds X, VI and VIII constitute a striking demonstration of the subtle effects by which alkyl substituents influence product isolation, a more dramatic transformation was ob-

served by increasing the size of the alkyl substituents on the substrate molecule. Thus, changing a methyl substituent in X to an ethyl group in XIVb altered the product form from pure tropilidene to a tropilidene/norcaradiene equilibrium. The results from the decompositions in p-ethyltoluene and p-cymene also indicate that the tropilidene/norcaradiene equilibrium only exists when the large diphenyltriazole moiety is vicinal to the larger substituent.

It is evident that steric interactions between the alkyl substituent and the diphenyltriazole moiety account for the above observations. It is tempting to postulate that the increased non-bonded steric interactions between the diphenyltriazole group and the alkyl substituents cause the relative ground-state free energy of the tropilidene tautomer to approach or surpass the ground-state free energy of the norcaradiene isomer. The interactions result in a norcaradiene/tropilidene equilibrium where it is now possible for the large diphenyltriazole moiety to relieve steric strain by adopting the norcaradiene conformation; thus easing non-bonded interactions between itself and the alkyl substituents, or triene portion of the tropilidene tautomer. In addition, an increase in the relative ground-state free energy of the exo-tropilidene isomer of compounds XIII, XIVb, and XVb due to steric interaction between the larger alkyl substituent and the diphenyltriazole group would favor a shift in the equilibrium

towards the endo-tropilidene isomer. The decompositions of diazo compound IV in p-ethyltoluene, p-cymene, and 4-tert-butyltoluene clearly demonstrate that electronic factors do not influence the tropilidene-norcaradiene equilibrium, nor govern the position of attack of the carbene moiety. However, it would be interesting to investigate whether a combination of electronic and steric factors could influence the tropilidene-norcaradiene equilibrium observed for some of the adducts isolated from decomposition of IV in poly-substituted benzenes. Alteration of the electron-releasing capabilities in a series of para substituted toluenes and tert-butylbenzenes should furnish the desired information bearing on this point.

REFERENCES

1. (a) H. Meerwein, H. Disselnkötter, F. Rappen, H. von Rintelen, and H. van De Vloed, Justus Liebigs Ann. Chem., 604, 151 (1957); (b) W. von E. Doering and L.H. Knox, J. Amer. Chem. Soc., 72, 2305 (1950); (c) ibid., 75, 257 (1953).

2. E. Buchner and T. Curtius, Chem. Ber., 18, 2377 (1885).

3. (a) E. Buchner, Chem. Ber., 21, 2637 (1888); (b) W. Brown and E. Buchner, Chem. Ber., 34, 982 (1901) and intermediate publications.

4. W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, J. Amer. Chem. Soc., 78, 5448 (1956).

5. R. Wehner and H. Günther, ibid., 97, 924 (1975).

6. (a) R. Hoffmann, Tetrahedron Lett., 2907 (1970); (b) G. Maier, Angew. Chem., Int. Ed., 6, 402 (1967).

7. (a) E. Vogel, W. Wiedmann, H. Kiefer and W. F. Harrison, Tetrahedron Lett., 673 (1963); (b) P. Radlick and W. Rosen, J. Amer. Chem. Soc., 88, 3461 (1966); (c) R. Darins, T. Threlfull, M. Pesaro, and A. Eschenmoser, Helv. Chem. Acta., 46, 2893 (1963).

8. (a) R. Huisgen and G. Juppe, Chem. Ber., 94, 2332 (1961); (b) E. Müller, H. Kessler, and H. Suhr, Tetrahedron Lett., 423 (1965); (c) H. Nozaki, M. Yamabe and R. Noyori, Tetrahedron, 21, 1657 (1965).

9. E. Ciganek, J. Amer. Chem. Soc., 87, 652, 1149 (1965).

10. E. Ciganek, ibid., 89, 1454 (1967).

11. D. Schonleber, Angew. Chem., 81, 83 (1969).

12. (a) M. Jones, Jr., and S. D. Reich, J. Amer. Chem. Soc., 89, 3935 (1967); (b) H. Tsuruta, S. Mori and T. Mukai, Chem. Lett., 1127 (1974).

13. T. Mukai, H. Kubota and T. Toba, Tetrahedron Lett., 3581 (1967).

14. G. E. Hall and J. D. Roberts, J. Amer. Chem. Soc., 93, 2203 (1971).

15. E. M. Bruckmann, Ph.D. Thesis, University of Michigan, 1971.

16. A. C. Cope, A. C. Haven, F. L. Ramp and E. R. Trumbull, J. Amer. Chem. Soc., 74, 4867 (1952).

17. H. Günther, W. Peters and R. Wehner, Chem. Ber., 106, 3683 (1973).

18. K. Conrow, M. E. H. Howden and D. Davis, J. Amer. Chem. Soc., 85, 1929 (1963).

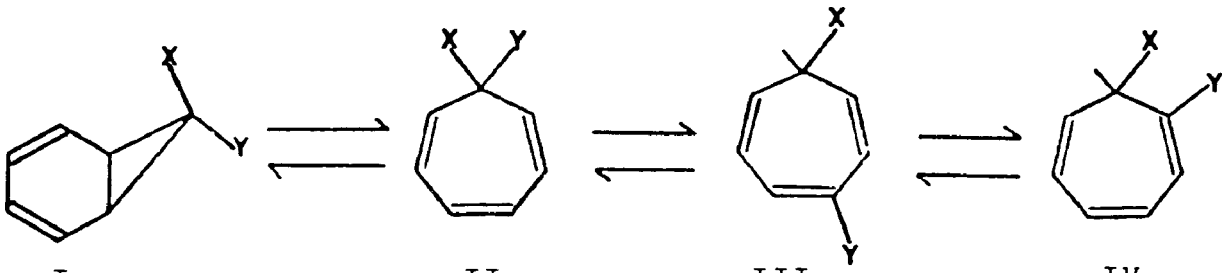
CHAPTER III

THE THERMAL REARRANGEMENTS OF 1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL ADDUCTS OBTAINED BY DECOMPOSITION OF 5-DIAZOMETHYL-1,4-DIPHENYL-1,2,3-TRIAZOLE IN POLYSUBSTITUTED AROMATIC SUBSTRATES:

1. Introduction:

Degenerate rearrangements are intramolecular reactions in which the structural integrity of the substrates has been retained, although atoms have been interconverted by virtue of bond rotations or electron shifts.[1] The best known example of this is the thermal rearrangement of bullvalene to itself *via* successive Cope rearrangements.[2] The vocabulary associated with thermal processes has expanded since 1964 with the recognition that the course of thermal rearrangements is controlled in many instances by quantum mechanical considerations.[3]

There are several types of thermal degenerate rearrangement pathways available to the norcaradiene and tropilidene adducts isolated from the thermal decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in polysubstituted arene substrates. The first, and of lowest energy, is the degenerate Cope rearrangement between the norcaradiene and tropilidene tautomers, which was discussed fully in Chapter II. Following the degenerate Cope rearrangement is the thermally degenerate 1,5-hydrogen shift of tropilidene systems.[4]



I II III IV

This reaction, which takes place readily at about 100°C, is called the "skin" or "epidermal" rearrangement of tropilidene, in contrast to rearrangement of the carbon skeleton which occur at still higher temperatures.[5] The rearrangement is quite facile, presumably because it is electronically allowed and sterically possible in a suprafacial manner.[3] Most reported 1,5-hydrogen shifts have an activation energy of approximately 30 kcal/mole, with a minimum value of 26 kcal/mole observed for the isomerization of 2,5,7-triphenylnorcaradiene[5] (Table XV). Considerable experimental evidence has been obtained concerning the 1,5-hydrogen shift rearrangement.[6]

E. M. Bruckmann[9] observed that norcaradiene V, when heated to 80-100°C, rearranged quantitatively to a new substance of the same elemental composition. A firm assignment of the structure, however, was not possible at that time. Extension of Bruckmann's work on the mesitylene adduct V to other adducts obtained from decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in polysubstituted aromatic substrates, the structural assignment of the rearranged materials, and the energetics of the rearrange-

Table XV

Kinetic Parameters for Some Intramolecular 1,5-Hydrogen-Transfer Reactions[a]

Reaction	Phase[b]	Temp. °C	Analysis[b]	Log A sec^{-1}	E_a kcal/mole	$\Delta S^{\ddagger}$ e.u.	Ref.
cis-2-methyl-1,3-pentadiene 4-methyl-1,3-pentadiene	Gas.	200-287	Glpc	11.2	32.8	-12.4	7a
cis-1-methyl-2-vinyl-cyclopropane cis-1,4-hexadiene	Gas.	166-220	Glpc	11.0	31.2	-13.2	7b
cis-1,3-Hexadiene cis,trans-2,4-hexadiene	Gas.	202-245	Glpc	10.8	32.5	-13.4	7c
7-Methyl-1,3,5-cycloheptatriene 3-methyl-1,3,5-cycloheptatriene	Gas.	129-226	Glpc	12.6	33.3	-4.9	7d
7-Phenyl-1,3,5-cycloheptatriene 3-phenyl-1,3,5-cycloheptatriene	Liq.	80-121	PMR	10.8	27.6	-11.6	7c
7D-1,3,5-cycloheptatriene 3D-1,3,5-cycloheptatriene	Liq.	98-140	PMR	11.2	31.5	-11.1	4
2,5,7-Triphenylnorcaradiene 1,3,5-triphenyl-1,3,5-cycloheptatriene	Liq.	110-131	PMR	- -	26.0	-12.7	6

Table XV continued

Reaction	Phase[b]	Temp. °C	Analysis[b]	Log A sec^{-1}	E_a kcal/mole	$\Delta S^{\dagger}$ e.u.	Ref.
1,3,5-Triphenyl-1,3,5- cycloheptatriene 1,3,6-triphenyl-1,3,5-cycloheptatriene	Liq.	110-131	PMR	- -	27.8	-13.4	6

[a] For additional liquid-phase data compare Reference 8.

[b] Liq. stands for liquid, glpc for gas-liquid partition chromatography, and PMR for proton magnetic resonance.

ments begins with a reexamination of the thermal rearrangement of the mesitylene adduct V.

2. Statement of the Problem:

The reexamination of the thermal rearrangement of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (V) and other selected adducts derived from the thermal decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole was undertaken. The kinetics of the rearrangements were determined. A comparison between the alkyl group's size, positioning on the substrate molecule, and the type of ring (i.e., whether tropilidene or norcaradiene) is interpreted in terms of the current theories on thermally degenerate rearrangements. In addition, the energetics of the rearrangement are related to the tropilidene/norcaradiene valence tautomerization problem discussed in Chapter II.

3. Results and Discussion:

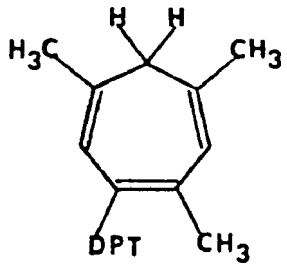
A) Thermal Rearrangement of 1,3,5-Trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (V).

When V was heated in solution to 80-100°C, it rearranged quantitatively to a new substance with the same elemental composition. The PMR spectrum, in addition to two diagnostic multiplets for the ten aromatic protons of 1,4-diphenyl-1,2,3-triazole, displayed a broad, two-proton

signal at δ 5.77, an AB quartet centered at 2.23 (J = 10 cps, two protons) and three methyl signlets at 1.96, 1.87 and 1.60 ppm. The chemical shift of the AB quartet requires that both protons be attached to a saturated carbon, of which there is only one in cycloheptatriene. The ^{13}CMR spectrum (Table XVI) of the rearranged material showed only four alkyl carbon atoms, of which three are accounted for

Table XVI

^{13}CMR of 1,4,6-Trimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (VII). Chemical Shifts in ppm Relative to TMS



C-7	39.1	triplet
1-CH_3	24.8	quartet
4-CH_3	21.0	quartet
6-CH_3	24.3	quartet
vinyl and aromatic carbons	122.5 to 140.1[a]	

[a] Individual assignment of the vinyl and aromatic carbon atoms was impossible due to the complexity of the region.

by the three methyl groups. The coupled spectrum indicates a triplet for the remaining saturated carbon atom, which

three are accounted for by the three methyl groups. The coupled spectrum indicates a triplet for the remaining saturated carbon atom, which can only be interpreted as a methylene group. This clearly negates the possibility that V had simply undergone a Cope rearrangement to the non-conjugated tropilidene VI. However, a Cope rearrangement to the non-conjugated tropilidene followed by a 1,5-hydrogen shift, or a direct 1,5-hydrogen shift with concerted cyclopropyl ring opening would result in the formation of the conjugated tropilidene VII.

Cycloheptatriene VII corresponds well with the ^{13}CMR spectrum, but the AB quartet present in the PMR for the methylene group requires further analysis. It is conceivable that the proximity of the methyl group vicinal to the diphenyltriazole moiety could slow the rapid equilibration of the two non-planar boat conformations of the tropilidene VII,[10] a circumstance which could account for the chemical non-equivalence of the methylene hydrogens. However, models clearly indicate that this is not likely. On the other hand, if the large diphenyltriazole moiety cannot freely rotate past the vicinal methyl group, as models demonstrate, then two frozen isomeric conformations are possible, as in the cases of ortho-tetrasubstituted biphenyls.[11] Without free rotation, the C_7-hydrogens feel the shielding or deshielding effect of either the N-phenyl or C-phenyl group, depending on whether they are in a <u>syn</u> or <u>anti</u> orientation. With rapid equilibration of the two

non-planar conformers of the tropilidene VII, 50% of the C_7-hydrogens are continually perturbed by the N-phenyl group, and the other 50% by the C-phenyl group (Figure 7). This results in their chemical non-equivalence and accounts for the AB quartet observed in the PMR spectrum. A structure assignment of 1,4,6-trimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (VII) as the rearranged compound isolated from norcaradiene V is thus in excellent agreement with all features of the PMR and ^{13}CMR spectra.

The AB quartet, resulting from hindered rotation of the diphenyltriazole moiety past the vicinal methyl substituent, should collapse to a singlet if free rotation of the diphenyltriazole moiety could be obtained. To this end, the variable-temperature PMR spectrum of VII was examined. However, even at 160°C, the PMR spectrum of VII retains the AB quartet, indicating the large energy of activation required to rotate the diphenyltriazole group past the vicinal methyl substituent.

The kinetics for the thermal rearrangement of V to VII were investigated. The valence isomerization can be envisioned as occurring via two routes (Figure 8). Route (a) involves an initial reversible Cope rearrangement to the non-conjugated tropilidene VI, followed by an irreversible 1,5-hydrogen shift to the isolated product VII. Route (b) proceeds directly to the conjugated tropilidene VII via a concerted 1,5-hydrogen shift, possibly through an intermediate such as VIII.

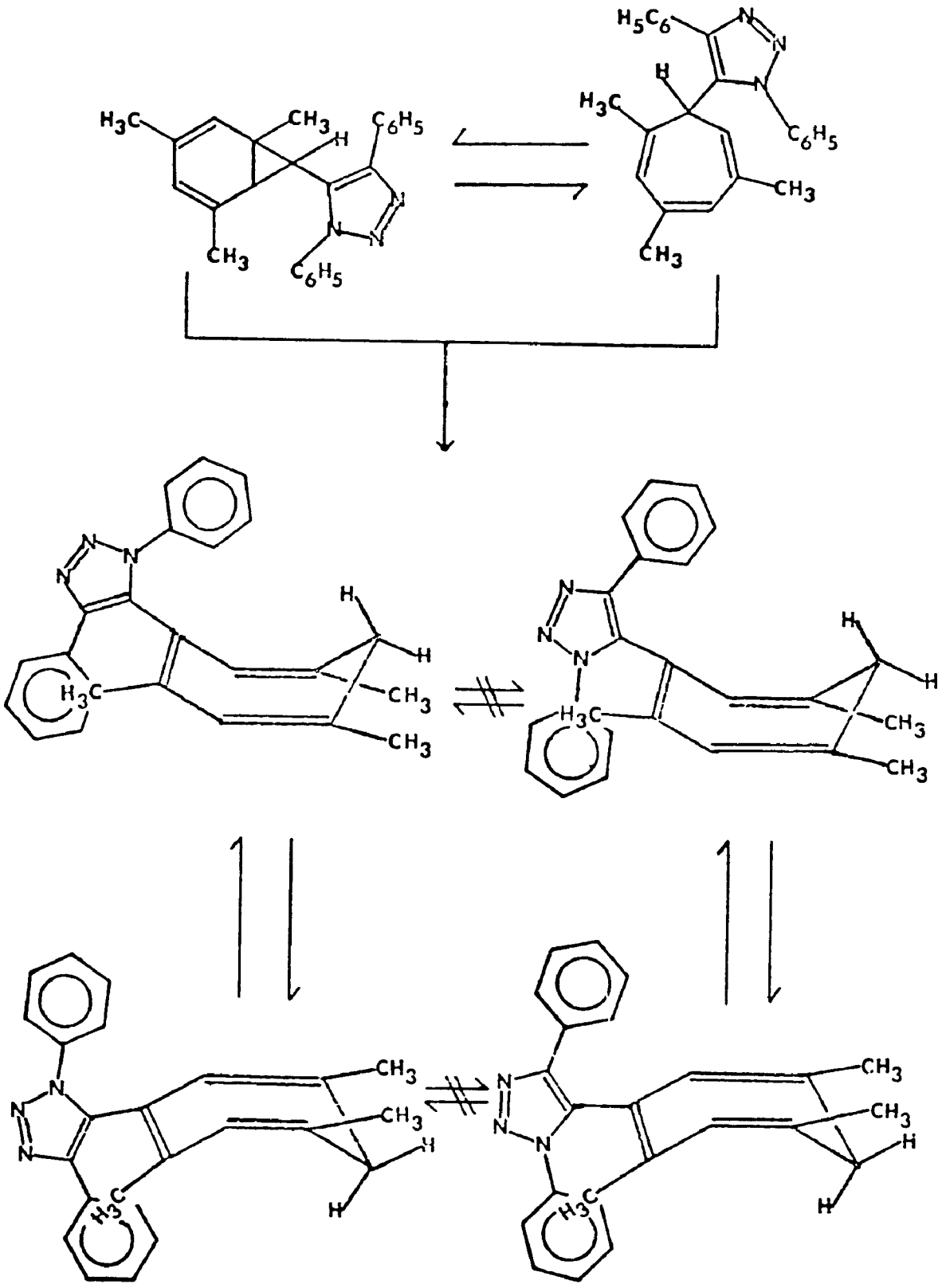
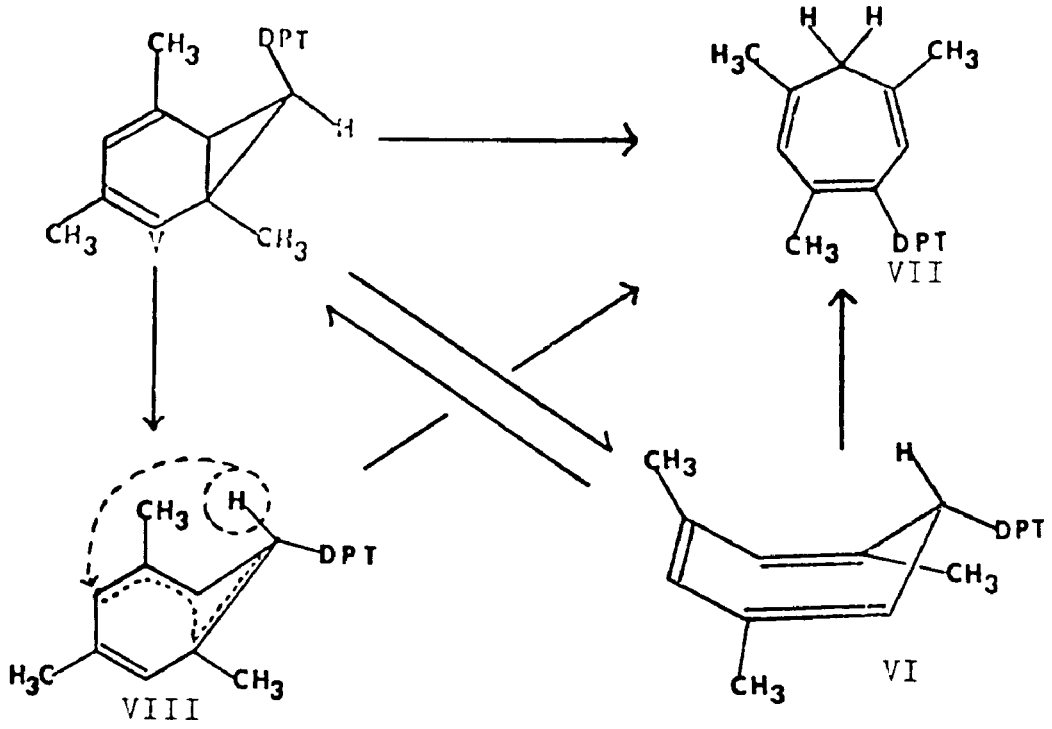


Figure 7. Schematic representation of the chemical non-equivalence generated by the hindered rotation of the diphenyltriazole moiety past the vicinal substituent.

Figure 8. Schematic representation of the possible reaction pathways for thermal isomerization of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-norcaradiene to 1,4,6-trimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene.



The kinetic data shown in Figures 9 and 10 (interpreted in Tables XVII and XVIII) were obtained by measuring areas of the methyl signals of V and the methyl signals of VII in their PMR spectra. The reaction was found to be first-order in V with an activation energy (E_a) 24.75 ± 0.73 kcal/mole and a $\Delta S^{\ddagger}$ -14.84 eu. Most reported 1,5-hydrogen shifts have an E_a of approximately 30 kcal/mole,[7] with a minimum value of 26 kcal/mole observed for the isomerization of 2,5,7-triphenylnorcaradiene.[6] The energy difference between reported 1,5-hydrogen shifts and that observed for the thermal rearrangement of V to VII of from 3- to 5-kcal/mole supports the earlier postulation (Chapter I and Chapter II) of an increased ground-state energy for

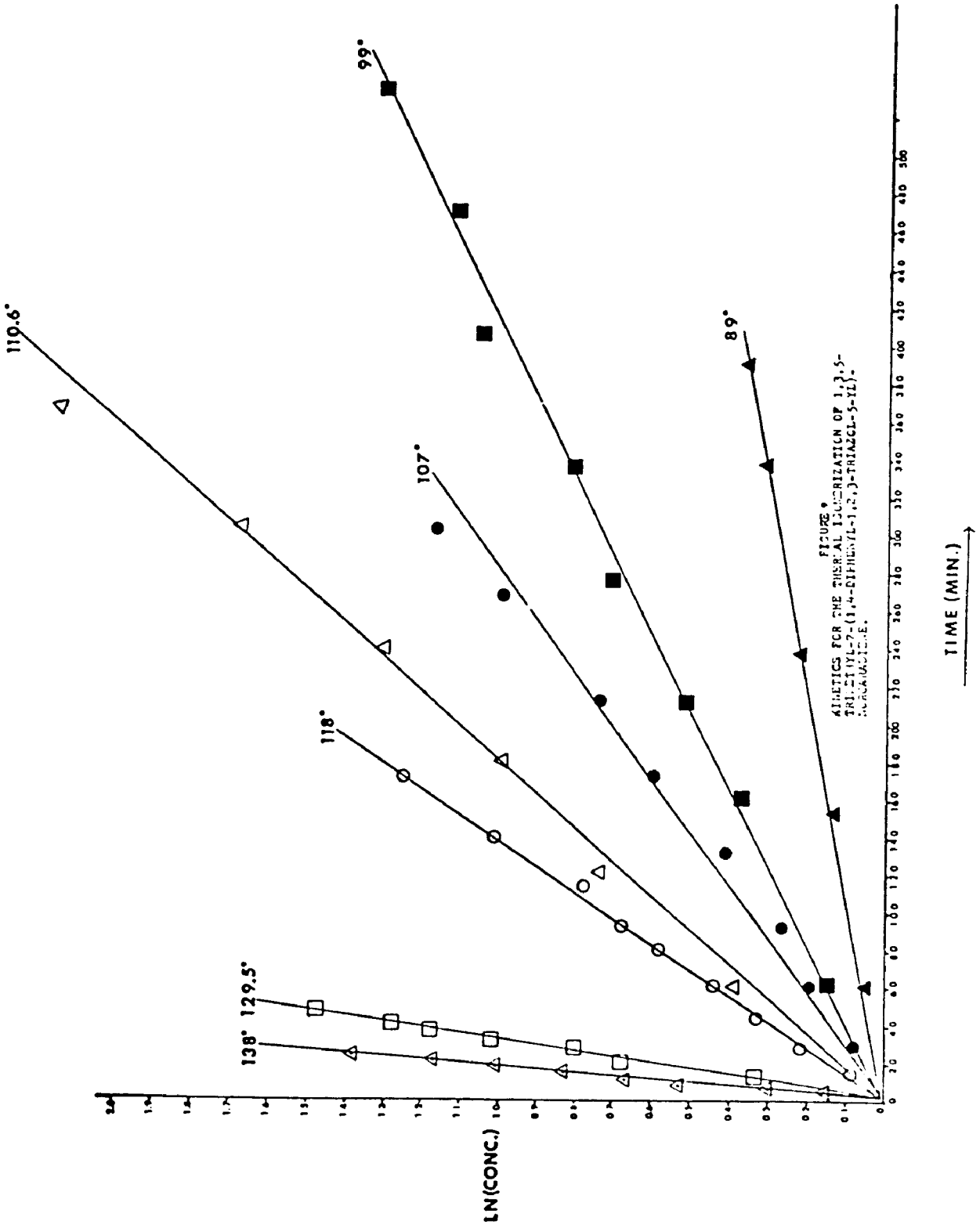


Figure 9. Kinetics for the thermal isomerization of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-norcaradiene.

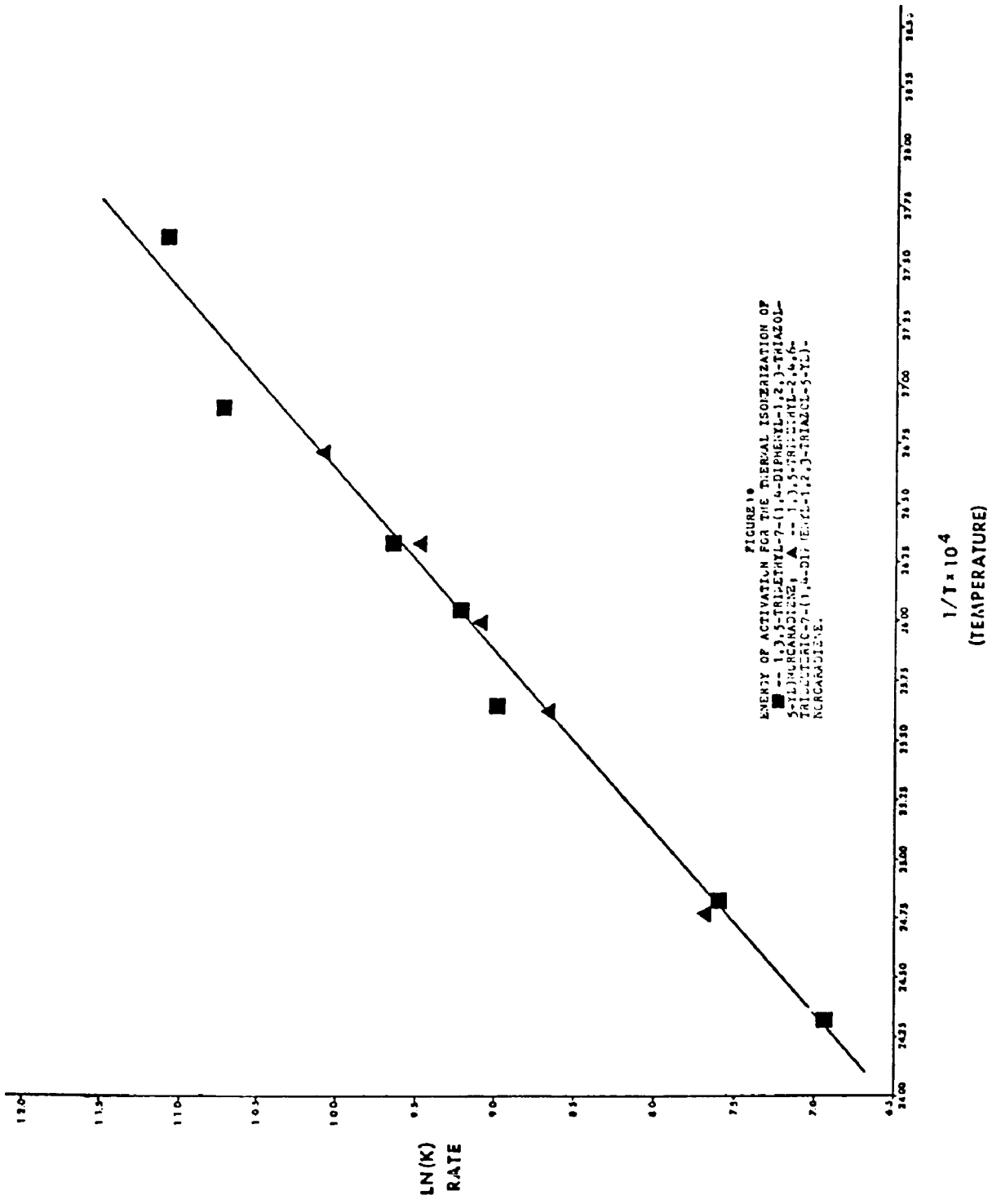


Figure 10. Energy of activation for the thermal isomerization of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene and 1,3,5-trimethyl-2,4,6-trideuterio-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene.

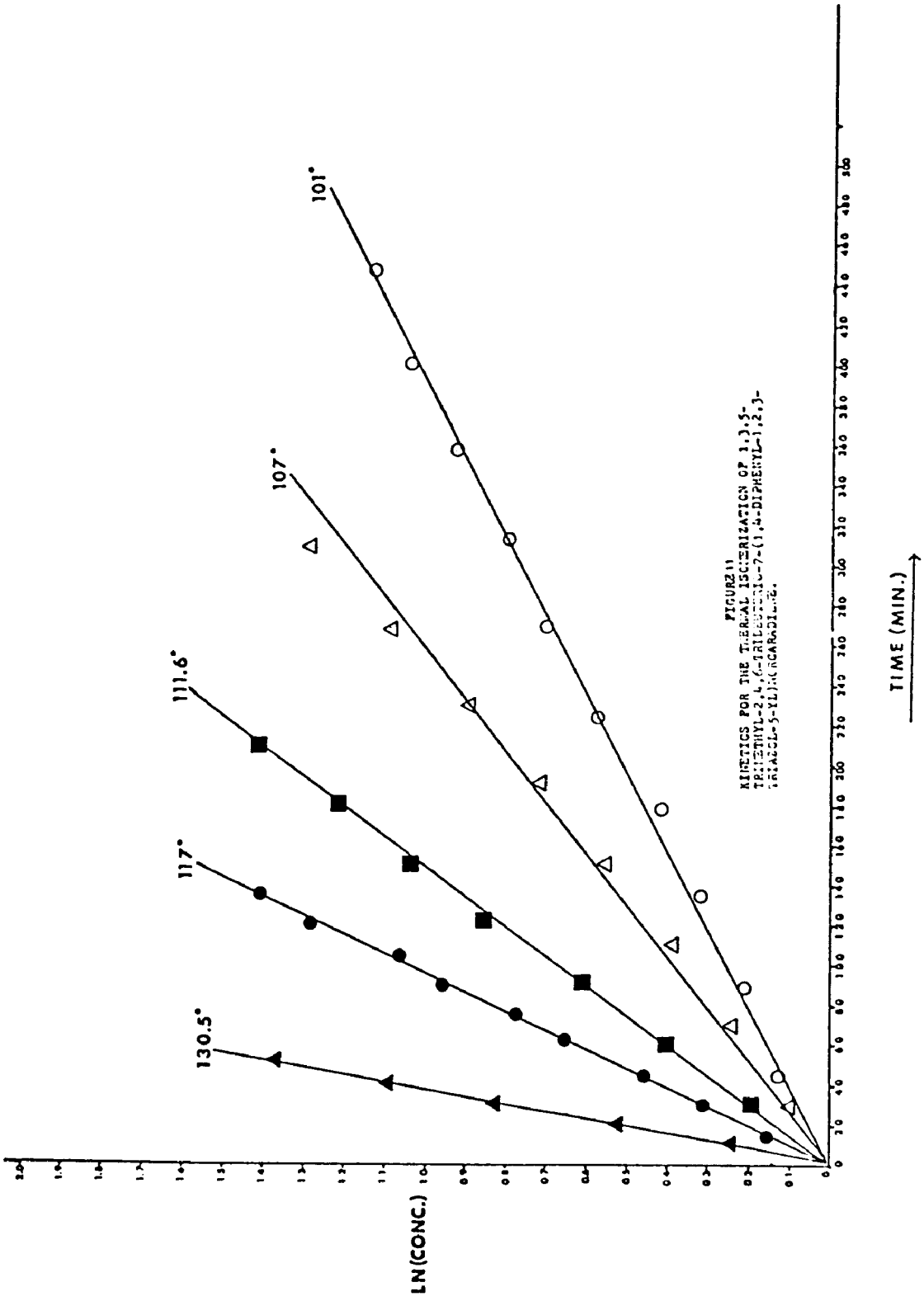


Figure 11. Kinetics for the thermal isomerization of 1,3,5-trimethyl-2,4,6-trideuterio-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene.

Table XVIII

Activation Parameters for the Thermal Isomerization of Adduct V to VII[a]

	Mesitylene Adduct	2,4,6-Trideuterio-mesitylene Adduct
$E_{a_{\pm}}$, kcal/mole	24.75 ± 0.73	24.51 ± 0.35
$\Delta H^{\ddagger}$, kcal/mole	23.99	23.75
$\Delta S^{\ddagger}$, e.u.	-14.84	-15.41
Log A	10.09	9.97

[a] In this work, calculations were made from a mean temperature, 110°C.

Table XVII

Kinetics of the Thermal Rearrangement of 1,3,5-Trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene to the Conjugated Tropilidene Isomer

Mesitylene Adduct V

Temp., °C	K, sec^{-1} x 10^5	Deviation %
89.0	1.50	4.0
100.0	4.11	3.1
107.0	6.65	1.5
110.6	9.78	4.2
118.0	12.5	2.1
129.5	52.8	4.8
138.0	95.2	2.4

2,4,6-Trideuteriomesitylene Adduct

Temp., °C	K, sec^{-1} x 10^5	Deviation %
100.0	4.17	1.9
107.0	7.51	3.1
111.5	11.4	1.6
117.0	17.4	3.1
130.0	47.1	0.7

the initial adduct V. Since the norcaradiene V was shown to be in a dynamic equilibrium with its tropilidene tautomer VI (Chapter II, p. 119), and in light of the present knowledge concerning 1,5-hydrogen shifts, it is reasonable to assume that the hydrogen shift occurs through intermediate VI, Figure 8. The low activation energy for the valence isomerization of 2,5,7-triphenylnorcaradiene, the only known norcaradiene with a hydrogen atom at the 7-position, reported by T. Mukai and coworkers,[6] who postulated a transition state such as VIII, seems unlikely in light of our current findings.

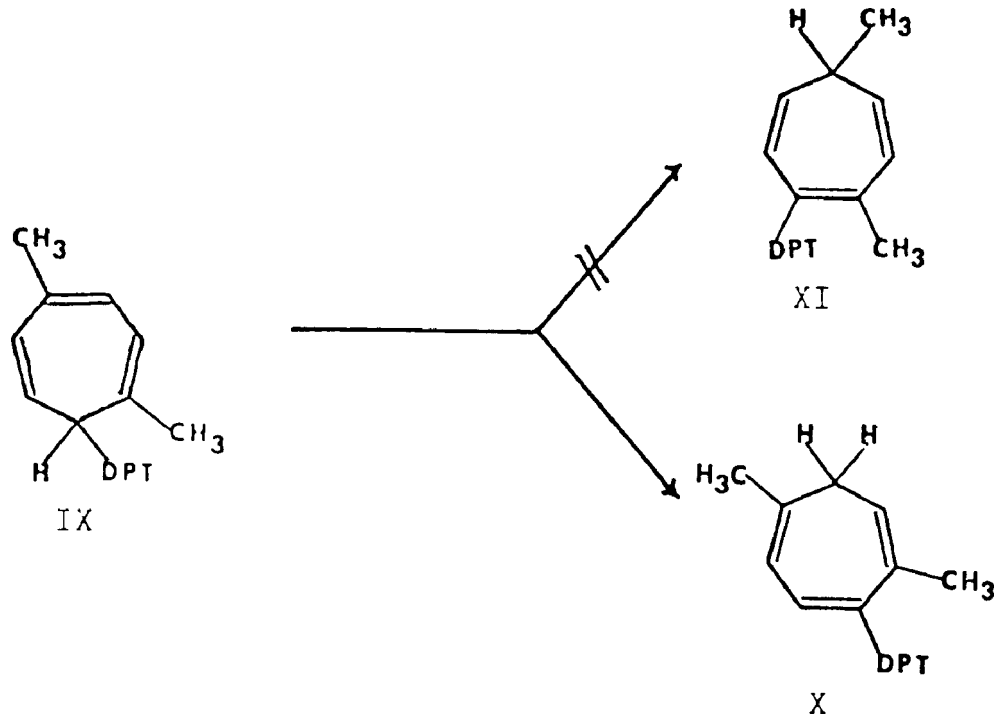
Additional kinetic data shown in Figures 10 and 11 (interpreted in Tables XVII and XVIII) were obtained from the thermal rearrangement of the 1,3,5-trimethyl-2,4,6-trideuterio-7-(1,4-diphenyl-1,2,3-triazole-5-yl)norcaradiene. The reaction was again found to be first-order in norcaradiene with E_a 24.51 ± 0.35 kcal/mole and $\Delta S^{\dagger}$ -15.41 eu. The ratio k_H/k_D = 1.004 clearly indicates that the ring hydrogen atoms do not participate in the rate-determining step in the rearrangement of norcaradiene V to tropilidene VII. After prolonged heating of the tropilidene VII under the reaction conditions used in obtaining the kinetic data, no subsequent 1,5-hydrogen shift products were detected.

B) <u>Thermal Rearrangement of 1,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (IX)</u>.

The low activation energy observed for the thermal

rearrangement of norcaradiene V to tropilidene VII, and the unusual PMR spectrum of tropilidene VII, prompted further investigations on the thermal rearrangements of the adducts obtained from decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in polysubstituted aromatic substrates. When IX was heated in solution to 110°C, it rearranged quantitatively to a new substance with the same elemental composition as the cycloheptatriene precursor. Of the two possible isomeric tropilidenes formed during the 1,5-hydrogen shift, only one was isolated. The structure 1,5-dimethyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene (X) was assigned on the basis of the following PMR spectrum. The two diagnostic multiplets for the ten aromatic protons of 1,4-diphenyl-1,2,3-triazole appeared at δ 7.86 and 7.40 ppm. The three olefinic hydrogens appeared as a doublet centered at δ 6.50 ($J_{3,2}$ = 6.0 cps), a doublet centered at 5.80 ($J_{2,3}$ = 6.0 cps), and the terminal olefinic hydrogen appeared as a triplet centered at 5.18 ppm ($J_{6,7}$ = 7.4 cps). The methyl groups appeared as singlets at δ 1.96 and 1.52 ppm. The methylene group appeared as a very broad hump centered at δ 2.20 ppm.

It is evident from the PMR spectrum that only one isomeric tropilidene was formed during the thermolysis. However, like the tropilidene VII obtained from the thermal rearrangement of norcaradiene V, the broad hump present in the PMR for the methylene group merits further analysis. The AB quartet observed in the PMR spectrum of



tropilidene VII results from hindered rotation of the diphenyltriazole moiety past the vicinal methyl substituent. In the mesitylene case, adduct V, the diphenyltriazole moiety and the methyl substituent are both attached to the same double bond in the tropilidene ring, and even at 160°C no coalescence of the AB quartet was observed. However, in tropilidene X, the vicinal arrangement of diphenyltriazole and methyl substituent is now on two different double bonds and the energy barrier to rotation of the diphenyltriazole moiety past the methyl substituent is lowered. Verification was obtained from the variable-temperature spectra of tropilidene X (Figure 12). At 118°C the PMR spectrum of X displayed a clean doublet for the methylene group centered at δ 2.20 ppm ($J_{7,6}$ = 7.4 cps), clearly indicating completely free rotation of the diphenyltriazole moiety

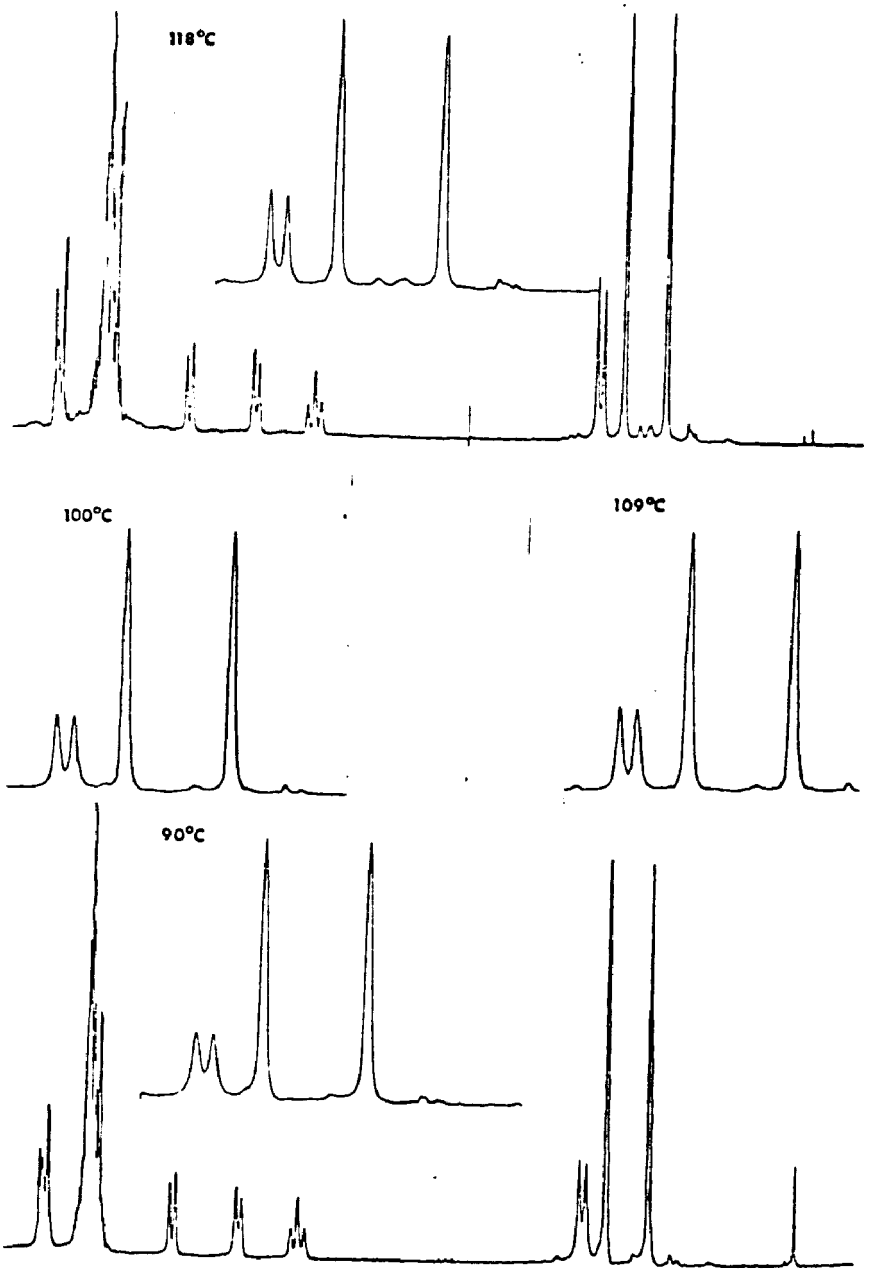


Figure 12. Variable temperature PMR spectra of 1,5-dimethyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene. $CDCl_3$.

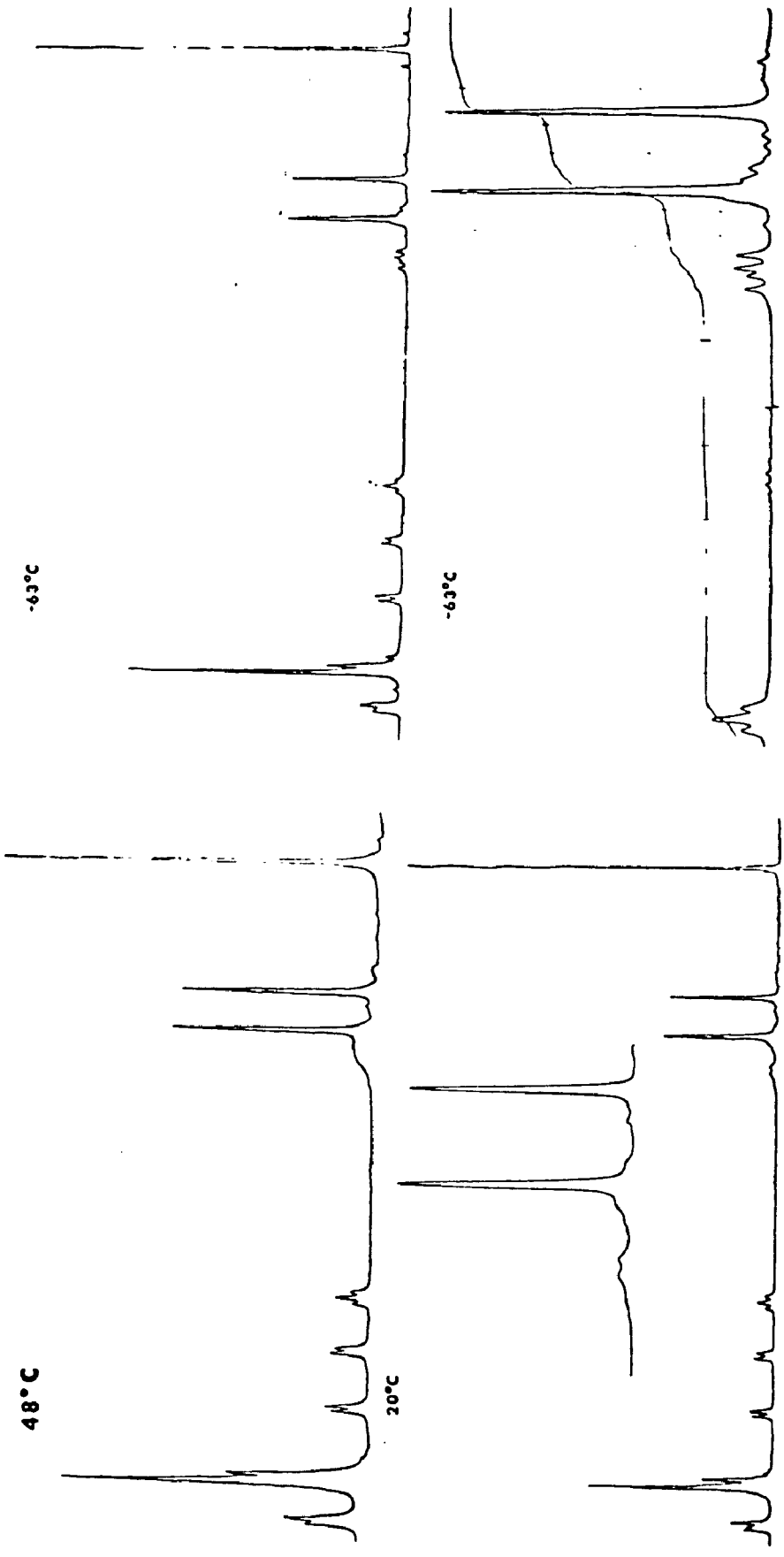


Figure 12 continued.

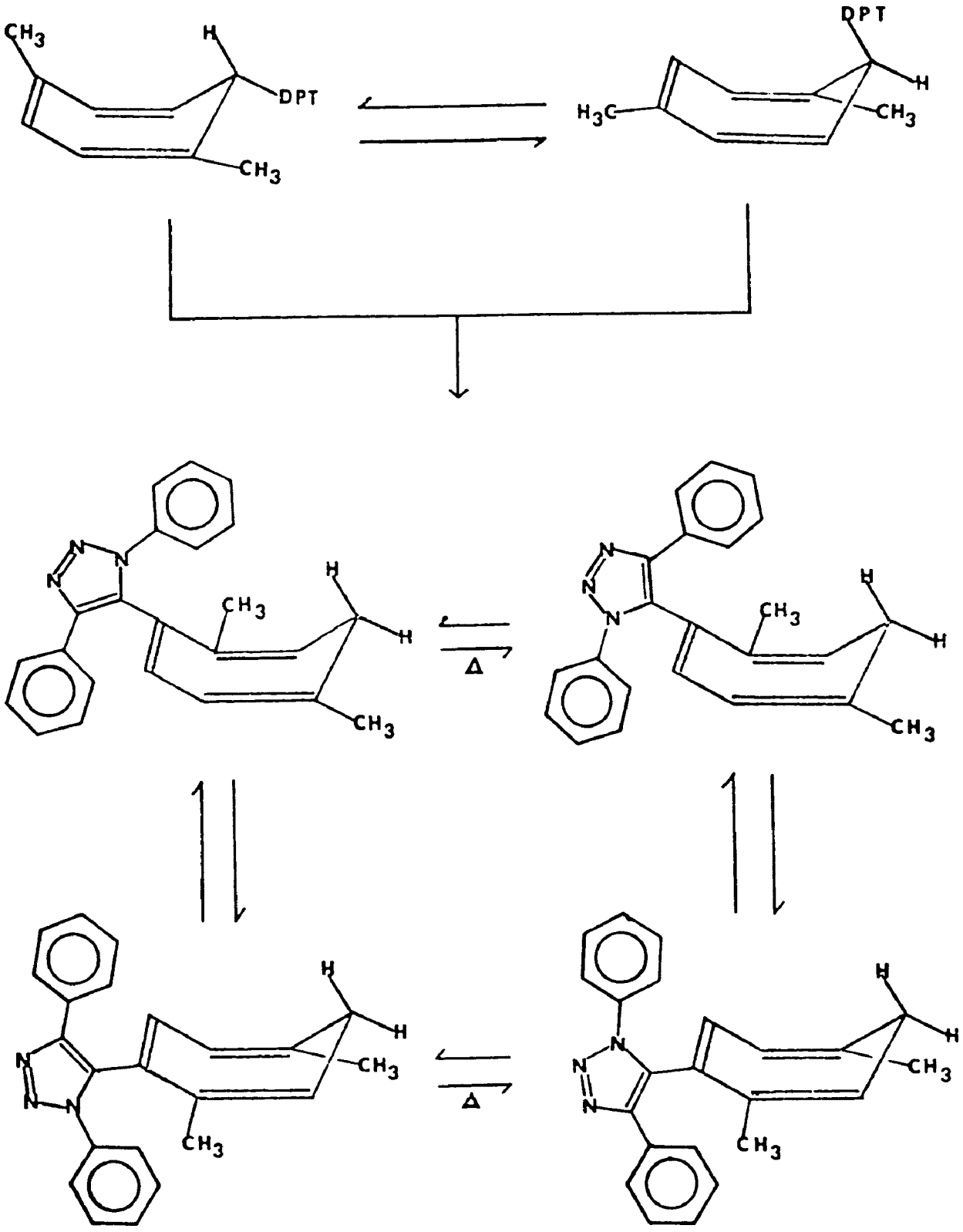


Figure 13. Schematic representation of the chemical non-equivalence generated by the hindered rotation of the diphenyltriazole moiety past the vicinal substituent.

past the vicinal methyl group. At -63°C the PMR spectrum of X displayed two AB quartets, appearing as doublet AB quartets, split by the C_6-hydrogen ($J_{6,7}$ = 7.4 cps). The doublet AB quartets were centered at δ 2.48 and 1.94 ppm, respectively. Again, as in tropilidene VII, with rapid equilibration of the two nonplanar conformers of X, 50% of the C_7-hydrogen are continually perturbed by the N-phenyl group and the other 50% by the C-phenyl group (Figure 13). At -63°C this results in the chemical non-equivalence of C_7-hydrogens and accounts for the AB quartets observed in the PMR spectrum. The structural assignment of 1,5-dimethyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene (X) as the sole isolated rearranged compound from cycloheptatriene IX is thus in agreement with all features of the PMR spectrum.

Examination of the variable-temperature PMR spectra, depicted in Figure 12, indicates a coalescence temperature of 40°C for the interconversion of the two diphenyltriazole forms. The rotation of the diphenyltriazole moiety past the vicinal methyl substituent was found to have an energy of activation of 17.3 ± 0.3 kcal/mole, with a coalescence temperature (T_c) of 40°C and a relative rate (k^1) of rotation of 143.9 sec^{-1}.[12]

$$K^1 = \pi\Delta\nu/\sqrt{2} = R(kT/he^{-E_a/RT})$$

$$E_a = 2.303\ R\ T_c\ (10.319 - \log_{10}K^1 + \log_{10}\ T_c)$$

$$T_c = 40°C$$

$$K^1 = 143.9\ sec^{-1}$$

$$E_a = 17.34\ kcal/mole$$

These results, coupled with the observations on the tropilidene XII, are the first examples of hindered rotation of substituents on tropilidene rings. They also support the earlier postulates (Chapters I and II) of the interactions between the large diphenyltriazole moiety and the alkyl substituents on the arene substrate and resulting adducts.

The kinetics for the thermal rearrangement of IX to X were investigated. The kinetic data shown in Figures 14 and 15 (interpreted in Tables XIX and XX) were obtained by measuring areas of the methyl signals of IX and the methyl signals of X in their PMR spectra. The reaction was found to be first-order in IX with E_a 26.9 ± 1.1 kcal/mole and $\Delta S^{\dagger}$ -10.64 eu. The E_a is in close agreement with reported 1,5-hydrogen shifts (Table XV).

C) Thermal Rearrangement of 2,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XII).

When XII was heated in solution to 110°C, it rearranged quantitatively to a new substance with the same elemental composition. The structure 1,6-dimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene XIII was assigned on the basis of the following PMR spectrum. The two diagnostic multiplets for the ten aromatic hydrogens of 1,4-diphenyl-1,2,3-triazole appeared at δ 7.75 and 7.32 ppm, two protons and eight protons, respectively. The three internal olefinic hydrogens appeared as a doublet

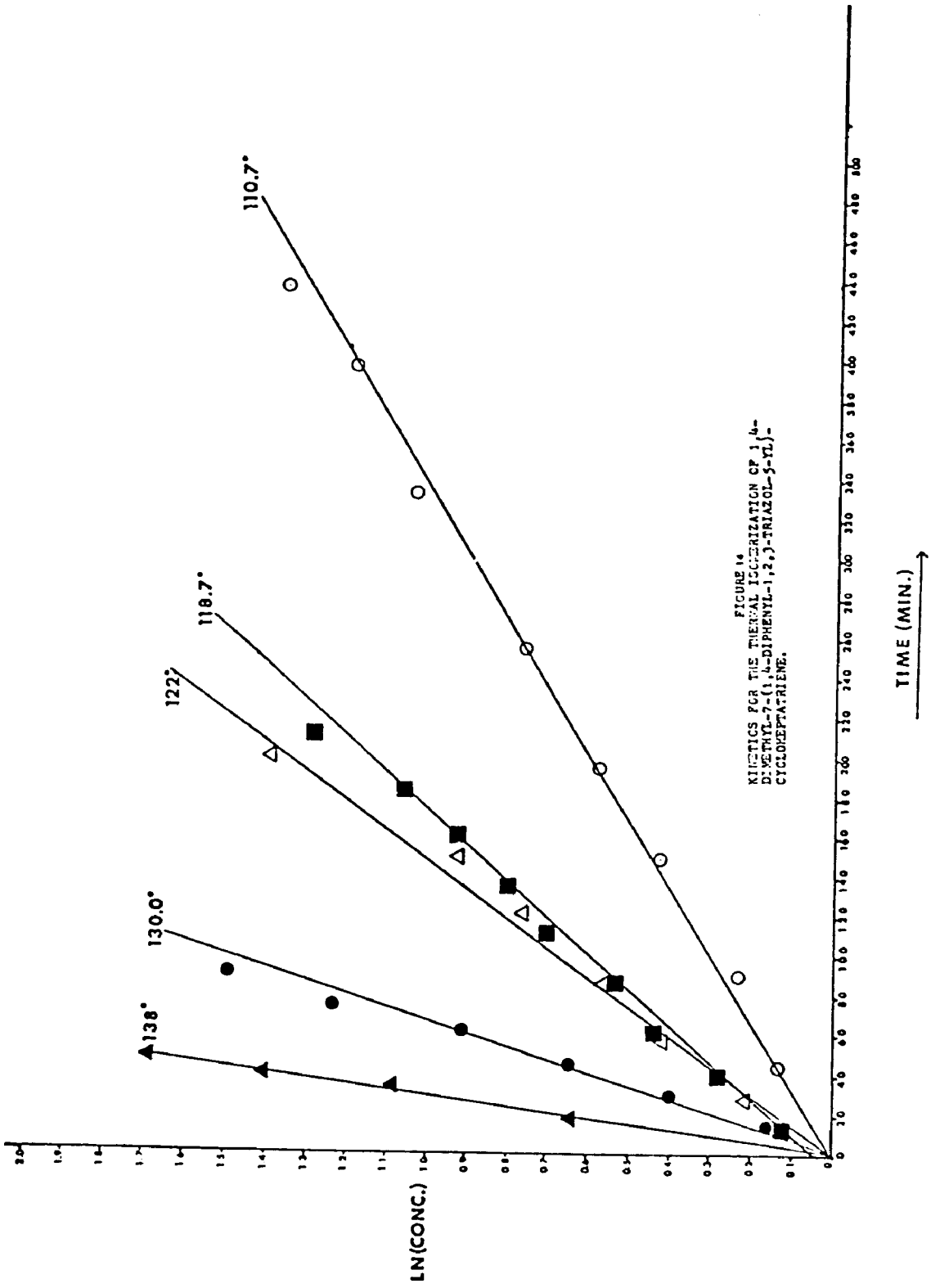


Figure 14. Kinetics for the thermal isomerization of 1,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl) cycloheptatriene.

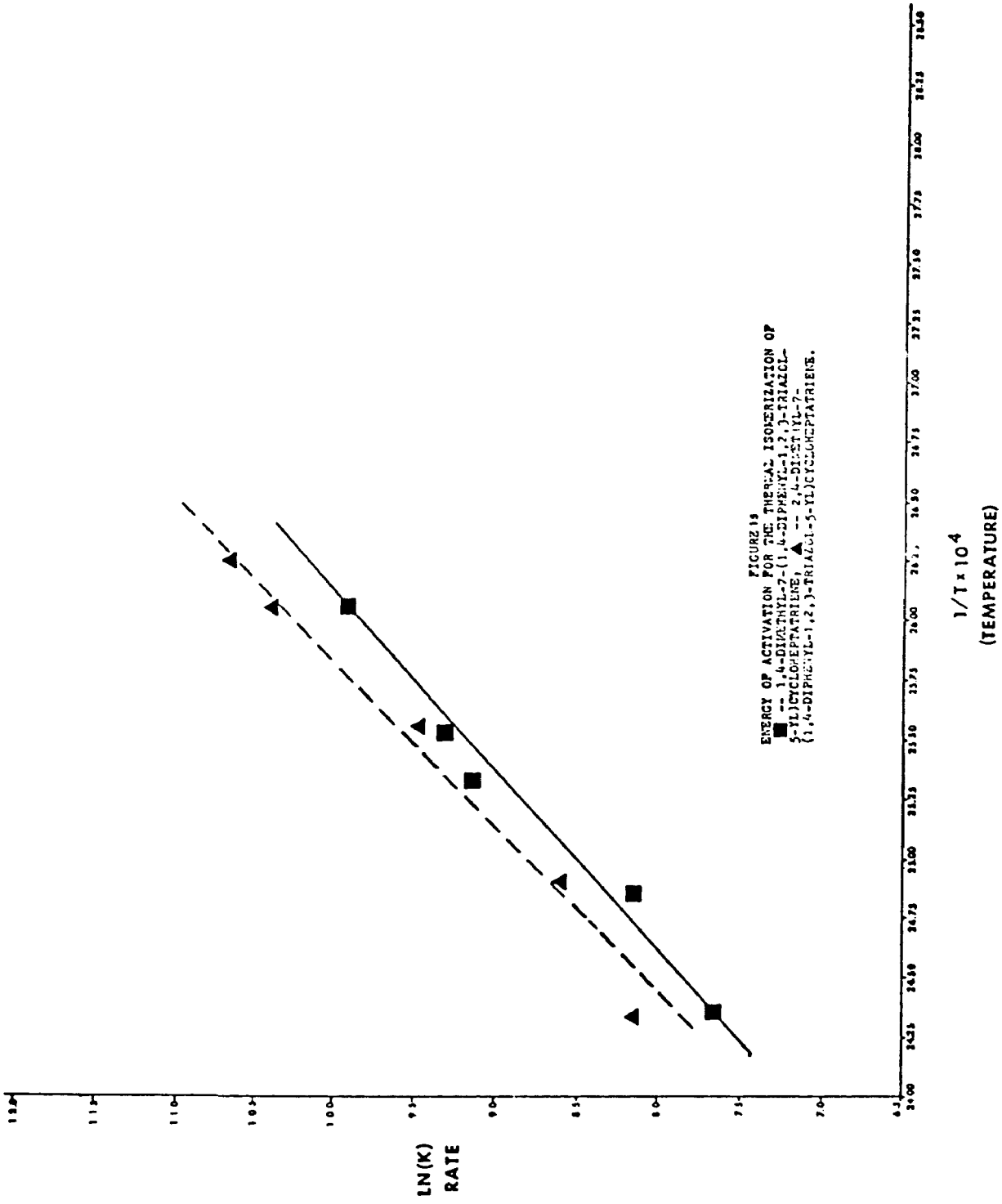


Figure 15. Activation parameters for the thermal isomerization of 1,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene and 2,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene.

Table XIX

Kinetics of the Thermal Rearrangement of 1,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene to 1,5-Dimethyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene

p-Xylene Adduct:

Temp., °C	K, sec^{-1} x 10^5	Deviation, %
110.7	5.31	2.0
118.5	9.58	4.1
122.0	10.9	5.0
130.0	29.8	1.9
138.0	50.9	0.2

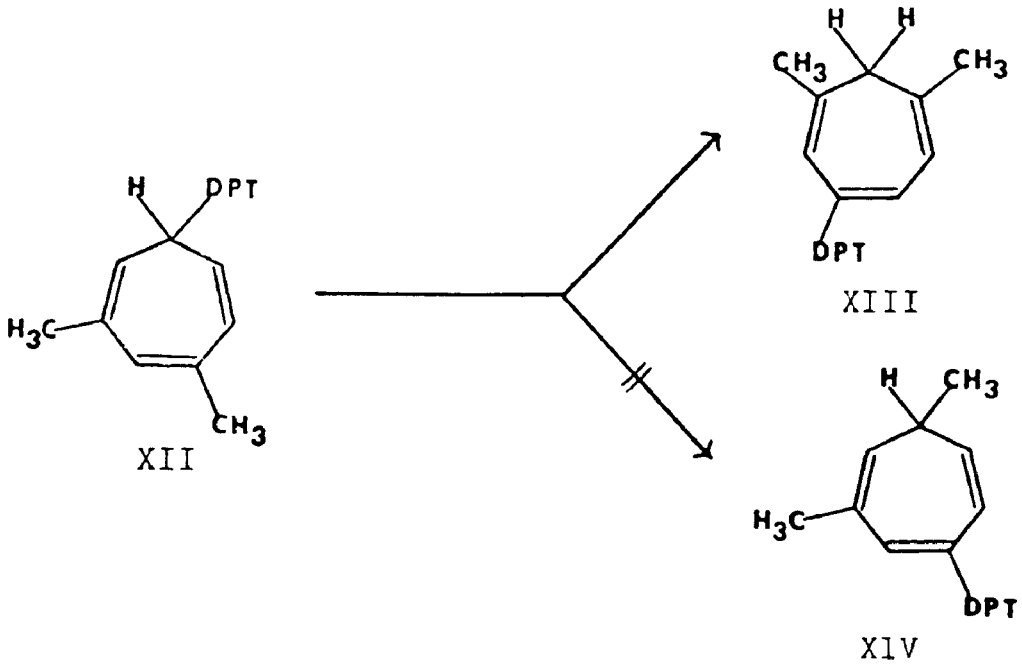
Table XX

Activation Parameters for the Thermal Isomerization of 1,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene to 1,5-Dimethyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene[a]

E_a, kcal/mole	26.9 ± 1.1
$\Delta H^{\dagger}$, kcal/mole	26.1
$\Delta S^{\dagger}$, e.u.	-10.64
Log A, sec^{-1}	11.01

[a] In this work, calculations were made from a mean temperature, 125°C.

centered at δ 6.32 ($J_{4,5}$ = 6.0 cps), a doublet centered at 5.80 ($J_{5,4}$ = 6.0 cps), and a singlet at 5.71 ppm. The methylene group appeared as a singlet at δ 2.22 and the two methyl groups appeared as singlets at 1.95 and 1.83 ppm. It is interesting to note that the thermal rearrangements of V, IX and XII yielded only one of the two possible isomeric tropilidenes. In each case, only products arising from a 1,5-hydrogen shift to the unsubstituted atom of the tropilidene ring were formed. During the thermal rearrangements, no products resulting from a 1,5-hydrogen shift to the alkyl-substituted position were detected.



The variable temperature PMR spectrum of adduct XIII showed no coalescence of the methylene absorption down to -63°C, indicating no hindrance to rotation of the diphenyltriazole moiety in the absence of vicinal substituents.

The kinetics for the thermal rearrangement of XII to XIII were investigated. The kinetic data shown in Figures

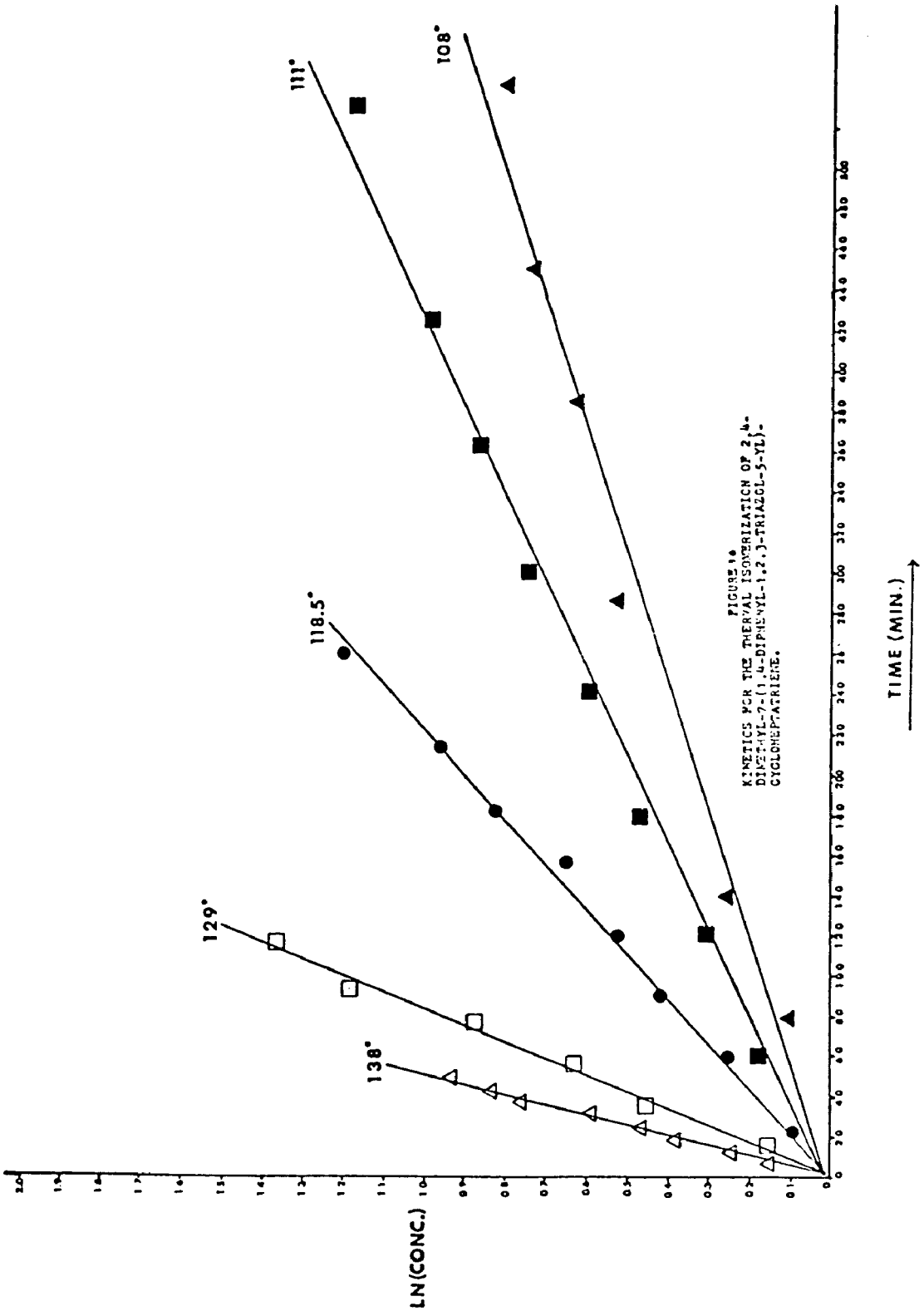


Figure 16. Kinetics for the thermal isomerization of 2,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene.

Table XXI

Kinetics of the Thermal Rearrangement of 2,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene to 1,6-Dimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene

Temp., °C	m-Xylene Adduct: K, sec^{-1} x 10^5	Deviation, %
108.0	2.31	9.5
111.0	3.08	2.9
118.5	7.93	2.2
129.0	20.0	3.9
138.0	31.3	3.5

Table XXII

Activation Parameters for the Thermal Isomerization of 2,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene to 1,6-Dimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene[a]

E_a, kcal/mole	27.9 ± 1.1
$\Delta H^{\dagger}$, kcal/mole	27.1
$\Delta S^{\dagger}$, e.u.	-8.81
Log A, sec^{-1}	11.41

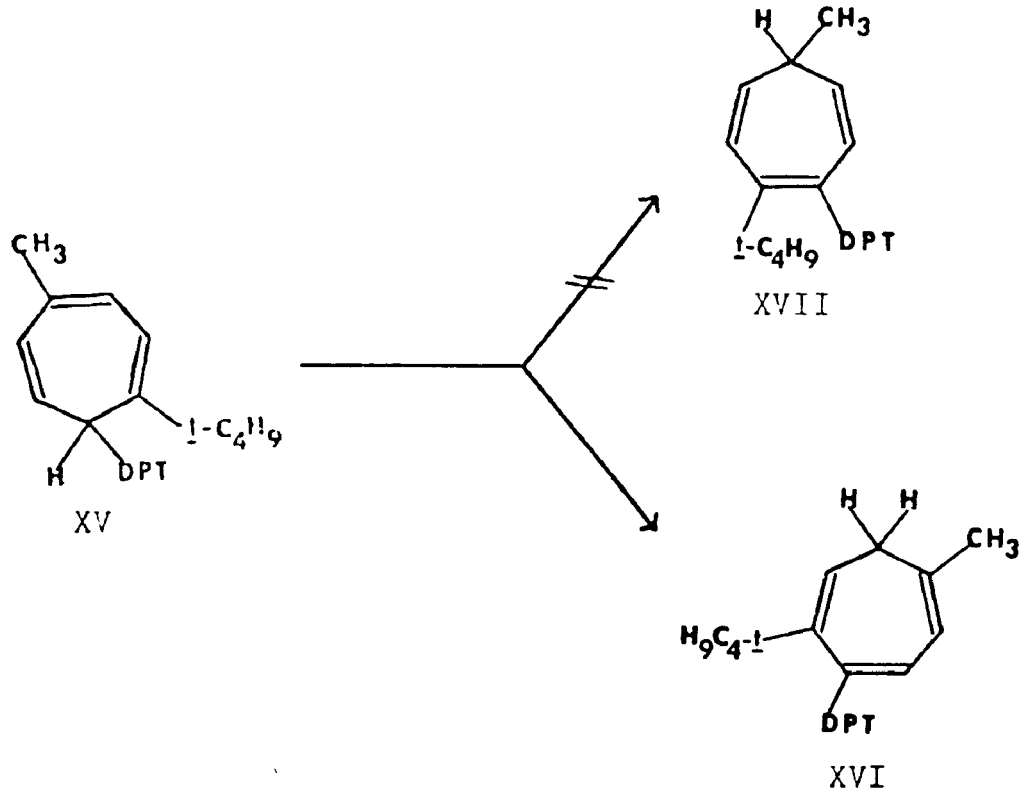
[a] In this work, calculations were made from a mean temperature, 125°C.

15 and 16 (interpreted in Tables XXI and XXII) were determined by measuring areas of the methyl signals of XII and the methyl signals of XIII in their PMR spectra. The reaction was found to be first-order in XII, with E_a 27.9 ± 1.1 kcal/mole and $\Delta S^{\dagger}$ -8.81 e.u. The E_a is in close agreement with reported 1,5-hydrogen shifts (Table XV).

D) Thermal Rearrangement of 1-tert-Butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XV).

Like the mesitylene adduct V, cycloheptatriene XV was shown to be in a dynamic equilibrium between its tropilidene and norcaradiene forms (Chapter II, p. 133). When XV was heated in solution to 80-100°C, it rearranged quantitatively to a new substance with the same elemental composition. The PMR spectrum, in addition to two diagnostic multiplets for the ten aromatic protons of 1,4-diphenyl-1,2,3-triazole, displayed a complex series of multiplets centered at δ 6.04, 5.85 and 5.43 ppm, which integrated for three protons and were assigned to olefinic hydrogens. The methyl and tert-butyl groups both appeared as three singlets at δ 1.71, 1.58 and 1.51 for the methyl group, integrating for a total of three hydrogens, and 1.12, 1.05 and 0.95 ppm for the tert-butyl group integrating for a total of nine protons. The methylene group appeared as very broad multiplets centered at δ 1.6 ppm. The chemical

shifts clearly indicate that the initial adduct has undergone a 1,5-hydrogen shift to the conjugated tropilidene XVI by comparison with the observations made on adducts VII and X. However, the complexity of the spectrum, especially the tert-butyl and methyl absorptions, requires further explanation. The first factor influencing the PMR spectral

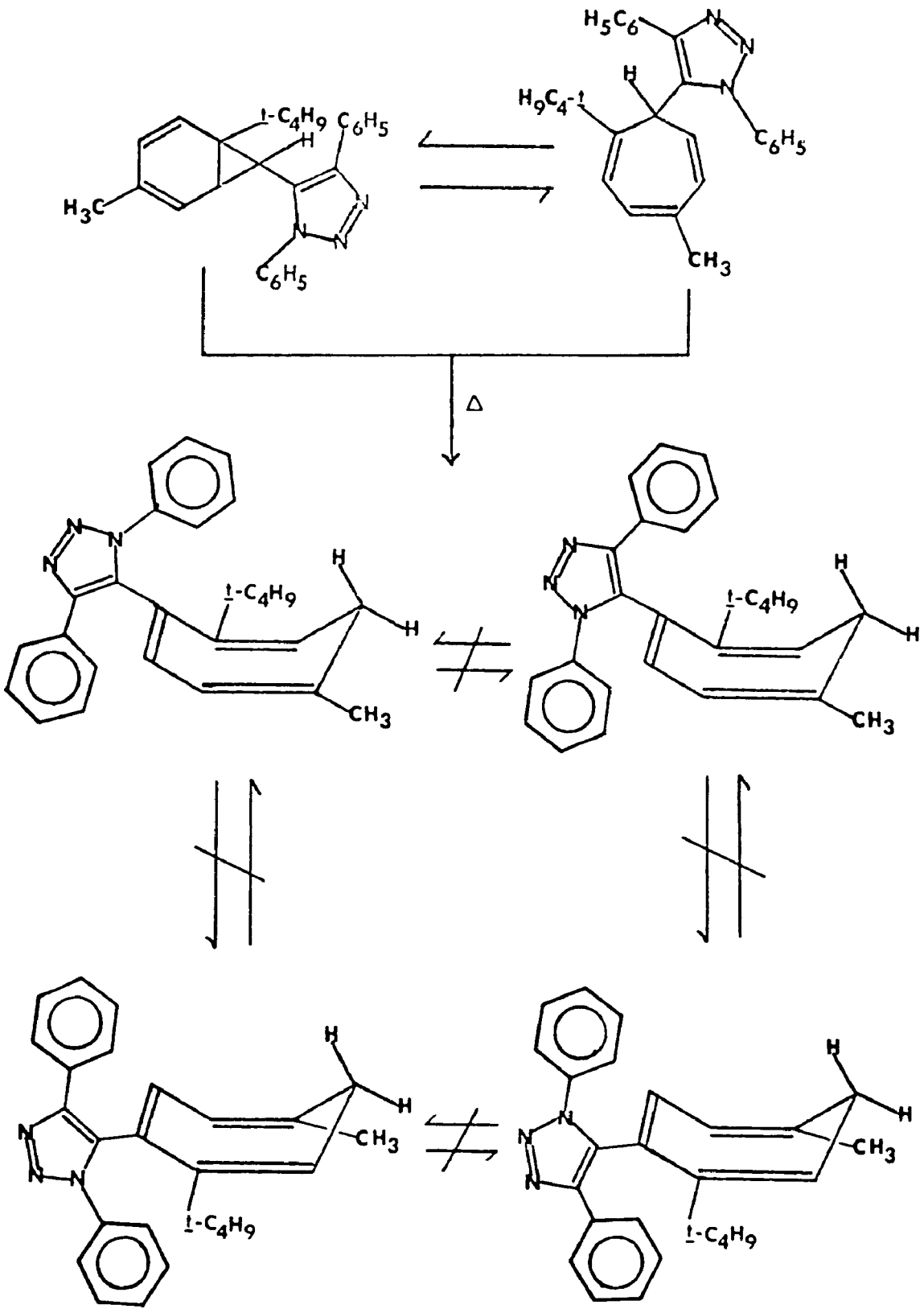


behavior is the hindered rotation of the large diphenyltriazole moiety past the vicinal tert-butyl group. Like the p-xylene adduct X, the vicinal relationship restricts rotation of the diphenyltriazole group and thus forces the methylene hydrogens to become non-equivalent. However, unlike the p-xylene case, the energy barrier to rotation for the diphenyltriazole moiety past the vicinal tert-butyl substituent must be extremely large, and rotation

would never be observable.

This would account for the complexity of the methylene group; however, the spectral behavior of the methyl group and tert-butyl group would not be affected. If, however, the ring interconversion of the two non-planar tropilidene conformations of the rearranged adduct XVI were frozen out by steric interactions between the diphenyltriazole group and the tert-butyl group, as models clearly demonstrate, the resulting PMR spectrum would become increasingly complex. It is therefore believed that the rearranged adduct XVI exists as a mixture of the two non-planar tropilidene conformers, which are not in equilibrium at room temperature, a fact that implies an activation energy of 15-20 kcal/mole or higher. A firm assignment of the structure will have to await additional experimental evidence. In particular, the possibility that two 1,5-hydrogen shifts have occurred, yielding a mixture of XVI and XVII, cannot be completely discounted. However, no support for such a mixture can be found in the other rearrangements already discussed.

The kinetics for the thermal rearrangement of XV to XVI were investigated. The data shown in Figures 17 and 18 (interpreted in Tables XXIII and XXIV) were obtained by measuring areas of the tert-butyl signal of XV versus an internal standard of acetonitrile in their PMR spectra. The reaction was found to be first-order in XV with E_a 24.85 ± 0.37 kcal/mole and $\Delta S^{\dagger}$ -14.52 e.u. As with the



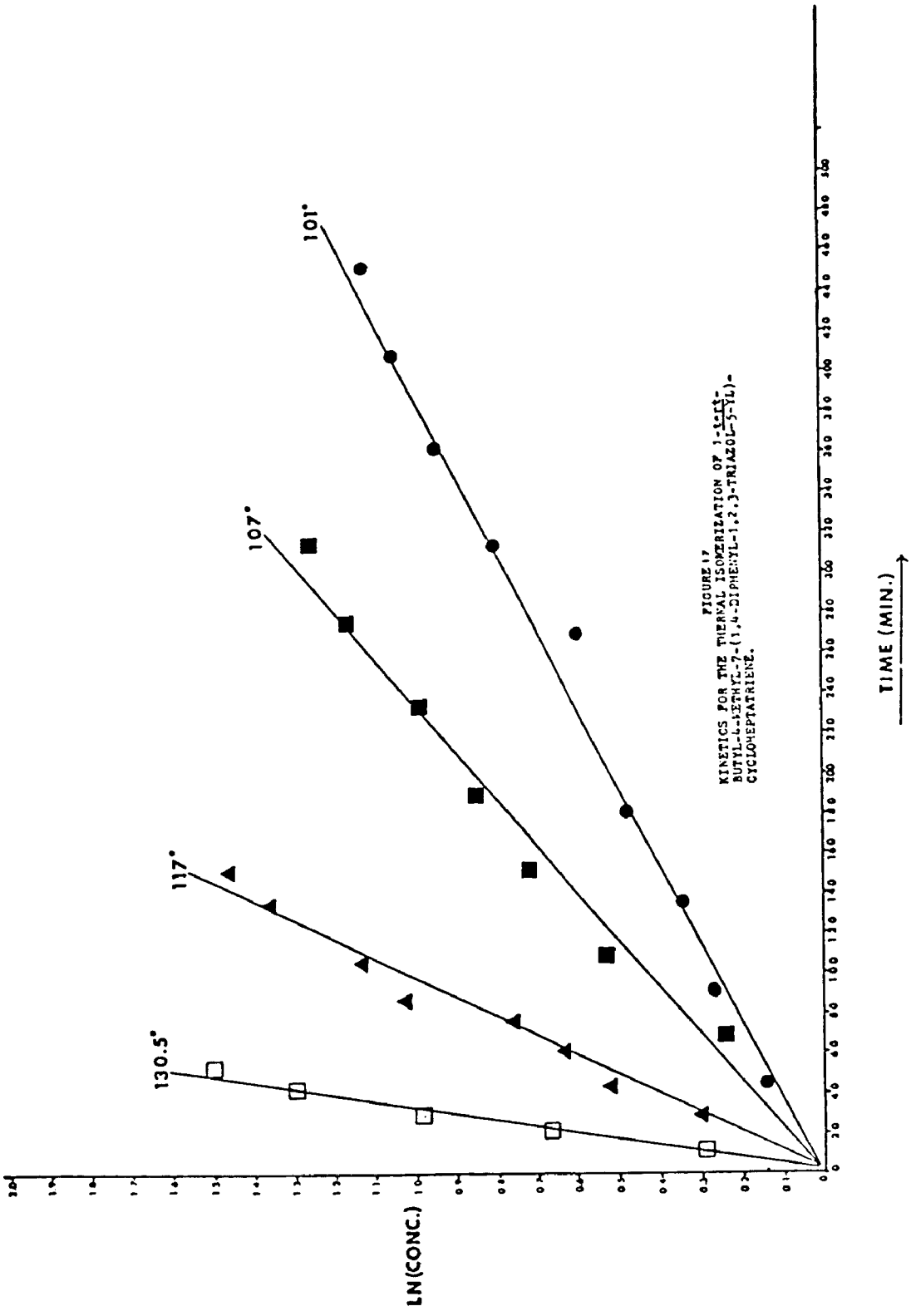


Figure 17. Kinetics for the thermal isomerization of 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene.

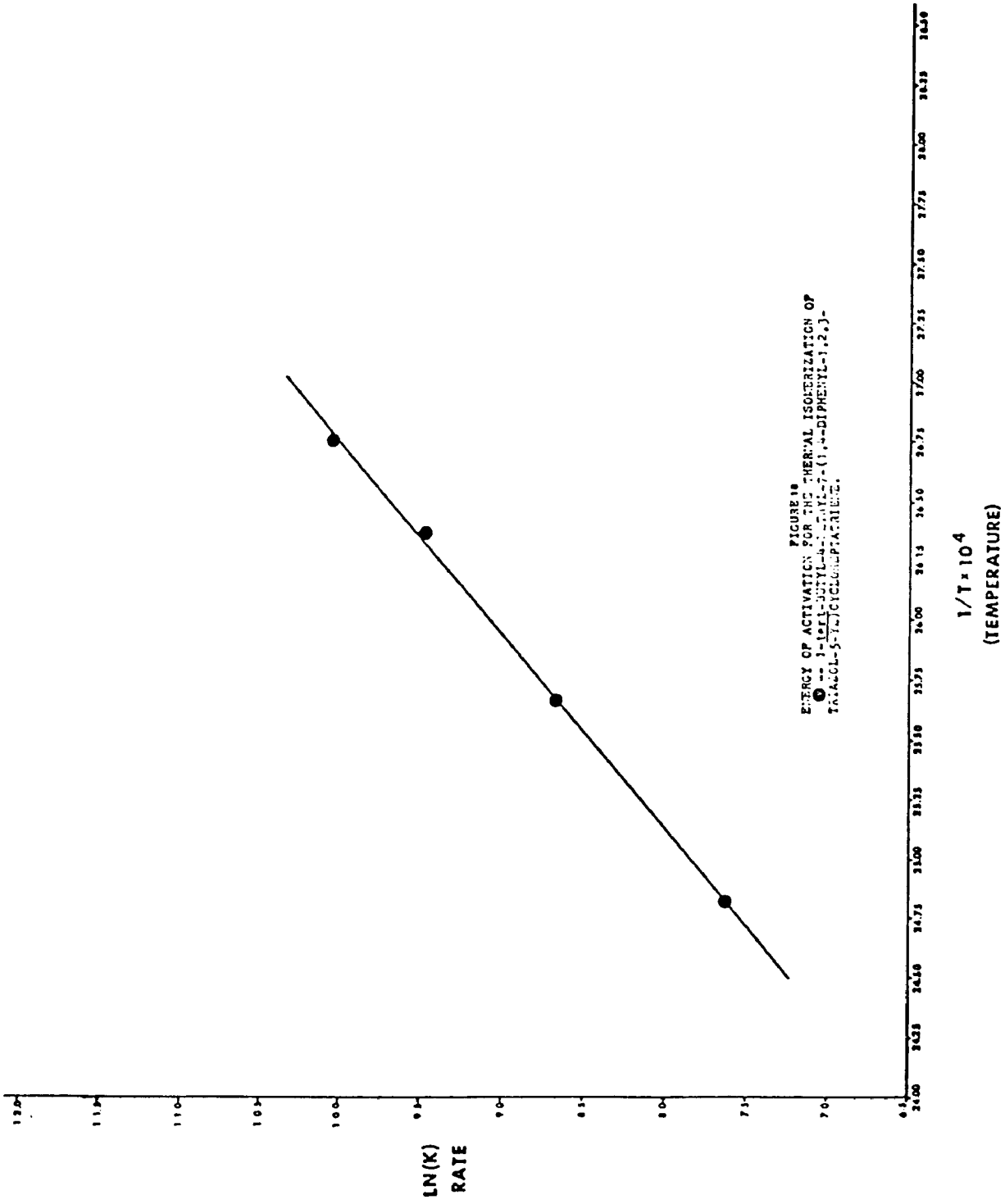


Figure 18. Activation parameters for the thermal isomerization of 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene.

mesitylene adduct V, an energy difference between reported 1,5-hydrogen shifts and that observed for the thermal rearrangement of XV to XVI of from 3- to 5-kcal/mole supports the earlier postulate (Chapters I and II) of an increased ground-state free energy for the initial adduct XV. Since the tropilidene XV was shown to be in a dynamic equilibrium with its norcaradiene tautomer (Chapter II, p. 133), and in light of the present knowledge concerning 1,5-hydrogen shifts, it is reasonable to assume that the hydrogen shift occurs through intermediate XVIII, Figure 19. The low activation energy for the isomerization of 2,5,7-triphenylnorcaradiene, adduct V and adduct XV, the only known norcaradienes with a hydrogen atom at the 7-position, support the postulate of an increased ground-state free energy.

E) Thermal Rearrangement of 1,3,4,6-Tetramethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (XIX).

The thermal rearrangement of norcaradiene XIX required unusually high temperatures. When XIX was heated in solution to 130°C it rearranged quantitatively to a new substance with the same elemental composition. Examination of the reaction at periodic intervals revealed that the isomerization proceeded through a series of intermediates. After prolonged heating, the PMR spectrum displayed only

Table XXIII

Kinetics of the Thermal Rearrangement of 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene to 1-methyl-5-tert-butyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene

4-tert-Butyltoluene Adduct:

Temp., °C	K, sec^{-1} x 10^5	Deviation, %
106.0	4.24	5.6
107.0	7.88	12.1
117.0	17.2	5.5
130.5	50.3	5.6

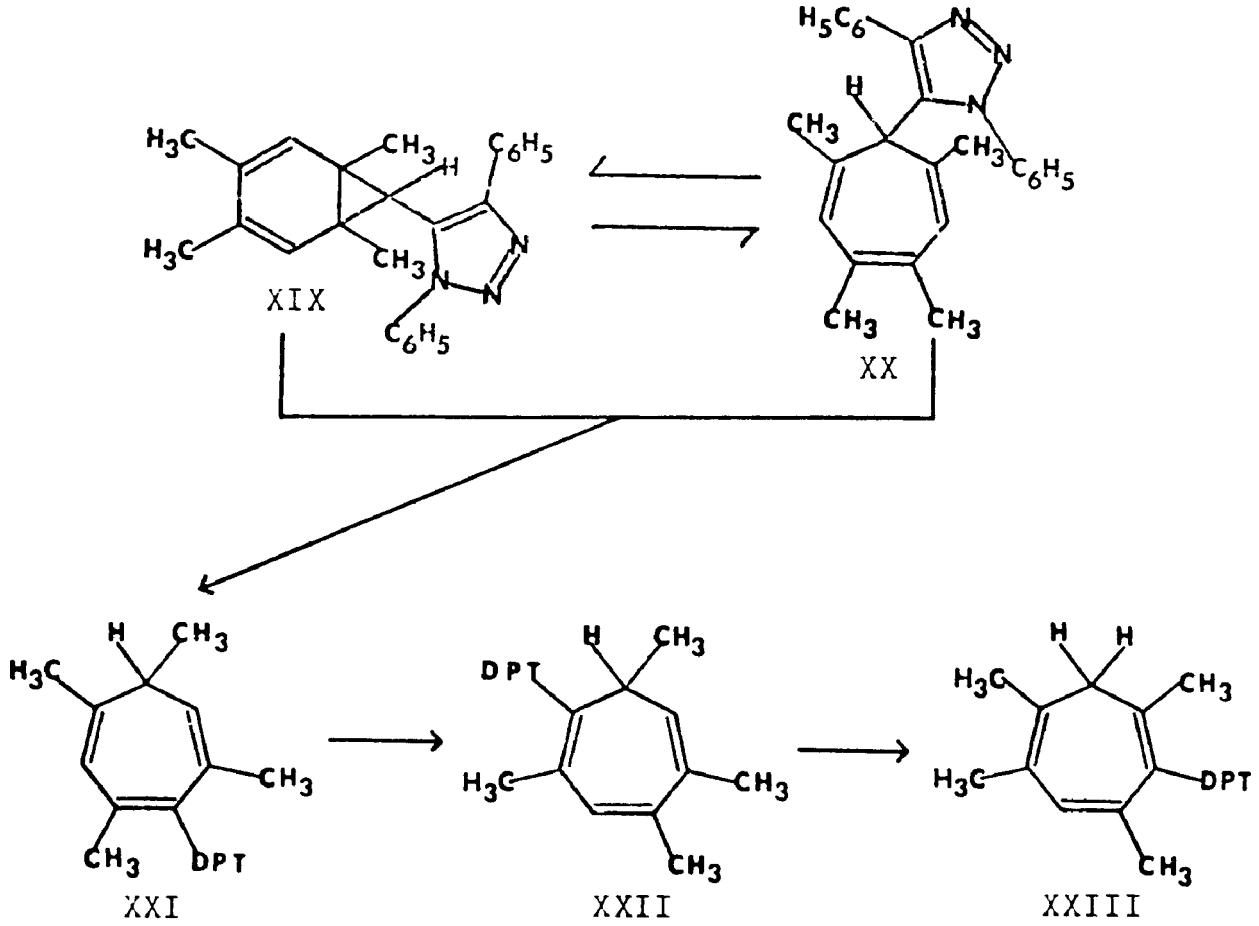
Table XXIV

Activation Parameters for the Thermal Isomerization of 1-tert-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene to 1-methyl-5-tert-butyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene[a]

E_a, kcal/mole	24.85 ± 0.37
$\Delta H^{\ddagger}$, kcal/mole	24.09
$\Delta S^{\ddagger}$, e.u.	-14.52
Log A, sec^{-1}	10.17

[a] In this work, calculations were made from a mean temperature, 110°C.

one isomeric tropilidene. Of the four possible isomeric tropilidenes formed by consecutive 1,5-hydrogen shifts, the structure 1,3,5,6-tetramethyl-2-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XXIII) assigned to the compound on the basis of the following PMR spectrum: An aromatic region typical of the 1,4-diphenyl-1,2,3-triazole moiety; and a two-proton multiplet centered at δ 7.72 shifted downfield from the large eight-proton multiplet centered at 7.30 ppm. The vinylic hydrogen appeared as a singlet at δ 6.15, the methylene group appeared as a singlet at 2.30 and the four methyl groups appeared as singlets at 1.90, 1.75, 1.65 and 1.61 ppm, respectively.



It is interesting to note the increased temperature required to initiate thermal isomerization. The large diphenyltriazole moiety is flanked on the 1- and 6-positions by methyl substituents. As molecular models demonstrate, considerable steric nonbonded interactions occur between the diphenyltriazole and methyl substituents during the Cope rearrangement of norcaradiene XIX to tropilidene XX. These interactions are believed responsible for the increased temperature required to initiate the thermal rearrangement.

A secondary feature observed during the thermal rearrangement of XIX is the final isolation of tropilidene XXIII. In all previously examined rearrangements, only one 1,5-hydrogen shift was observed before a stable tropilidene tautomer was formed. During the isomerization of XIX, at least two intermediate tropilidene isomers were formed, which could not be isolated in pure form. However, upon the arrival of the migrating hydrogen atom at 2- or 5-position no further rearrangements were observed, clearly indicating that XXIII is an energy well for the system.

Finally, the methylene group of tropilidene XXIII is not affected by the diphenyltriazole moiety in the 2-position, unlike the mesitylene adduct VII, the p-xylene adduct X or the 4-tert-butyltoluene adduct XVI, in which the chemical shift of the methylene hydrogens is strongly influenced by the diphenyltriazole moiety in the 3- or 4-position of the tropilidene ring.

Unfortunately, the complexity of the spectrum precluded the possibility for obtaining any kinetic data on this thermal rearrangement.

4. Experimental:

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. A Varian T-60, T-60A or a Joel 100 HMz Nuclear Magnetic Resonance Spectrometer were used for the scanning of NMR spectra and variable-temperature NMR spectra. In general, thin-layer chromatography was effected by the use of Eastman Chromagram Sheets, Type 6060 (silica gel with fluorescent indicator). Preparative pre-coated silica gel plates by Brinkman (2 mm) were used for preparative thin-layer chromatography. Column chromatography was done on Woelm neutral alumina or silica gel with fluorescent indicator, "dry-column chromatography grade," or with J. T. Baker Florisil (60-100 mesh).

Elemental analysis were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

A) Thermal Rearrangement of Selected 1,4-Diphenyl-1,2,3-triazol-5-yl Adducts.

(1) Thermal Rearrangement of 1,3,5-Trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (V).

A solution of 200 mg of 1,3,5-trimethyl-7-(1,4-

diphenyl-1,2,3-triazol-5-yl)norcaradiene in 20 ml of absolute ethanol was refluxed overnight. The ethanol was removed under aspirator vacuum; 200 mg of a yellow oil remained, and crystallized on standing; mp 146-148°C. On the basis of the PMR spectrum, compound VII was identified as 1,4,6-trimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene: δ 7.74 (m, 2H aromatic), 7.40 (m, 8H aromatic), 5.77 (br s, 2H C=CH-C=C; C=CH-C=C), 2.23 (AB quartet, 2H methylene CH_2), 1.96 (s, 3H methyl), 1.87 (s, 3H methyl) and 1.60 ppm (s, 3H methyl). Two recrystallizations from 95% ethanol gave an analytically pure sample, mp 147-148°C, m/e = 353.

Anal. Calcd for $C_{24}H_{23}N_3$:
C, 81.54; H, 6.57; N, 11.90.
Found: C, 81.50; H, 6.63; N, 11.95.

(2) Thermal Rearrangement of 1,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (IX).

A solution of 100 mg of compound IX in 20 ml of reagent grade toluene was refluxed for 24 hr. The toluene was removed under aspirator vacuum, leaving 100 mg of a yellow oil, which was chromatographed on a column of 15 g of 60-100 mesh Florisil. The column was eluted with benzene and each fraction was examined by TLC after concentration, and one of similar composition were combined. The only fractions amounted to 96 mg (essentially quanti-

tative conversion) which crystallized during evaporation of the eluent under aspirator vacuum; mp 138-142°C. On the basis of the PMR spectrum, the rearranged adduct was identified as 1,5-dimethyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene: ($CDCl_3$) δ 7.86 (m, 2H aromatic), 7.40 (m, 8H aromatic), 6.50 (d, $J_{3,2}$ = 6 Hz; 1 H C=C-CH=C), 5.80 (d, $J_{2,3}$ = 6 Hz; 1 H C=CH-C=C), 5.18 (t, $J_{6,7}$ = 7.4 Hz; 1 H C-CH=C), 2.20 (broad bump, 2H methylene CH_2), 1.96 (s, 3H methyl) and 1.52 ppm (s, 3H methyl). Recrystallization from a diethyl ether/petroleum ether (bp 30-60°C) mixture gave white needles of analytical purity, mp 146-147°C, m/3 = 339.

Anal. Calcd for $C_{23}H_{21}N_3$:
C, 81.36; H, 6.23; N, 12.38.
Found: C, 81.20; H, 6.16; N, 12.35.

(3) Thermal Rearrangement of 2,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XII).

A solution of 100 mg (0.0003 mole) of cycloheptatriene XII in 20 ml of reagent grade toluene was refluxed 24 hr. The toluene was removed under aspirator vacuum, leaving 100 mg of a yellow oil, which was triturated with two 10-ml portions of petroleum ether (bp 30-60°C) and cooled, whereupon 89 mg (approximately quantitative conversion) of a white crystalline material precipitated; mp 152-155°C. On the basis of the PMR spectrum, the rearranged material

was identified as 1,6-dimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XIII); ($CDCl_3$) δ 7.75 (m, 2H aromatic), 7.32 (m, 8H aromatic), 6.32 (d, $J_{4,5}$ = 6 Hz; CH C=C-CH=C), 5.80 (d, $J_{5,4}$ = 6 Hz; 1H C=CH-C=C), 5.71 (s, 1H C=CH-C=C), 2.22 (s, 2H methylene CH_2), 1.95 (s, 3H methyl) and 1.83 ppm (s, 3H methyl). Recrystallization from a diethyl ether/petroleum ether (bp 30-60°C) mixture gave a white solid of analytical purity; mp 158-160°C, m/e = 339.

Anal. Calcd for $C_{23}H_{21}N_3$:
C, 81.36; H, 6.23; N, 12.38.
Found: C, 81.21; H, 6.26; N, 12.42.

(4) Thermal Rearrangement of 1-tert-Butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene (XV).

A solution of 250 mg (0.0006 mole) of cycloheptatriene XV in 20 ml of reagent grade benzene was refluxed for 24 hr. The benzene was removed ~~under aspirator~~ vacuum, leaving 250 mg of a yellow oil, which was chromatographed on a column of 25 g of Florisil (60-100 mesh). The column was eluted with a benzene/diethyl ether mixture (10:1) and each fraction was examined by TLC after concentration. Only one fraction was isolated, which amounted to 225 mg of colorless oil (essentially quantitative conversion). On the basis of the PMR spectrum, the rearranged adduct was identified as 1-methyl-5-tert-butyl-4-(1,4-diphenyl-1,2,3-

triazol-5-yl)cycloheptatriene (XVI): ($CDCl_3$) δ 7.70 (m, 2H aromatic), 7.40 (m, 8H aromatic), 6.04, 5.85, and 5.43 (m, 3H vinylic), 1.71, 1.58, 1.51 (three singlets, 3H methyl), 1.12, 1.05, 0.95 (three singlets, 9H tert-butyl) and 1.60 ppm (very broad multiplet, 2H methylene). The oil was dissolved in the minimum amount of diethyl ether; an equal portion of petroleum ether (bp 30-60°C) was added and the resulting solution was cooled, whereupon a white crystalline material precipitated; mp 146-147.5°C.

Anal. Calcd for $C_{26}H_{27}N_3$:
C, 81.85; H, 7.13; N, 11.01.
Found: C, 81.90; H, 7.13; N, 11.05.

B) Kinetics of the Thermal Rearrangement of Selected 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole Adducts.

The kinetics of the thermal isomerization of five polysubstituted adducts derived from the thermal decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in polysubstituted aromatic substrates were determined. The isomerizations were conducted in sealed 5-mm NMR tubes. Prior to use they were cleaned with chromic/sulfuric acid solution, followed by 10N sodium hydroxide, and were then rinsed repeatedly with distilled water, followed by rinsings with reagent grade acetone and then were baked for 24 hr in a drying oven at about 100°C.

Solutions were prepared by placing 20 to 50 mg of the adduct in an NMR tube and dissolving it with approximately

0.5 ml of deuteriochloroform containing 1% of tetramethylsilane. The tubes were then repeatedly evacuated and flushed with dry nitrogen and were finally sealed under vacuum (approximately half atmosphere). In cases where the complexity of the PMR spectrum did not allow for the direct measurement of the disappearance of starting material and appearance of product, an internal standard of acetonitrile was added. Prior to isomerization, all tubes were examined by PMR spectroscopy to insure the purity of the substrate and that an adequate concentration of reactant was present.

All PMR data were obtained on a Varian T60 or T60-A spectrometer. The tube and content were placed in a constant temperature vapor, which had previously reached equilibration. After an appropriate time the tube was removed from the vapor and immediately cooled by being placed in a cold water bath, which completely quenched any further isomerization. In general, the methyl peaks were used to monitor the progress of the reaction. To this end, the aliphatic region of the PMR spectrum was expanded and the relative areas of the methyl peaks of the starting material and the area of the methyl peaks of the product were integrated an average of five times. The average value obtained from these integrations was used to determine the kinetic parameters.

The average numerical values obtained (each an average of five measurements) were treated in the following manner.

A plot of the ln $X/(X_{0+1})$ *versus* time was used to obtain the rates, where X_0 equals the ratio of starting material to product obtained from the PMR integrations. The ratios thus obtained are tabulated in Table XXV, together with measured integral counts and times. The zero point was not included in the computer data set for any of the runs.

(5) Spectra:

On the following pages are reproduced the PMR, ^{13}CMR and mass spectra of the novel compounds encountered in this study. Their special features and diagnostic value have been discussed in the previous pages.

All PMR and ^{13}CMR spectra were determined from solutions in $CDCl_3$ with TMS as internal standard.

Table XXV

Relative Rates for the Thermal Rearrangement of Selected 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole Adducts

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
(1) 1,3,5-Trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene:					
Run I 89°C					
1	3.6	-0.0457	-0.0437	-4.3	
2	9.18	-0.1177	-0.1274	8.3	
3	14.22	-0.2105	-0.2030	-3.5	
4	20.22	-0.3025	-0.2930	-3.1	
5	23.52	-0.3334	-0.3425	2.7	
					-1.5×10^{-5}
		standard deviation = 6.47×10^{-7}			
Run II 99°C					
1	3.6	-0.1342	-0.1454	8.4	
2	9.6	-0.3955	-0.3922	-0.8	
3	12.6	-0.5196	-0.5156	-0.7	
4	16.5	-0.6931	-0.6761	-2.5	
5	20.1	-0.8018	-0.8241	+2.8	
6	24.42	-1.0520	-1.0018	-4.8	

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%,Difference	Slope, sec^{-1}
7	28.08	-1.0980	-1.1524	4.9	
8	31.68	-1.3140	-1.3005	-1.0	
					-4.11×10^{-5}
		standard deviation = 1.31×10^{-6}			
Run III 107.0°C					
1	1.8	-0.0777	-0.0538	-30.8	
2	3.6	-0.1788	-0.1734	- 3.0	
3	5.4	-0.2808	-0.2930	4.3	
4	7.8	-0.4355	-0.4525	3.9	
5	10.2	-0.5983	-0.6120	2.2	
6	12.6	-0.7668	-0.7715	0.6	
7	15.9	-0.9903	-0.9908	0.04	
8	18.3	-1.1690	-1.1503	-1.6	
					-6.65×10^{-5}
		standard deviation = 1.05×10^{-6}			
Run IV 110.6°C					
1	3.6	-0.3795	-0.3256	-14.2	
2	7.2	-0.6823	-0.6776	- 0.7	

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
3	10.8	-0.9935	-1.0296	3.6	
4	14.4	-1.3120	-1.3817	5.2	
5	18.0	-1.6970	-1.7337	2.1	
6	21.9	-2.1969	-2.1151	-3.7	
					-9.78×10^{-5}
		standard deviation = 4.26×10^{-6}			
Run V 118.0°C					
1	0.9	-0.0935	-0.0904	-3.3	
2	1.8	-0.2177	-0.2025	-6.9	
3	2.7	-0.3130	-0.3148	0.6	
4	3.6	-0.4265	-0.4270	0.1	
5	4.8	-0.5738	-0.5766	0.5	
6	5.6	-0.6783	-0.6763	-0.3	
7	6.9	-0.7840	-0.8384	6.9	
8	8.22	-1.0260	-1.0030	2.2	
9	10.2	-1.2650	-1.2499	-1.3	
					-1.25×10^{-4}
		standard deviation = 2.75×10^{-6}			

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
Run VI 129.5°C					
1	0.6	-0.3326	-0.3515	5.7	
2	1.2	-0.6772	-0.6683	-1.3	
3	1.5	-0.8007	-0.8267	3.3	
4	1.8	-1.0530	-0.9852	-6.4	
5	2.1	-1.1697	-1.1436	-2.2	
6	2.4	-1.2384	-1.3020	5.1	
7	2.7	-1.4663	-1.4605	-0.4	
					-5.28×10^{-4}
		standard deviation = 2.58×10^{-5}			
Run VII 138.0°C					
1	0.18	-0.1626	-0.1598	-1.7	
2	0.36	-0.3184	-0.3313	4.0	
3	0.54	-0.5288	-0.5027	-4.9	
4	0.72	-0.6646	-0.6742	1.4	
5	0.9	-0.8329	-0.8457	1.5	
6	1.08	-1.0413	-1.0171	-2.3	
7	1.26	-1.1449	-1.1886	3.8	

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
8	1.44	-1.3863	-1.3601	-1.8	
					-9.53×10^{-4}
		standard deviation = 2.29×10^{-5}			

(2) 1,3,5-Trimethyl-2,4,6-trideuterio-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene.

Run I 101°C				
1	2.7	-0.1458	-0.1138	-21.9
2	5.4	-0.2096	-0.2263	7.9
3	8.1	-0.3101	-0.3388	9.2
4	10.8	-0.4283	-0.4513	5.3
5	13.5	-0.5764	-0.5638	- 2.1
6	16.2	-0.7005	-0.6763	- 3.4
7	18.9	-0.7883	-0.7888	0.1
8	21.6	-0.9161	-0.9013	- 1.6
9	24.3	-1.0096	-1.0138	0.4
10	27.0	-1.1155	-1.1263	1.0

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
Run II 107.0°C					
1	3.6	-0.0826	-0.1346	62.8	
2	4.2	-0.2462	-0.1797	-27.0	
3	6.6	-0.3677	-0.3600	- 2.0	
4	9.0	-0.5260	-0.5403	2.7	
5	11.4	-0.7037	-0.7206	2.4	
6	13.8	-0.8979	-0.9009	0.3	
7	16.2	-1.0818	-1.0812	- 0.04	
8	18.6	-1.2729	-1.2616	- 0.9	
					-7.51×10^{-5}
		standard deviation = 2.46×10^{-6}			
Run III 111.5°C					
1	1.8	-0.1924	-0.1941	0.8	
2	3.6	-0.3885	-0.3987	2.6	
3	5.4	-0.5995	-0.6033	0.6	
4	7.2	-0.8361	-0.8078	-3.3	
5	9.0	-1.0216	-1.0124	-0.9	
6	10.8	-1.1895	-1.2170	2.3	
7	12.6	-1.4271	-1.4216	-0.4	

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
					-1.13×10^{-4}
		standard deviation = 1.98×10^{-6}			
Run IV 117.0°C					
1	0.9	-0.1500	-0.1477	-1.5	
2	1.8	-0.3001	-0.3047	1.5	
3	2.7	-0.4463	-0.4616	3.4	
4	3.6	-0.6527	-0.6186	-5.2	
5	4.5	-0.7506	-0.7756	3.3	
6	5.4	-0.9693	-0.9326	-3.7	
7	6.3	-1.0257	-1.0895	6.2	
8	7.2	-1.2993	-1.2465	-4.0	
9	8.1	-1.3863	-1.4035	1.2	
					-1.74×10^{-4}
		standard deviation = 5.56×10^{-6}			
Run V 130.5°C					
1	0.6	-0.2231	-0.2291	2.7	
2	1.2	-0.5142	-0.5119	-0.4	
3	1.8	-0.8023	-0.7948	-0.9	

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
4	2.4	-1.0798	-1.0776	-0.2	
5	3.0	-1.3544	-1.3604	0.4	
					-4.71×10^{-4}
		standard deviation = 3.58×10^{-6}			
(3) 1,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene.					
Run I 110.5°C					
1	2.7	-0.1251	-0.0965	-22.8	
2	5.4	-0.2182	-0.2401	10.0	
3	9.0	-0.4248	-0.4316	1.5	
4	11.7	-0.5787	-0.5752	-0.5	
5	15.3	-0.7472	-0.7667	2.6	
6	20.1	-1.0459	-1.0220	-2.2	
7	23.7	-1.1786	-1.2135	2.9	
8	26.1	-1.3683	-1.3411	-1.9	
					-5.31×10^{-5}
		standard deviation = 1.17×10^{-6}			

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
Run II 118.0°C					
1	0.9	-0.1144	-0.1225	7.1	
2	2.4	-0.2623	-0.2662	1.4	
3	3.6	-0.4054	-0.3812	-5.9	
4	5.1	-0.5321	-0.5249	-1.3	
5	6.6	-0.7031	-0.6686	-4.1	
6	8.1	-0.7851	-0.8123	3.4	
7	9.6	-0.9122	-0.9560	4.7	
8	11.1	-1.0384	-1.0997	5.9	
9	12.6	-1.3217	-1.2435	-5.9	
		standard deviation = 4.0×10^{-6}			-9.58×10^{-5}
Run III 122.0°C					
1	1.8	-0.1940	-0.1835	-5.4	
2	3.6	-0.4273	-0.3814	-10.7	
3	5.4	-0.5428	-0.5793	6.7	
4	7.2	-0.7591	-0.7772	2.3	
5	9.0	-0.9248	-0.9751	5.4	
6	12.3	-1.3863	-1.3379	-3.4	

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
					-1.09×10^{-4}
		standard deviation = 5.5×10^{-6}			
Run IV 130.0°C					
1	0.9	-0.1410	-0.1286	-8.8	
2	1.8	-0.4003	-0.3975	-0.7	
3	2.7	-0.6547	-0.6663	1.7	
4	3.6	-0.9028	-0.9352	3.5	
5	4.5	-1.2299	-1.2041	-2.0	
6	5.4	-1.4758	-1.4730	-0.1	
					-2.98×10^{-4}
		standard deviation = 5.96×10^{-6}			
Run V 130.0°C					
1	1.2	-0.6419	-0.6407	-0.1	
2	2.1	-1.0986	-1.0994	0.07	
3	2.7	-1.4027	-1.4051	0.1	
4	3.3	-1.7130	-1.7109	-0.1	
					-5.09×10^{-4}
		standard deviation = 1.56×10^{-6}			

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
(4) 2,4-Dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene.					
Run I 108.0°C					
1	4.8	-0.0953	-0.1548	62.4	
2	8.4	-0.2513	-0.2381	-5.2	
3	17.1	-0.5221	-0.4393	-15.8	
4	23.1	-0.5860	-0.5780	-1.3	
5	27.3	-0.6701	-0.6752	0.7	
6	32.7	-0.7608	-0.8001	5.1	
					-2.31×10^{-5}
		standard deviation = 2.27×10^{-6}			
Run II 111.0°C					
1	3.6	-0.1717	-0.2309	34.4	
2	7.2	-0.3026	-0.3420	13.0	
3	10.8	-0.4697	-0.4532	-3.5	
4	14.4	-0.5877	-0.5643	-3.9	
5	18.0	-0.7176	-0.6754	-5.8	
6	21.9	-0.8303	-0.7959	-4.1	
7	25.5	-0.9582	-0.9070	-5.3	

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
8	32.1	-1.1051	-1.1108	0.5	
9	35.7	-1.2237	-1.2219	- 0.1	
10	39.6	-1.3134	-1.3423	2.2	
11	43.2	-1.4169	-1.4535	2.5	
					-3.08×10^{-5}
		standard deviation = 9.16×10^{-7}			
Run III 118.5°C					
1	1.5	-0.0800	-0.0690	-13.7	
2	3.6	-0.2411	-0.2357	-2.2	
3	5.4	-0.3862	-0.3786	-1.9	
4	7.2	-0.5171	-0.5215	0.8	
5	9.3	-0.6359	-0.6882	8.2	
6	10.8	-0.8167	-0.8073	-1.1	
7	12.6	-0.9582	-0.9502	-0.8	
8	15.6	-1.2035	-1.1883	-1.2	
					-7.93×10^{-5}
		standard deviation = 1.88×10^{-6}			

Table XXV continued

Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
Run IV 129.0°C					
1	0.9	-0.1541	-0.1762	14.3	
2	2.1	-0.4519	-0.4168	-7.7	
3	3.3	-0.6346	-0.6573	3.5	
4	4.5	-0.8909	-0.8979	0.7	
5	5.7	-1.1904	-1.1384	-4.3	
6	6.9	-1.3437	-1.3790	2.6	
					-2.0×10^{-4}
		standard deviation = 7.86×10^{-6}			
Run V 138.0°C					
1	0.36	-0.1541	-0.1372	-10.9	
2	0.72	-0.2268	-0.2502	10.2	
3	1.08	-0.3760	-0.3631	-3.4	
4	1.44	-0.4519	-0.4761	5.3	
5	1.80	-0.5757	-0.5890	2.3	
6	2.16	-0.7537	-0.7020	-6.8	
7	2.52	-0.8060	-0.8149	1.1	
8	2.88	-0.9162	-0.9279	1.2	
					-3.13×10^{-4}

Table XXV continued

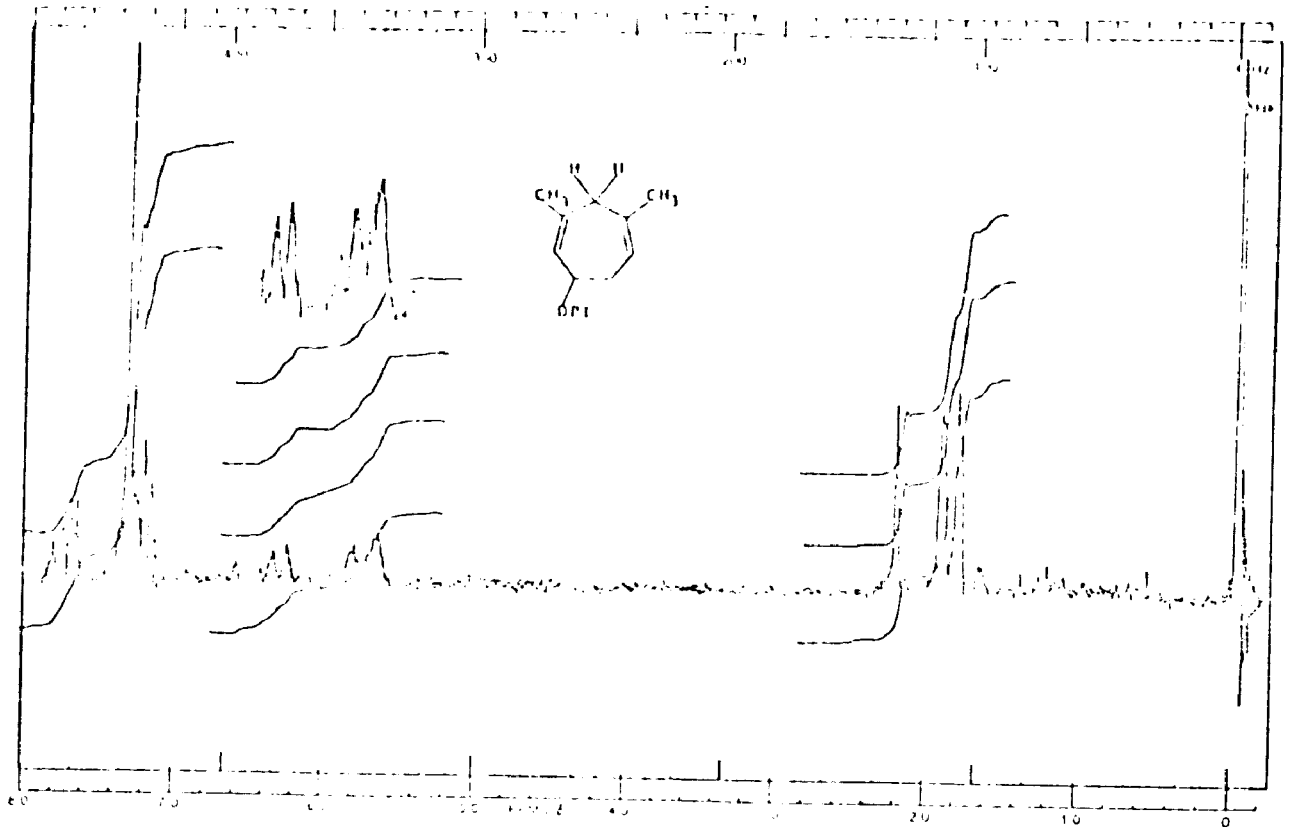
Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
		standard deviation = 1.19×10^{-5}			
(5) 1-tert-Butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene.					
Run I 101.0°C					
1	2.7	-0.1230	-0.1035	-15.8	
2	5.4	-0.2265	-0.2180	-3.7	
3	8.1	-0.3379	-0.3325	-1.5	
4	10.8	-0.4812	-0.4470	-7.0	
5	16.2	-0.5276	-0.6761	28.1	
6	18.9	-0.7965	-0.7906	-0.7	
7	21.6	-0.9403	-0.9051	-3.7	
8	24.3	-1.0392	-1.0197	-1.8	
9	27.0	-1.1545	-1.1342	-1.7	
					-4.24×10^{-5}
		standard deviation = 2.47×10^{-6}			
Run II 107.0°C					
1	4.2	-0.2464	-0.1913	-22.3	
2	6.6	-0.5280	-0.3805	-27.9	

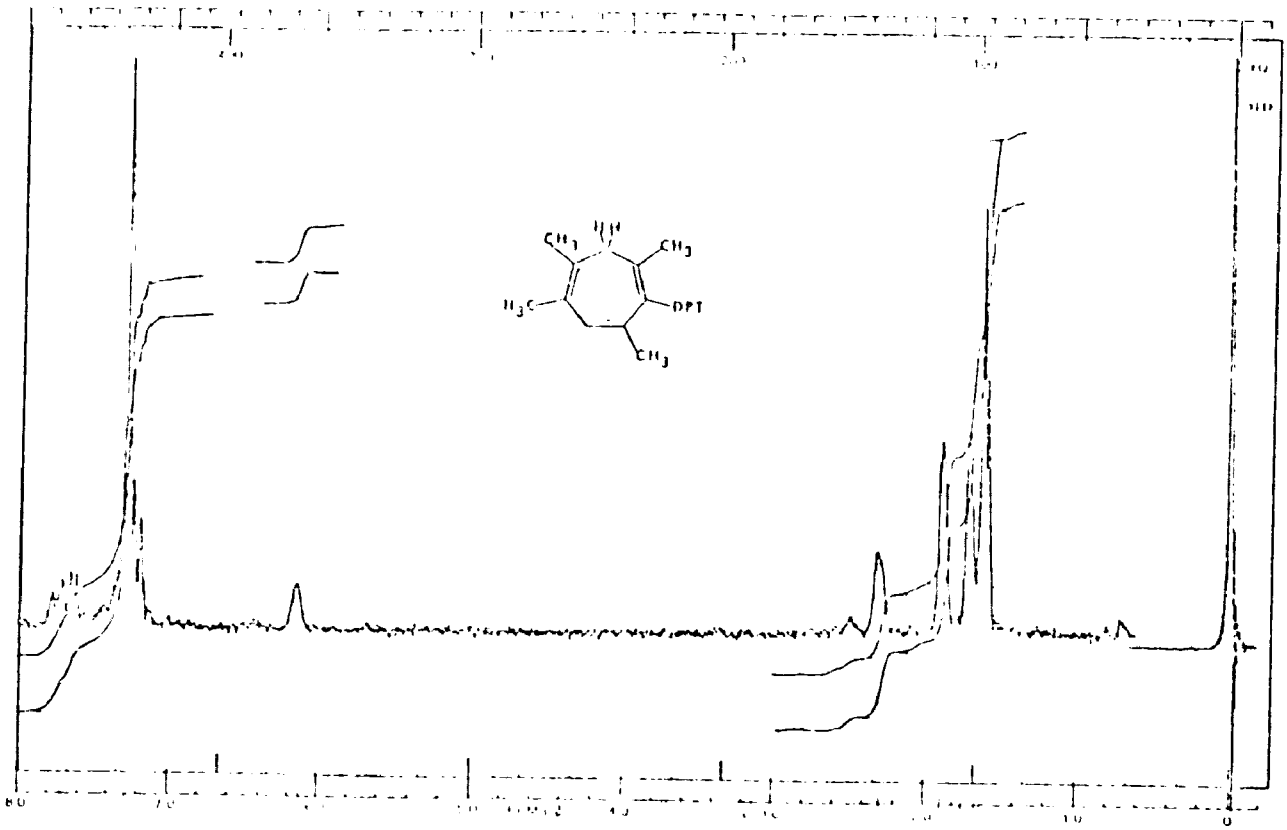
Table XXV continued

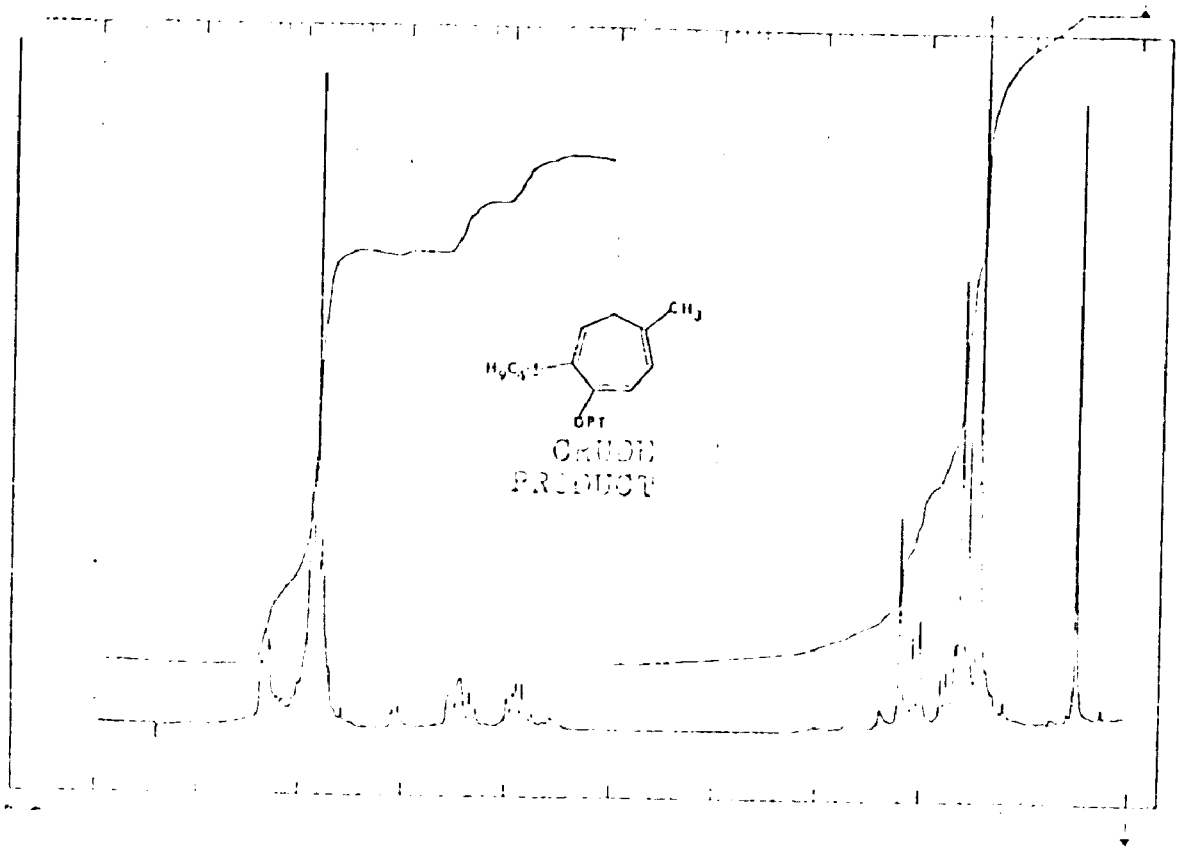
Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
3	9.0	-0.6330	-0.5696	-10.0	
4	11.4	-0.8278	-0.7587	-8.3	
5	13.8	-0.9622	-0.9478	-1.4	
6	16.2	-1.1479	-1.1370	-0.9	
7	18.6	-1.2166	-1.3261	8.9	
		standard deviation = 9.2×10^{-6}			7.88×10^{-5}
Run III 117.0°C					
1	1.8	-0.2902	-0.2869	-1.1	
2	2.7	-0.5177	-0.4422	-14.5	
3	3.6	-0.6050	-0.5974	-1.2	
4	4.5	-0.7193	-0.7526	4.6	
5	5.4	-1.0191	-0.9078	-10.9	
6	6.3	-1.0991	-1.0631	-3.2	
7	8.1	-1.3545	-1.3735	1.4	
8	9.0	-1.4550	-1.5287	5.0	
		standard deviation = 9.4×10^{-6}			1.72×10^{-4}

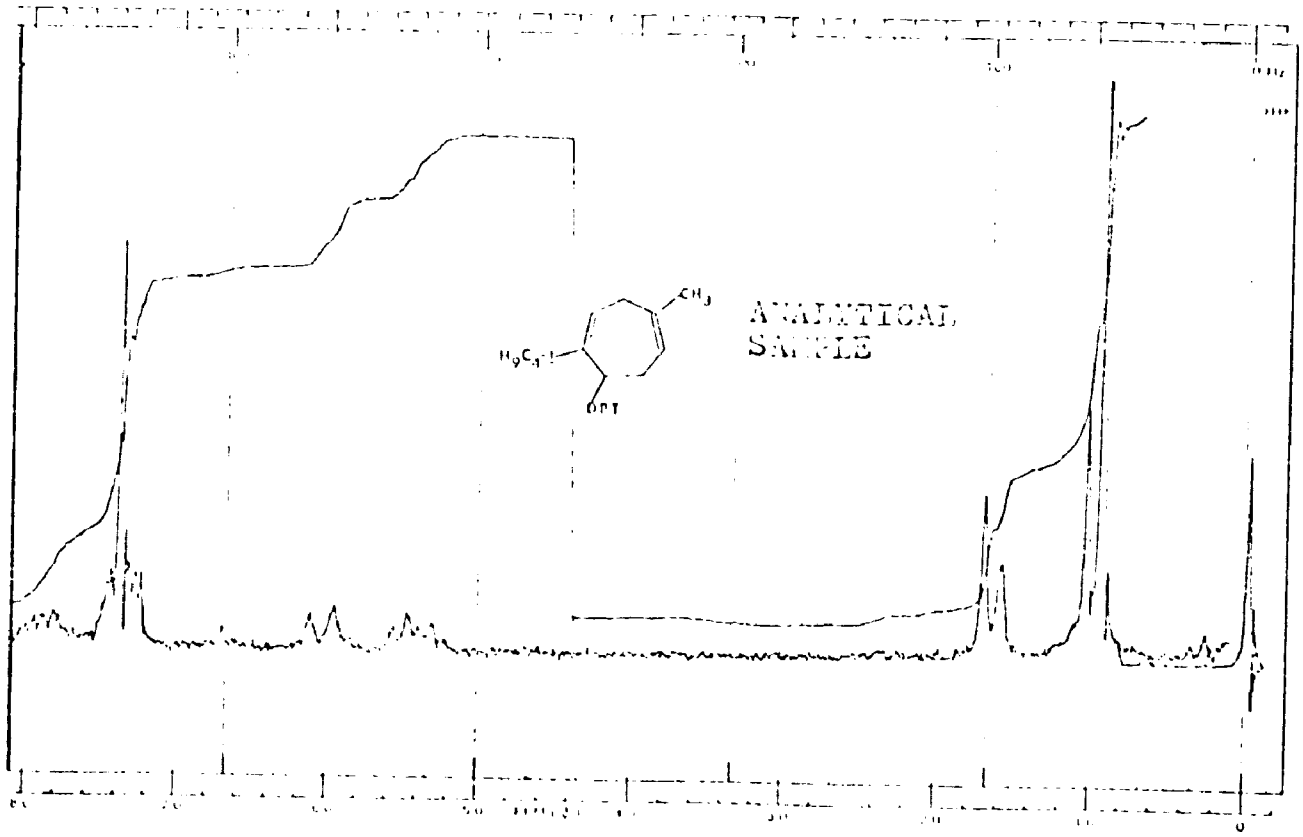
Table XXV continued

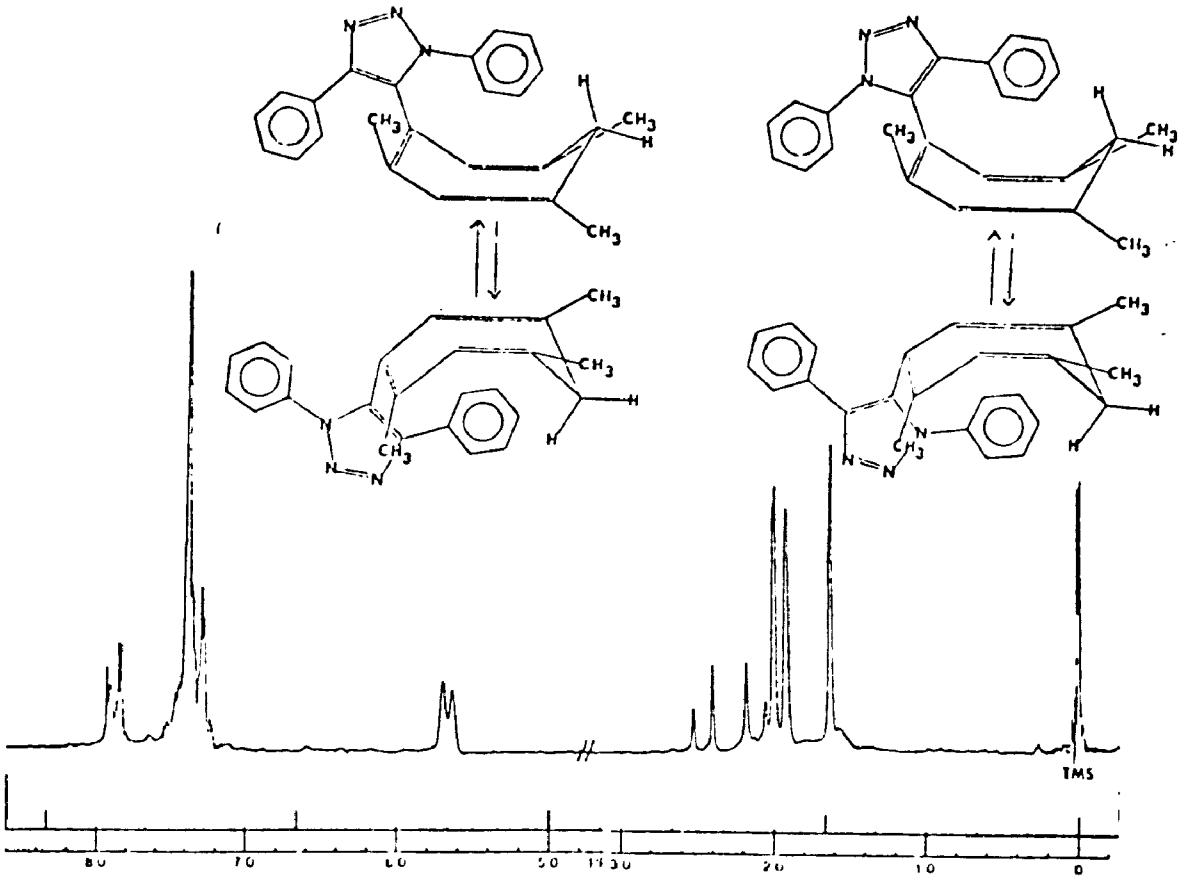
Data Point or Run #	Time, $sec^{-1} \times 10^3$	$\ln[X_0/(X_0+1)]$	Calc., $\ln[X/(X_0+1)]$	%, Difference	Slope, sec^{-1}
1	0.6	-0.2962	-0.3402	14.8	
2	1.2	-0.6675	-0.6425	-3.7	
3	1.8	-0.9711	-0.9448	-2.7	
4	2.4	-1.2953	-1.2471	-3.7	
5	3.0	-1.4937	-1.5494	3.7	
					5.03×10^{-4}
		standard deviation = 2.83×10^{-5}			


CH3
CH3
DPT

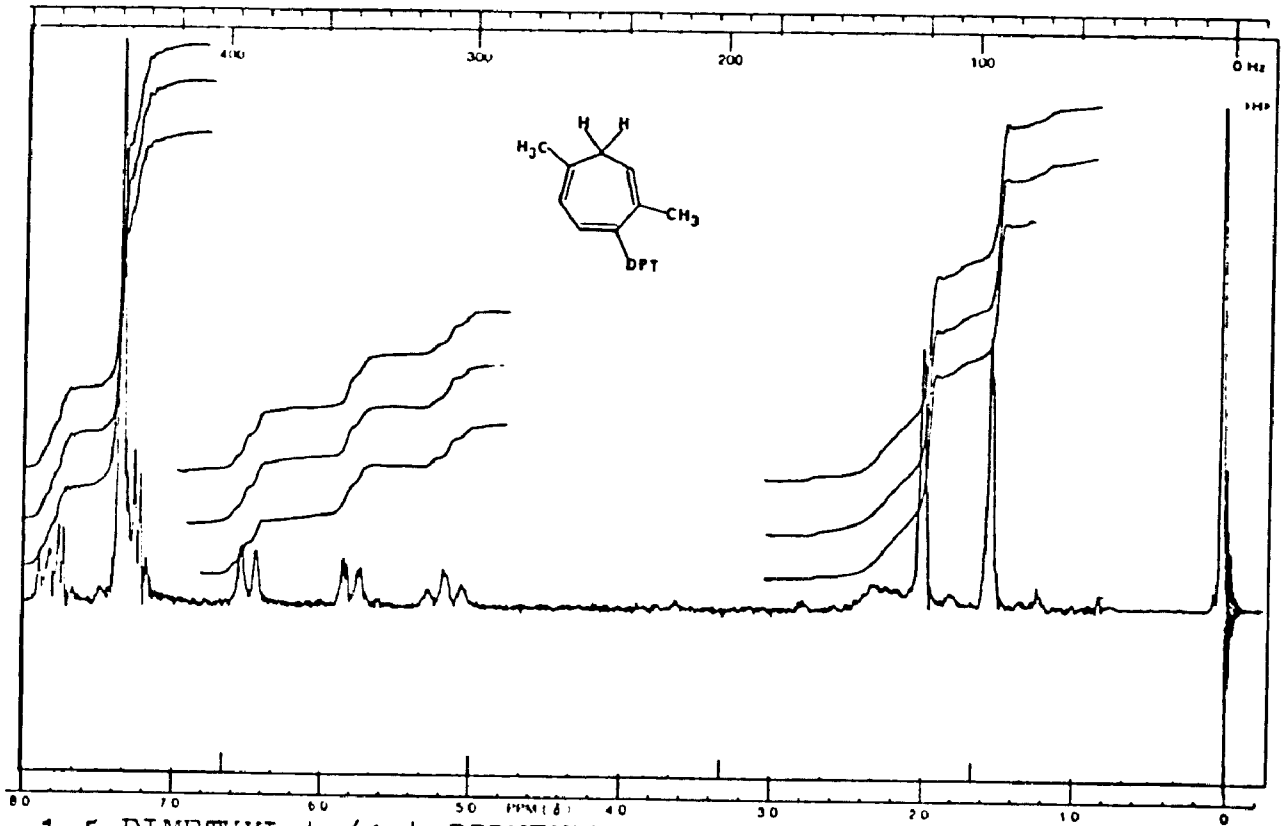

CH3
CH3
H3C
DPT
CH3


CRUDE
PRODUCT


ANALYTICAL
SAMPLE



1,4,6-TRIMETHYL-3-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)CYCLO-HEPTATRIENE



1,5-DIMETHYL-4-(1,4-DIPHENYL-1,2,3-TRIAZOL-5-YL)CYCLO-HEPTATRIENE

REFERENCES

1. J. J. Gajewski, in "Mechanics of Molecular Migrations," Vol. 4, B. S. Thyagarajan, Ed., John Wiley and Sons, Inc., New York, N.Y., 1971.

2. (a) W. von E. Doering and W. R. Roth, Angew. Chem. Int. Ed., 2, 115 (1963); (b) G. Schröder, Angew. Chem. Int. Ed., 2, 481 (1963).

3. (a) R. B. Woodward and R. Hoffmann, Angew. Chem. Int. Ed., 8, 781 (1969); (b) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Weinheim, 1971.

4. A. P. ter Borg, H. Kloosterziel, and N. van Meurs, Rec. Trav. Chim., 82, 717 (1963).

5. J. A. Berson and M. R. Willcott, III, J. Amer. Chem. Soc., 88, 2494 (1966).

6. T. Makai, H. Kubota, and T. Toda, Tetrahedron Lett., 3581 (1967).

7. (a) H. M. Frey and R. J. Ellis, J. Chem. Soc., 4770 (1965); (b) R. J. Ellis and H. M. Frey, ibid., Suppl. I, 5573 (1964); (c) M. H. Frey and B. M. Cope, ibid., Sect. A, 1701 (1966); (d) K. W. Egger, J. Amer. Chem. Soc., 89, 3688 (1967); (e) A. P. ter Borg and H. Kloosterziel, Rec. Trav. Chim., 82, 741 (1963).

8. (a) D. S. Gloss, R. S. Boikess, and L. Winstein, Tetrahedron Lett., 999 (1966); (b) W. R. Roth and J. König, Justus Liebigs Ann. Chem., 699, 24 (1966); (c) H. Kloosterziel and A. p. ter Borg, Rec. Trav. Chim., 84, 1305 (1965); (d) E. Weth and A. S. Dreiding, Proc. Chem. Soc., 59 (1964); (e) W. R. Roth, Tetrahedron Lett., 1009 (1964); (f) R. W. Murray and M. L. Kaplan, J. Amer. Chem. Soc., 88, 3527 (1966).

9. E. M. Bruckmann, Ph.D. Thesis, University of Michigan, 1971.

10. (a) W. E. Heyd and C. A. Cupas, J. Amer. Chem. Soc., 93, 6068 (1971); (b) F. A. L. Anet, ibid., 86, 458 (1964); (c) F. R. Heusen and L. A. Smith, ibid., 86, 956 (1964).

11. (a) A. Newman, P. Rutkin and K. Mislow, J. Amer. Chem. Soc., 80, 465 (1958); (b) also see V. Boekelheide, K. Galuszko, and K. S. Szeto, ibid., 96, 1578 (1974); (c) S. Rosenfeld and P. M. Keehn, Tetrahedron

Lett., 4021 (1973); for hindered rotation in cyclophanes.

12. A. Allerhand, H. S. Gutowsky, J. Jones, and R. A. Meinzer, J. Amer. Chem. Soc., 88, 3185 (1966).

APPENDIX I

A) Preliminary Investigations on the Thermal Decomposition of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole in Amine Substrates.

The experiments described here represent preliminary investigations on the thermal decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I) in amine substrates. The reaction of carbenes with various amines has not been extensively investigated.[1] The mild conditions used for the generation of 1,4-diphenyl-1,2,3-triazolylcarbene, and the high yields obtained from the decompositions in aromatic substrates recommended this carbene for the study of its reactions with amines. The reaction of carbene with an amine seems to proceed through an N-ylide intermediate,[2] which may then undergo a 1,2-hydrogen shift, as in the case of primary and secondary amines,[3] or a Stevens type of rearrangement, as in the case with tertiary amines.[4] To obtain a better understanding of the interaction between carbenes and amines, the following amines were chosen as reaction partners for 5-diazomethyl-1,4-diphenyl-1,2,3-triazole; aniline, N,N-dimethylaniline, N,N-diethylaniline, triethylamine and diisopropylethylamine.

Thermal Decomposition of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole in Aniline.

Thermolysis of 0.522 g (0.002 mole) of 5-diazomethyl-

1,4-diphenyl-1,2,3-triazole in 70 ml of dry, redistilled aniline gave a reddish-brown solution, which was filtered to remove a small amount of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde azine. The excess aniline was removed by vacuum distillation (0.1 mm) at room temperature, leaving a viscous, reddish-brown oil, which was triturated with four 25-ml portions of petroleum ether (bp 30-60°C). The combined petroleum ether extracts were refrigerated, whereupon 100 mg (25%) of a white, crystalline material, mp 142-153°C, precipitated. On the basis of the following PMR spectrum, it was identified as 5-(anilinomethyl)-1,4-diphenyl-1,2,3-triazole (II); ($CDCl_3$), δ 7.45 (m, 10H aromatic), 6.75 (m, 5H aromatic), 4.32 (d, 2H methylene), 4.00 (t, 1H amine). The infrared spectrum of the product showed the amine absorption at 3330 cm^{-1} and absorptions at 1600, 1500, 1017 and 975 cm^{-1}, indicating the presence of phenyl and 1,2,3-triazole rings. The evidence is consistent with the expected product of N-H insertion. An analytical sample was prepared by two recrystallizations from benzene, mp 158-160°C; m/e = 326.

Anal. Calcd for $C_{21}H_{18}N_4$:
C, 77.27; H, 5.56 ; N, 17.17.
Found: C, : H, ; N, .

Thermal Decomposition of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole in Triethylamine.

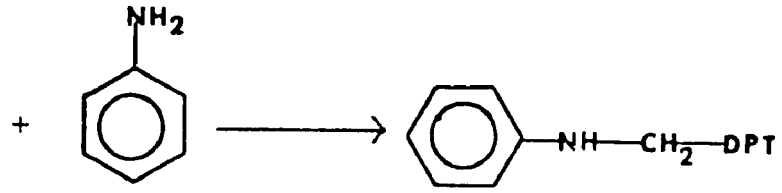
Thermolysis of 400 mg (0.0015 mole) of 5-diazomethyl-

1,4-diphenyl-1,2,3-triazole in 70 ml of dry, redistilled triethylamine gave a reddish-brown solution, which was filtered to remove a small amount of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde azine. The excess triethylamine was removed by vacuum distillation at room temperature, leaving a viscous, brown oil, which was triturated with two 25-ml portions of absolute ethanol. The combined ethanol extracts were refrigerated, whereupon 100 mg (20%) of a yellow, crystalline material, mp 119-121°C, precipitated. On the basis of the PMR spectrum, it was identified as 5-(1-diethylaminopropyl)-1,4-diphenyl-1,2,3-triazole (III); ($CDCl_3$), δ 7.50 (m, 10H aromatic), 2.94 (m, 3H triazolic methine hydrogen and methylene CH_2), 2.20 (q, 4H methylene) and 0.68 (t, 9H methyl). An analytical sample was prepared by recrystallization from petroleum ether (bp 30-60°C); mp 116-117°C; m/e = 334.

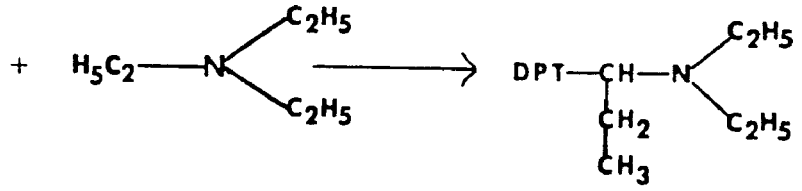
Anal. Calcd for $C_{21}H_{26}N_4$:
C, 75.42; H, 7.84 ; N, 16.76.
Found: C, 75.30; H, 7.70 ; N, 16.58.

Thermal Decomposition of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole in Diisopropylethylamine.

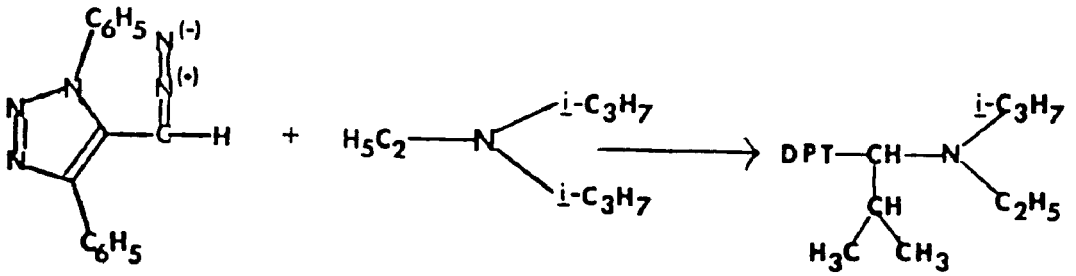
Thermolysis of 200 mg of recrystallized 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I) in 70 ml of distilled diisopropylethylamine and 5 ml of methylene chloride gave a brown solution after heating for ten hours at 55°C. The solution was filtered to remove a small amount of azine,



II

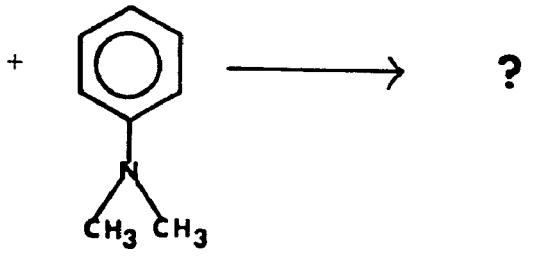


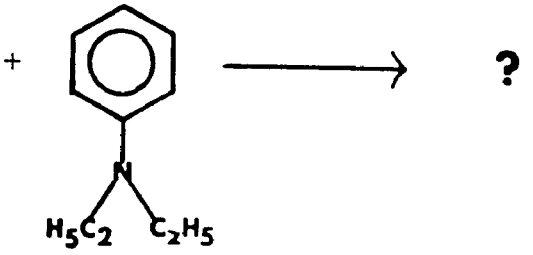
III



I

IV





and the excess amine was removed by vacuum distillation at room temperature, leaving a viscous, brown oil. The oil was chromatographed on a column of 50 g of 100-200-mesh alumina (activity III). The column was eluted with benzene and each fraction was examined by TLC after concentration; fractions of similar composition were combined. The major component was eluted first, and was dissolved in a minimal amount of petroleum ether (bp 30-60°C) and refrigerated, whereupon 120 mg (25%) of white plate-like crystals, mp 109-111°C, precipitated. On the basis of the PMR spectrum, it was identified as 5-(1-isopropylethylamino-2-methylpropyl)-1,4-diphenyl-1,2,3-triazole (IV); ($CDCl_3$) δ 7.50 (m, 10H aromatic), 3.00 [m, 5H:2H methylene (ethyl)]; 2H methine (isopropyl); 1H methine (triazolic), 0.90 (d, 6H methyls), 0.80 (t, 3H methyl) and 0.67 ppm (d, 6H methyls). Two recrystallizations from petroleum ether (bp 30-60°C) gave an analytical sample, mp 109-111°C, m/e = 362.

Anal. Calcd for $C_{23}H_{30}N_4$:
C, 76.21; H, 8.34 ; N, 15.46.
Found: C, 76.27; H, 8.20 ; N, 15.18.

Thermal Decomposition of 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole in N,N-Dimethylaniline and N,N-Diethylaniline.

Thermolysis of 0.522 g (0.02 mole) of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I) in 70 ml of either freshly distilled N,N-dimethylaniline or N,N-diethylaniline gave

a brown solution, which was freed from the amine by vacuum distillation (0.1 mm) at 50°C. The crude products were examined by thin-layer chromatography and found to contain a variety of products. Separation by preparative TLC on silica gel furnished only the component of highest R_f in reasonably pure form. Recrystallization of this fraction from acetone afforded 55.0 mg (16%) of a white solid, mp 171-172°C, identified as 1,4-diphenyl-1,2,3-triazole-5-carboaldehyde (NMR, IR, mixture melting point). All fractions were examined by NMR spectroscopy; however, no assignments were possible. Further experimentation is required in order to establish the identity of the products resulting from the thermal decomposition of diazo compound I in the above substrates.

B) Preliminary Investigations on the Preparation of Analogous Diazo Heterocycles:

(1) Preparation of 2-Diazomethyl-3-phenylthiophene.

The remarkable selectivity demonstrated by 5-diazomethyl-1,4-diphenyl-1,2,3-triazole[5] (I) towards aromatic cycloaddition reactions prompted further investigations on analogous heterocyclic diazo compounds. Following the procedure established by Gjos and Gronowitz,[6] 2-formyl-3-phenylthiophene (V) was prepared. Treatment of aldehyde V with anhydrous hydrazine yielded the corresponding hydrazone. Upon attempted purification, the crude hydrazone

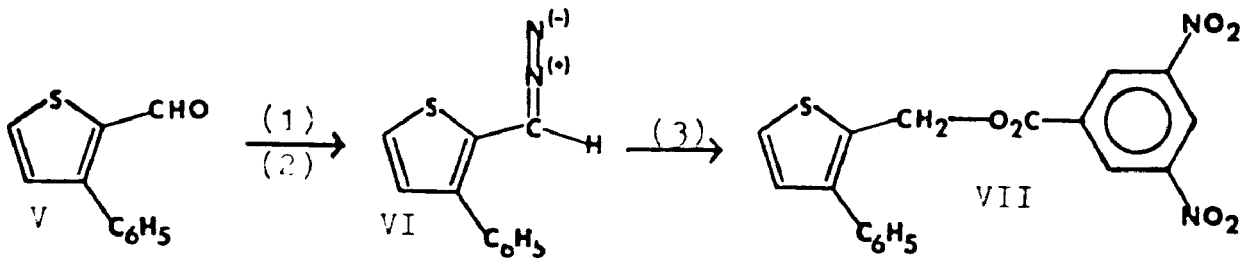
deteriorates quite rapidly with the formation of 3-phenylthiophene-2-carboxaldehyde azine. Therefore, the oily hydrazone was oxidized immediately without additional purification.

The oily hydrazone from 2 g of aldehyde was dissolved in 25 ml of methylene chloride and 3 ml of cyclohexylamine, and the solution was cooled with magnetic stirring in an ice-salt bath to -10°C. To this a solution 3 g of phenyliodose acetate in 30 ml of methylene chloride was added at a rate such that the temperature was maintained at 0°C. After addition was complete, the mixture was stirred for one more hour at about 0°C, and then cooled to -25°C. The cold mixture was freed from insoluble cyclohexylammonium acetate by suction filtration, the filtrate was extracted with four 100 ml portions of ice-water, and it was then dried over anhydrous potassium carbonate. The methylene chloride was removed in vacuo without external warming to leave a dark reddish-brown oil. A strong infrared absorption at 2050 cm^{-1} characteristic of the diazo function indicated the presence of 2-diazomethyl-3-phenylthiophene in the crude oil. All attempts to purify the diazo compound failed; complete decomposition occurred within a week. The reactivity of diazo compound VI was very similar to 2-diazomethylfuran and 2-diazomethylthiophene, which have half-lifes of two and 24 hours, respectively.[7]

Further evidence concerning the preparation of diazo

compound VI was obtained by treating a freshly prepared amount of the diazo compound with 3,5-dinitrobenzoic acid. The resulting 3,5-dinitrobenzoate derivative, VII, mp 131-132°C, was obtained. The PMR spectrum of VII showed a methylene absorption at δ 5.60 ppm, which is consistent for a methylene group substituted by an ester and aromatic functional group.

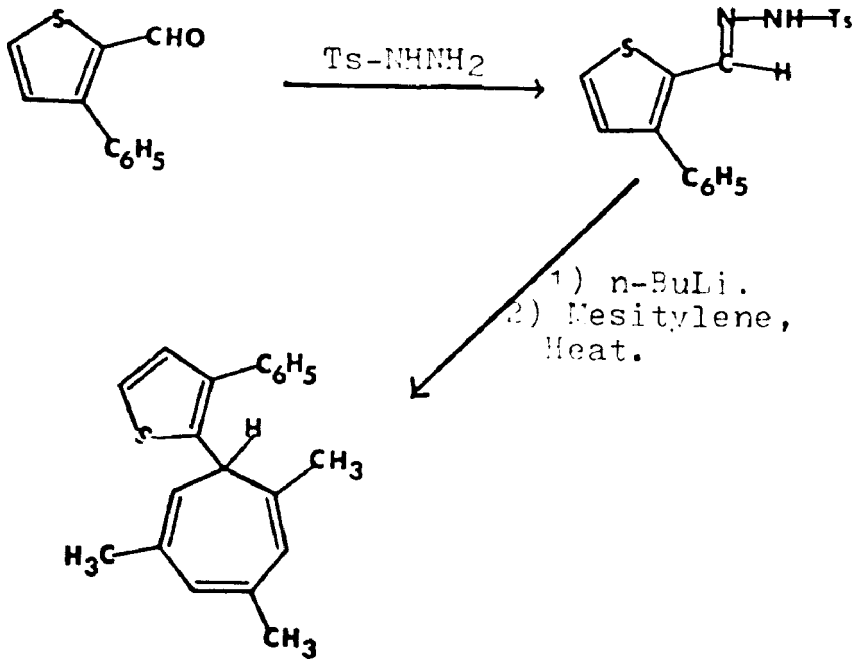
Anal. Calcd for $C_{18}H_{12}N_2O_6S$:
C, 56.24; H, 3.15; N, 7.30.
Found: C, 56.47; H, 3.18; N, 7.23.



1) NH_2NH_2; 2) Ph-I()Ac)$_2$;; 3) 3,5-dinitrobenzoic acid.

Since the diazo compound VI was impossible to isolate in pure form, the tosyl hydrazone of carboxaldehyde V was prepared, mp 67-69°C. The tosyl hydrazone of V was dissolved in a large excess of mesitylene followed by the addition of an equivalent amount of n-butyllithium. The resulting lithium salt was thermolyzed *in situ* at 60°C for two hours. Separation of the products resulted in an approximately 5% yield of the product resulting from carbene addition to the mesitylene. Based on the PMR spectrum, the adduct was identified as 1,3,5-trimethyl-7-(3-phenylthiophen-2-yl)cycloheptatriene (VIII); ($CDCl_3$) δ 7.32

(broad s, 6H aromatic), 7.08 (d, 1H thiophene), 6.18 (s, 1H CH=C-C=C), 5.88 (s, 1H C=C-CH=C), 5.37 (d, $J_{6,7}$ = 7.0 Hz; 1H C=CH-C), 3.43 (d, $J_{7,6}$ = 7.0 Hz; 1H C-CH-C), 1.99 (s, 3H methyl) and 1.82 ppm (s, 6H methyl). The mass spectrum of VIII showed a parent peak at m/e = 292, clearly indicating the presence of a 1:1 adduct of mesitylene and 2-diazomethyl-3-phenylthiophene.



(2) Preparation of 4-(1-diazoethyl)-1-benzyl-1,2,3-triazole (XII).

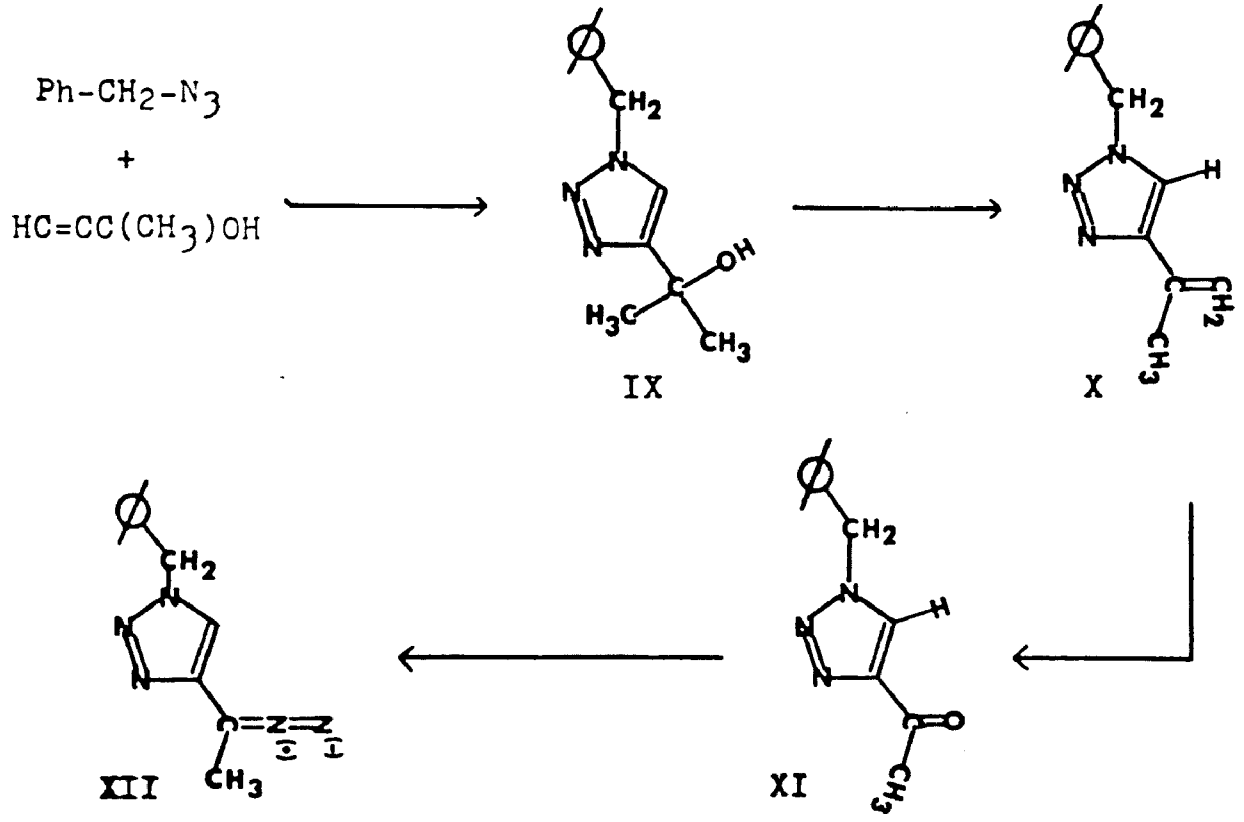
A solution of 70 ml of benzene, 6.65 g (0.05 mole) of benzyl azide[8] and 4.2 (0.05 mole) of 3-hydroxy-3-methylbutyne was refluxed for 48 hours. The resulting clear solution was concentrated by aspirator vacuum, leaving a clear oil, which crystallized on standing. Recrystallization from carbontetrachloride gave 5 g (80%) of 4-(2-hydroxy-2-methylethyl)-1-benzyl-1,2,3-triazole (IX), mp

79-81°C; PMR, ($CDCl_3$) δ 7.38 (s, 6H aromatic and triazolic), 5.50 (s, 2H methyline N-$\underline{CH_2}$-), 3.35 (s, 1H hydroxy OH) and 1.70 ppm (s, 6H methyls).

A solution of 1 g (0.0046 mole) of triazole IX and 6 g of dimethyl sulfoxide was heated for eight hours at 175°C, and was then cooled and poured into 125 ml of water. The crude material was extracted with two 50-ml portions of petroleum ether (bp 60-68°C), washed once with 100-ml portion of water, and dried over anhydrous potassium carbonate. Evaporation of the petroleum ether gave 0.47 g (55%) of a white crystalline material, mp 85-86°C, identified as 1-benzyl-4-isopropenyl-1,2,3-triazole (X). The PMR spectrum displayed the following absorptions; ($CDCl_3$), δ 7.43 (s, 1H triazolic), 7.35 (s, 5H aromatic), 5.72 (m, 1H vinylic), 5.52 (s, 2H methylene N-$\underline{CH_2}$-), 5.10 (m, 1H vinylic) and 2.17 ppm (s, 3H methyl).

Azonolysis of 2.50 g (0.0125 mole) of triazole X in 35 ml of chloroform followed by a reductive work-up with zinc and acetic acid afforded 1.75 g (70%) of a yellow-white crystalline material, mp 83-84°C. The PMR spectrum displayed the following absorptions, ($CDCl_3$), δ 8.00 (s, 1H triazolic), 7.32 (s, 5H aromatic), 5.60 (s, 2H methylene N-$\underline{CH_2}$-) and 2.67 ppm (s, 3H methyl), and the infrared spectrum displayed a strong absorption at 1625 cm^{-1} assigned to the carbonyl function. Based upon these spectral characteristics, compound XI was identified as 4-acetyl-1-benzyl-1,2,3-triazole.

Applying the sequence of carbonyl compound-hydrazone-diazo compound to the preparation of diazo compound XII seemed a logical extension, in view of the success experienced in the formation of diazo compound I. Conversion to the hydrazone was accomplished by treating 1.75 g of the ketone XI with 16 ml of anhydrous hydrazine, 8 ml of triethylamine in 50 ml of absolute ethanol. The crude hydrazone was not isolated, but instead was treated with phenyliodose acetate, yielding the desired diazo compound XII. A strong infrared absorption at 2080 cm^{-1} characteristic of the diazo function indicated the presence of 1-benzyl-4-(1-diazoethyl)-1,2,3-triazole in the crude oil. All attempts to purify the diazo compound failed, with complete decomposition to 4-acetyl-1-benzyl-1,2,3-triazole and intractible tars occurring within a few hours.



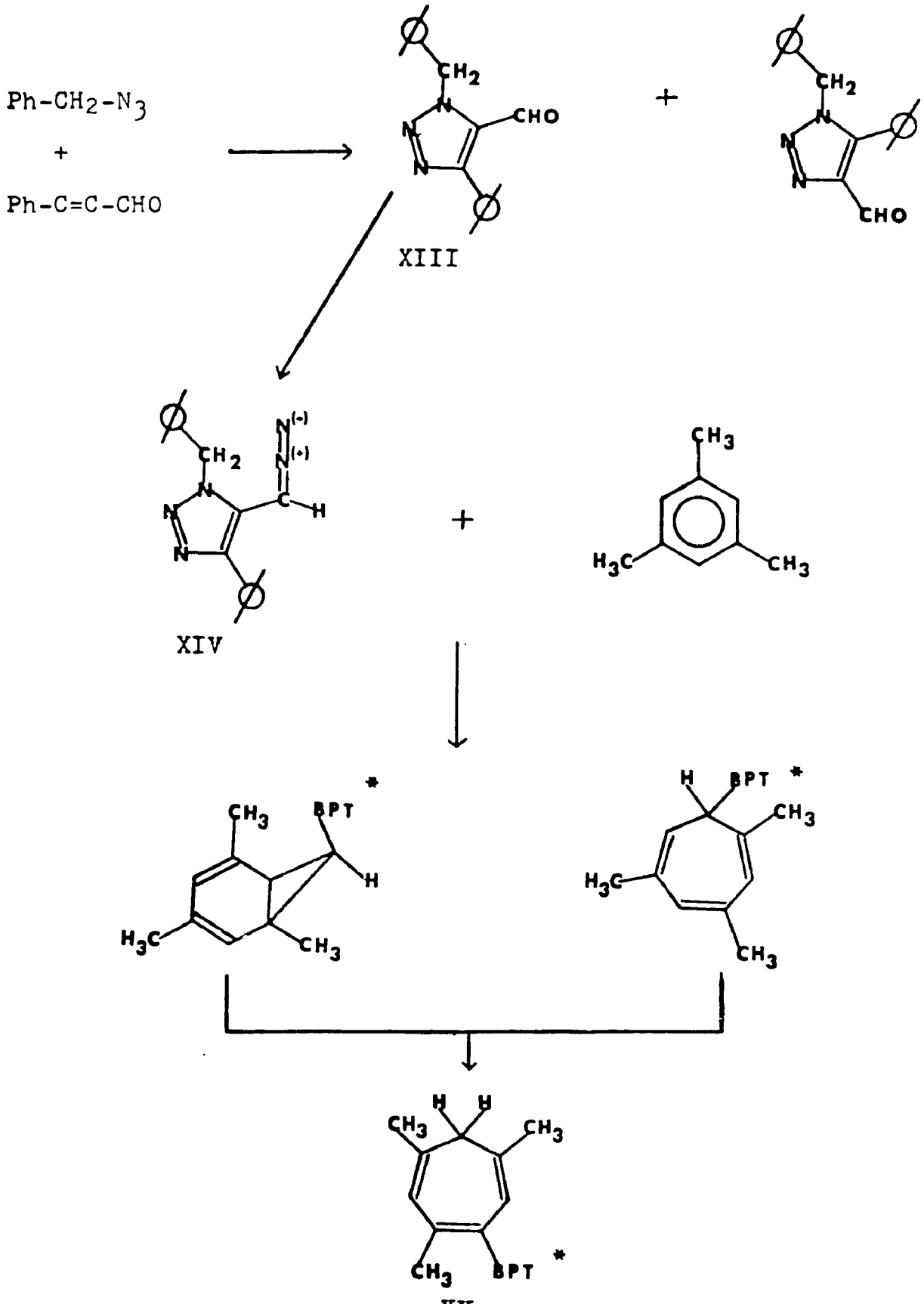
(3) Preparation of 1-Benzyl-5-diazomethyl-4-phenyl-1,2,3-triazole (XIV).

A solution of 65 ml toluene, 9.2 g (0.05 mole) of phenylpropargyl aldehyde[9] and 6.65 g (0.05 mole) of benzyl azide was refluxed for 24 hours. The resulting solution was concentrated by aspirator vacuum, leaving a yellowish oil. The PMR spectrum indicated that two isomeric aldehydes in a 1:1 ratio were formed during the cycloaddition reaction. Crystallization from a 50/50 mixture of carbon-tetrachloride/petroleum ether (bp 30-60°C) afforded 1-benzyl-5-formyl-4-phenyl-1,2,3-triazole (XIII) uncontaminated by the 4-formyl isomer: mp 111-112.5°C; PMR, ($CDCl_3$), δ 10.08 (s, 1H aldehyde), 7.50 (m, 10H aromatic) and 6.07 ppm (s, 2H methylene N-$\underline{CH_2}$-).

Applying the same sequence of carbonyl compound-hydrazone-diazo compound to the preparation of diazo compound XIV seemed logical in light of the successes experienced with other diazo heterocycles. Conversion to the hydrazone was accomplished by treating 1 g (0.0038 mole) of triazole XIII with 10 ml of anhydrous hydrazine, 5 ml of triethylimine in 200 ml of absolute ethanol. The crude hydrazone was not isolated. Instead the oily hydrazone was taken up in 40 ml of methylene chloride and treated with cyclohexylamine and phenyliodose acetate at 0°C. The resulting red solution was freed from insoluble cyclohexylammonium acetate by suction filtration; the filtrate was extracted with four 100-ml portions of ice-water, and

was then dried over anhydrous potassium carbonate. The methylene chloride was removed *in vacuo* without external warming to leave a dark red oil. A strong infrared absorption at 2090 cm^{-1} characteristic of the diazo function indicated the presence of 1-benzyl-5-diazomethyl-4-phenyl-1,2,3-triazole in the crude oil. The triazole function was established by the characteristic infrared absorptions at 1004 and 1023 cm^{-1}. All attempts to crystallize this diazo compound failed, however unlike the two previously described diazo heterocycles, diazo compound XIV seemed to have an extremely long half-life when refrigerated.

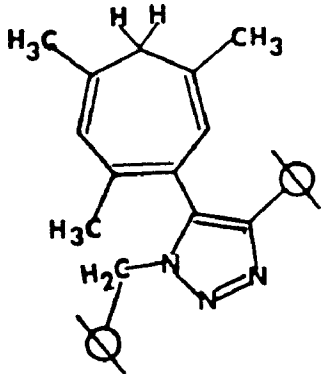
A freshly prepared quantity of diazo compound XIV was dissolved in 70 ml of reagent grade mesitylene. The solution was purged with N_2 gas for one hour, and placed in an oil-bath preheated to 75°C. The mesitylene was removed by vacuum distillation (0.1 mm) at room temperature. The crude brownish oil was chromatographed on a column of 50 g of alumina (100-200 mesh) with benzene. Fractions of similar composition were combined after concentration and examination by TLC. On the basis of its PMR and ^{13}CMR spectra, compound XV was identified as 1,3,6-trimethyl-4-(1-benzyl-4-phenyl-1,2,3-triazol-5-yl)cycloheptatriene; PMR, ($CDCl_3$), 7.68 (m, 2H aromatic), 7.15 (m, 8H aromatic), 5.72 (s, 1H C=C<u>H</u>-C=C), 5.50 (s, 1H C=C<u>H</u>-C=C), 5.18 (s, 2H methylene N-C<u>H_2</u>-), 2.29 (AB quartet, J = 12 Hz, 2H methylene C=C<u>H_2</u>-C), 1.92 (s, 3H methyl), 1.81 (s, 3H methyl), and 1.26 ppm (s, 3H methyl).



XV

* BPT = 1-BENZYL-4-PHENYL-1,2,3-TRIAZOLE

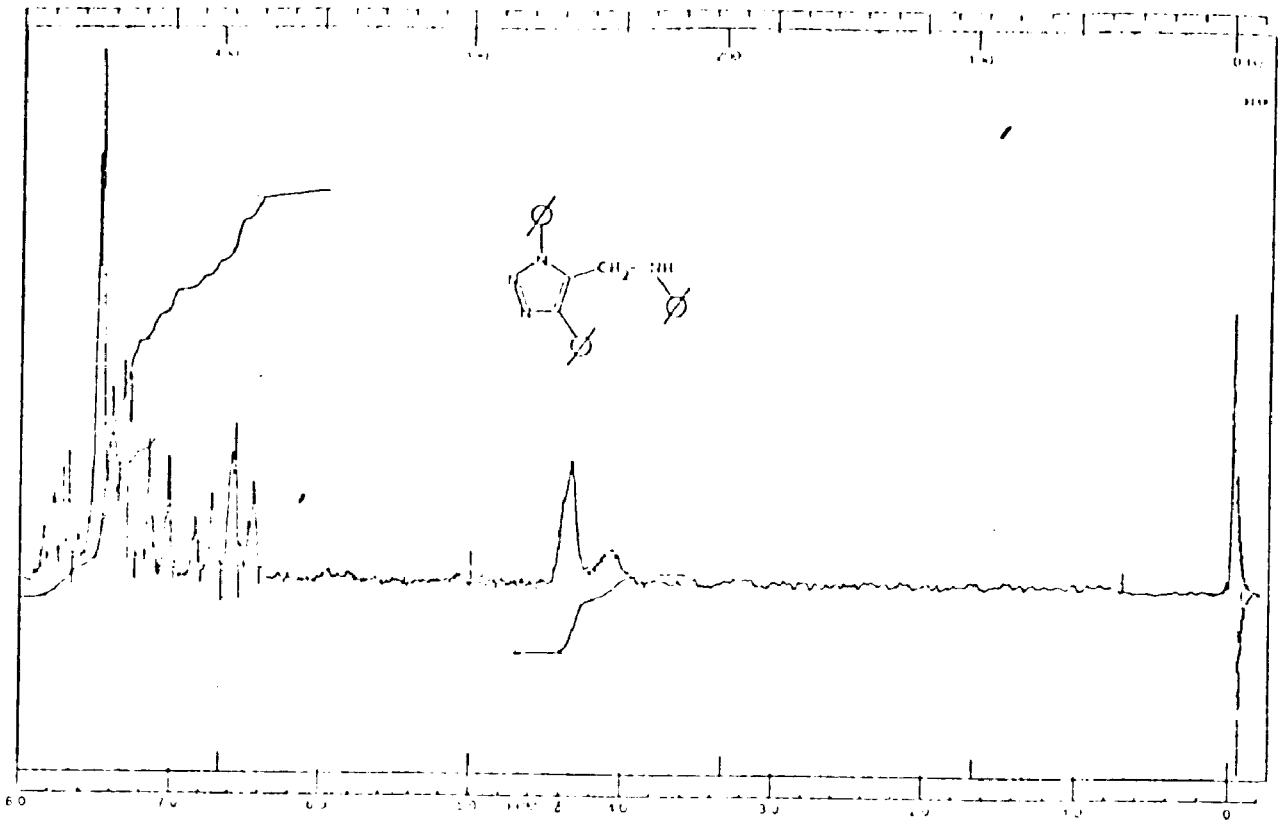
^{13}CMR, ($CDCl_3$)-Chemical Shifts Relative to TMS



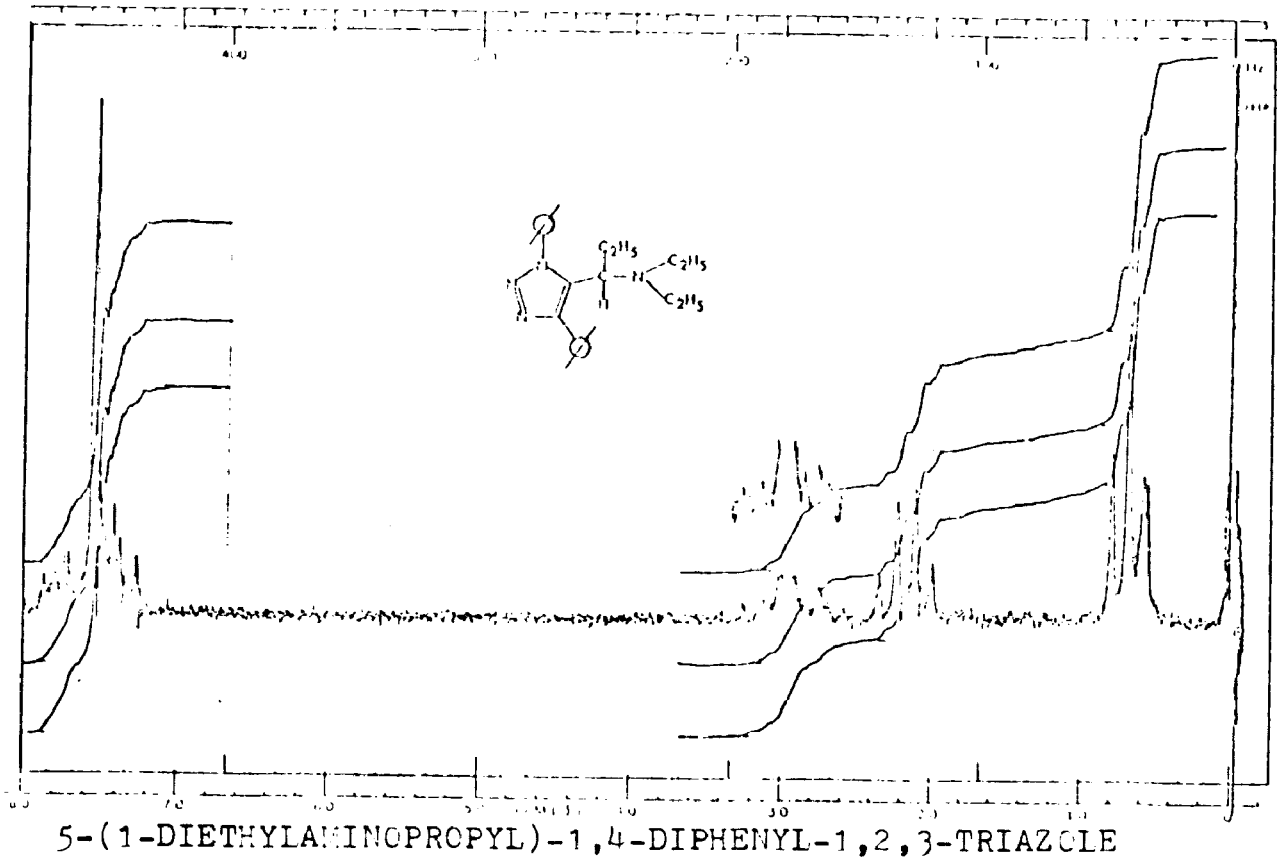
Carbonation	ppm	Coupled Spectrum
1-CH_3	24.3	quartet
3-CH_3	20.7	quartet
6-CH_3	24.7	quartet
7-CH_2	39.4	triplet
5-CH_2	51.7	triplet
vinyls and aromatic carbons		122.3-140.5[a]

[a] Due to the complexity of the vinylic and aromatic regions, individual assignments were impossible.

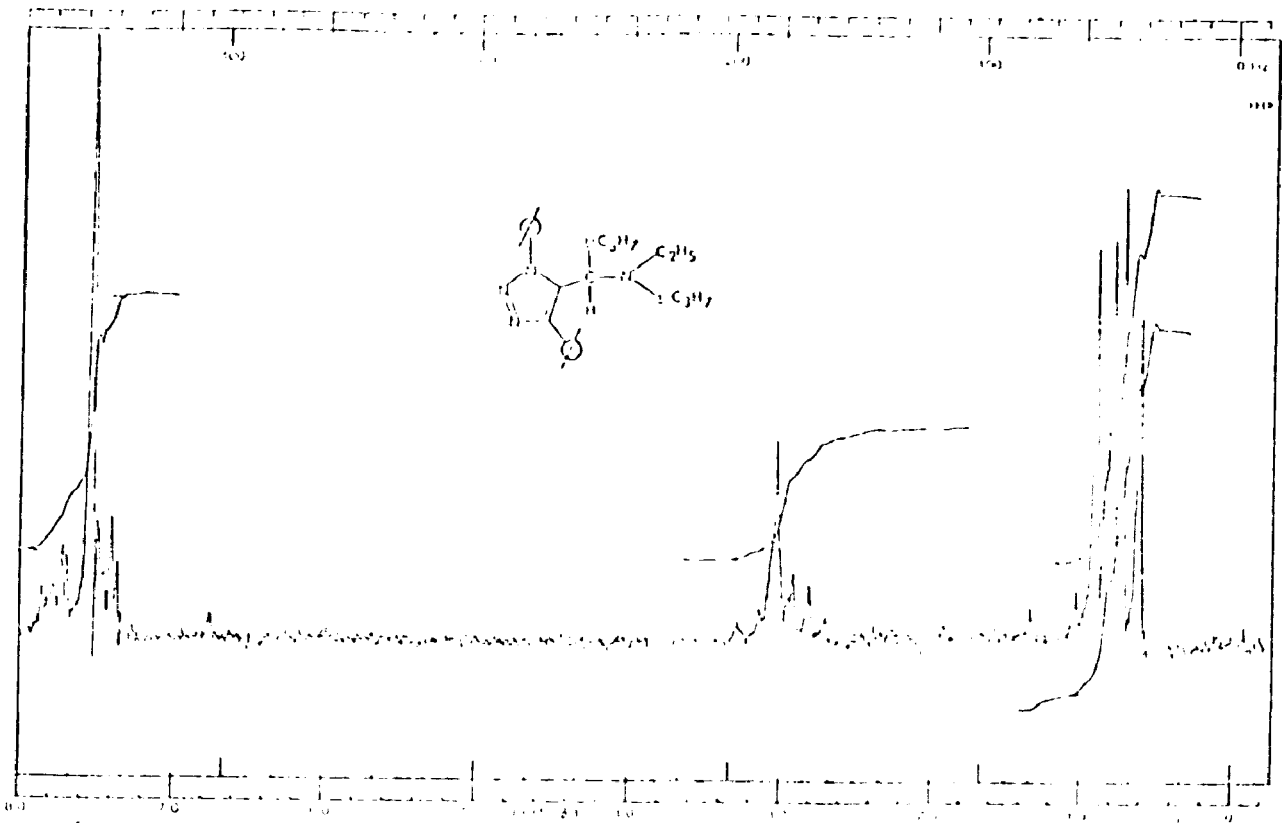
The results obtained (vide supra) are in excellent agreement with those discussed in Chapter I.



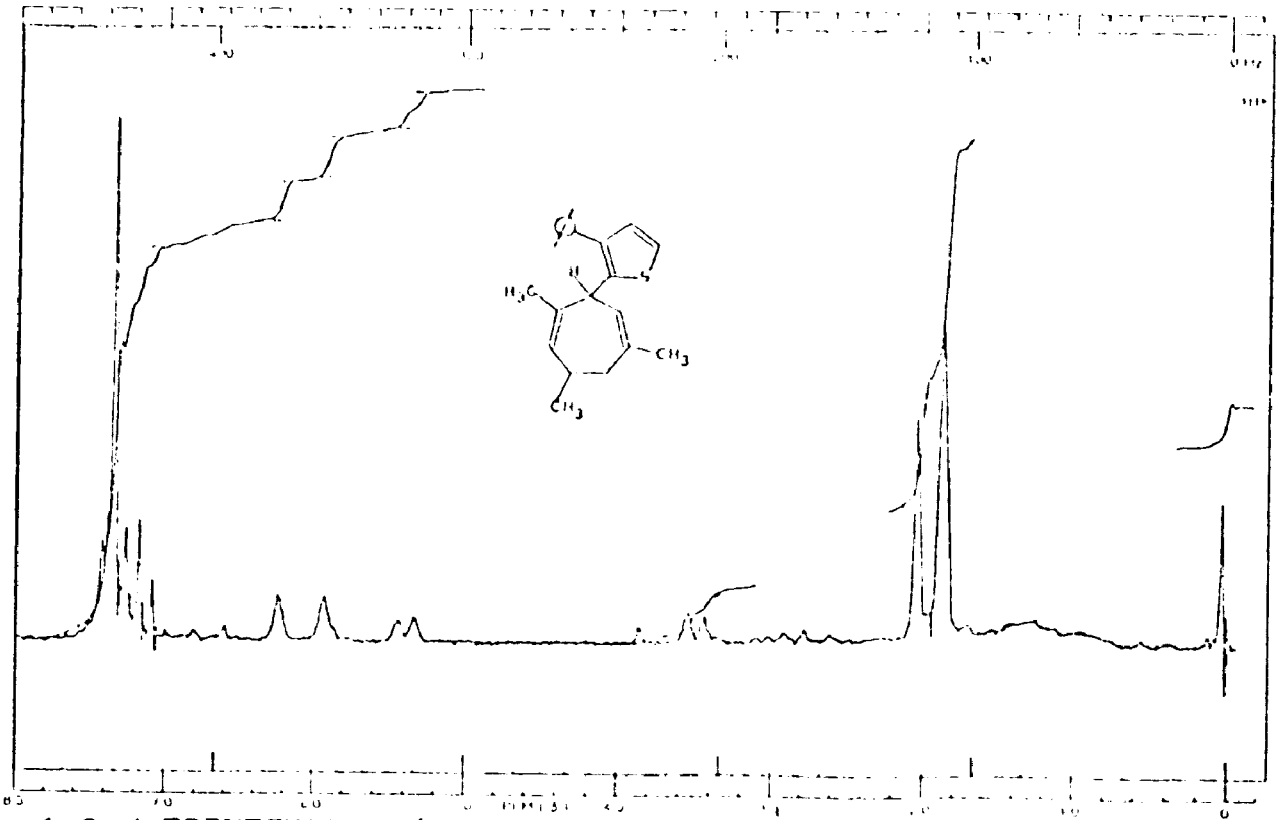
5-(ANILINOMETHYL)-1,4-DIPHENYL-1,2,3-TRIAZOLE



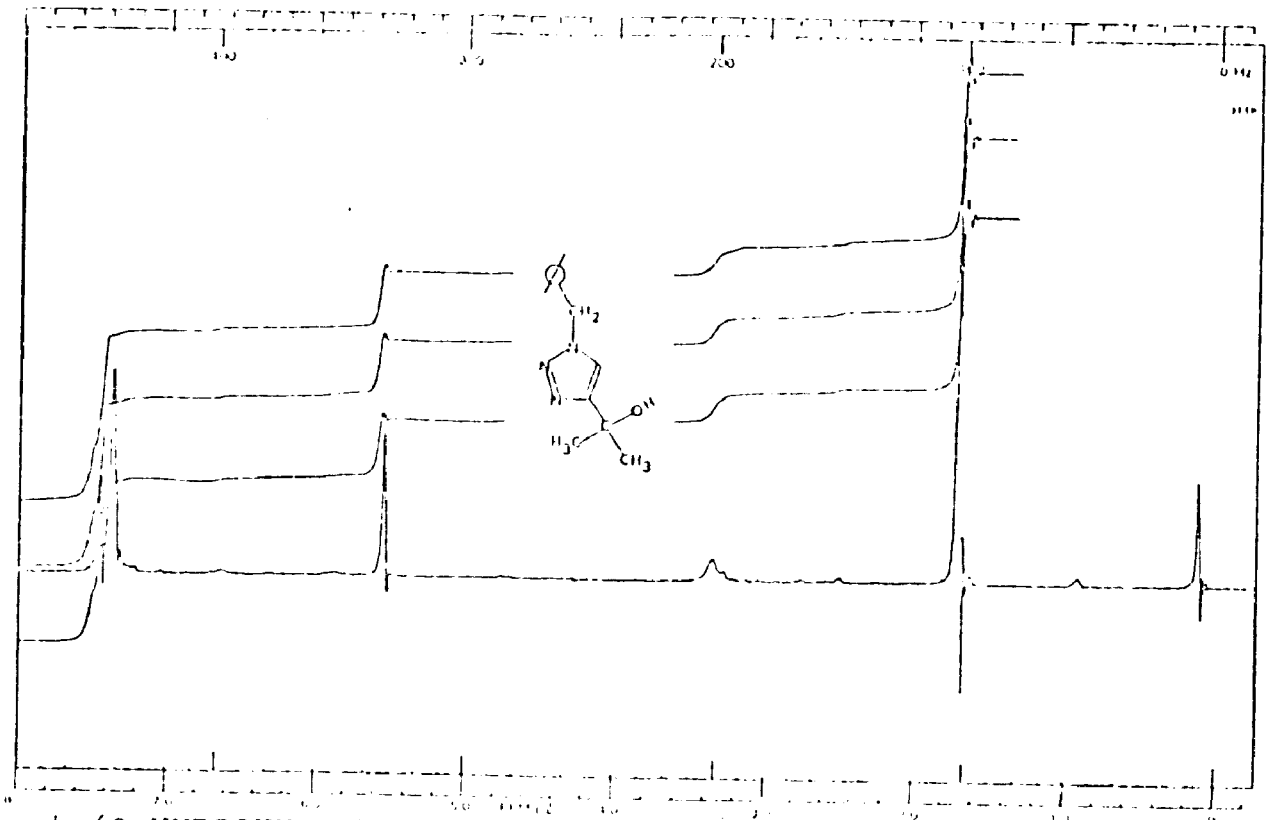
5-(1-DIETHYLAMINOPROPYL)-1,4-DIPHENYL-1,2,3-TRIAZOLE



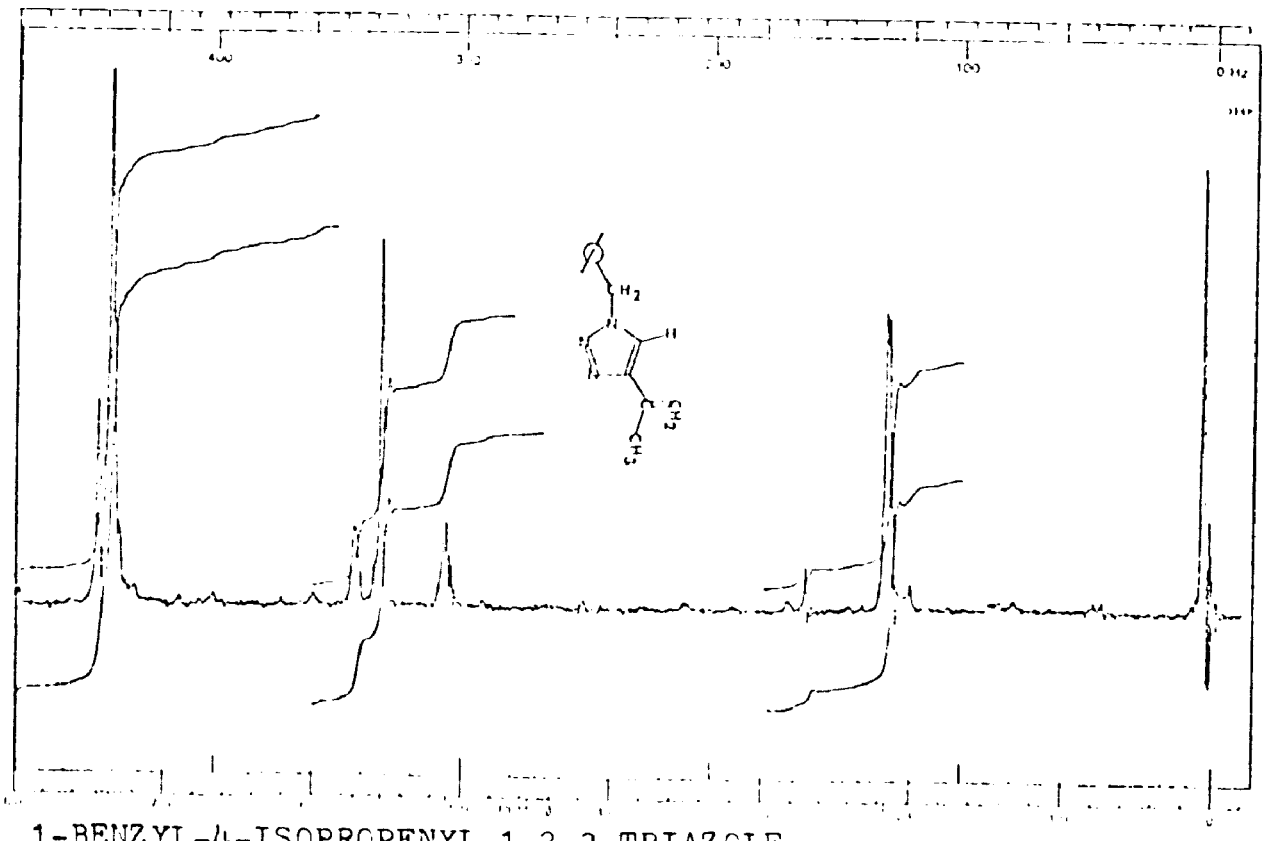
5-(1-ISOPROPYLETHYLAMINO-2-METHYLPROPYL)-1,4-DIPHENYL-1,2,3-TRIAZOLE



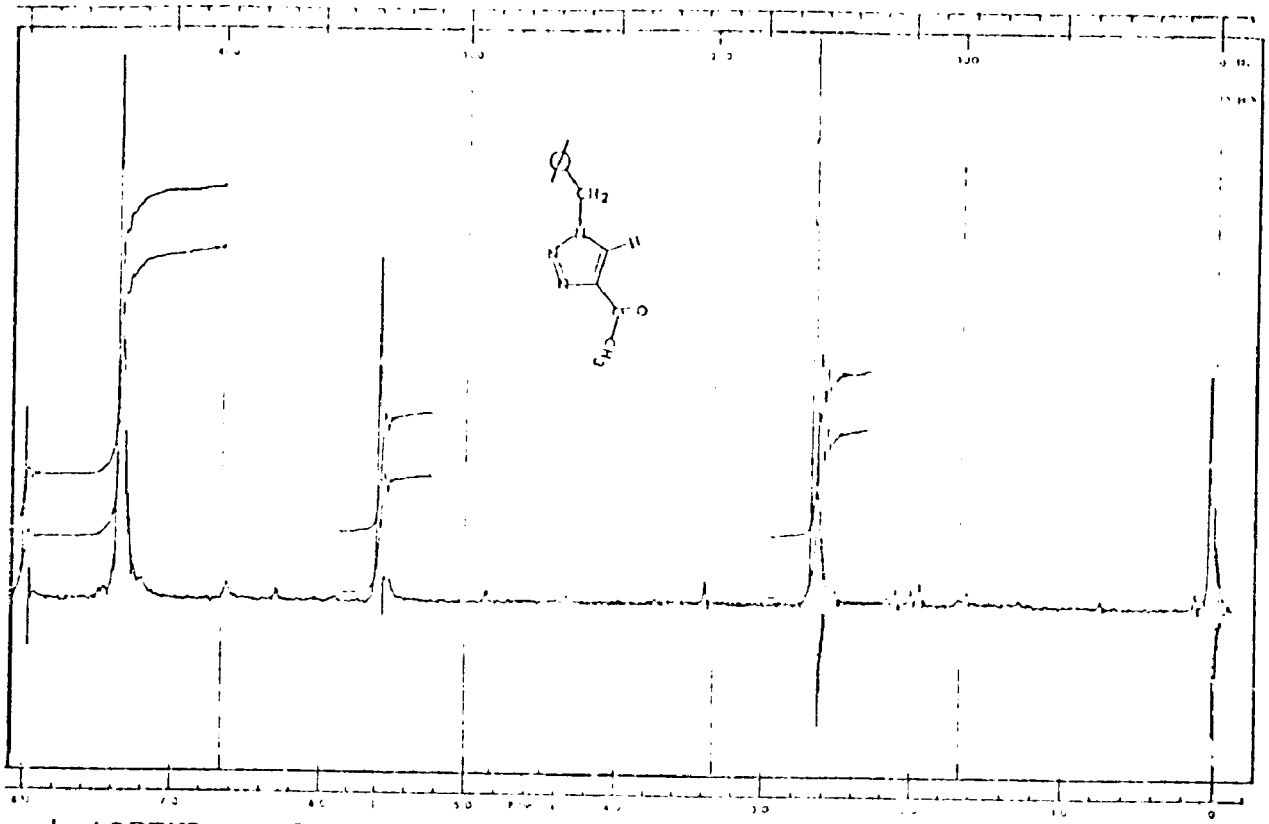
1,3,5-TRIMETHYL-7-(3-PHENYLTHIOPHEN-2-YL)CYCLOHEPTATRIENE



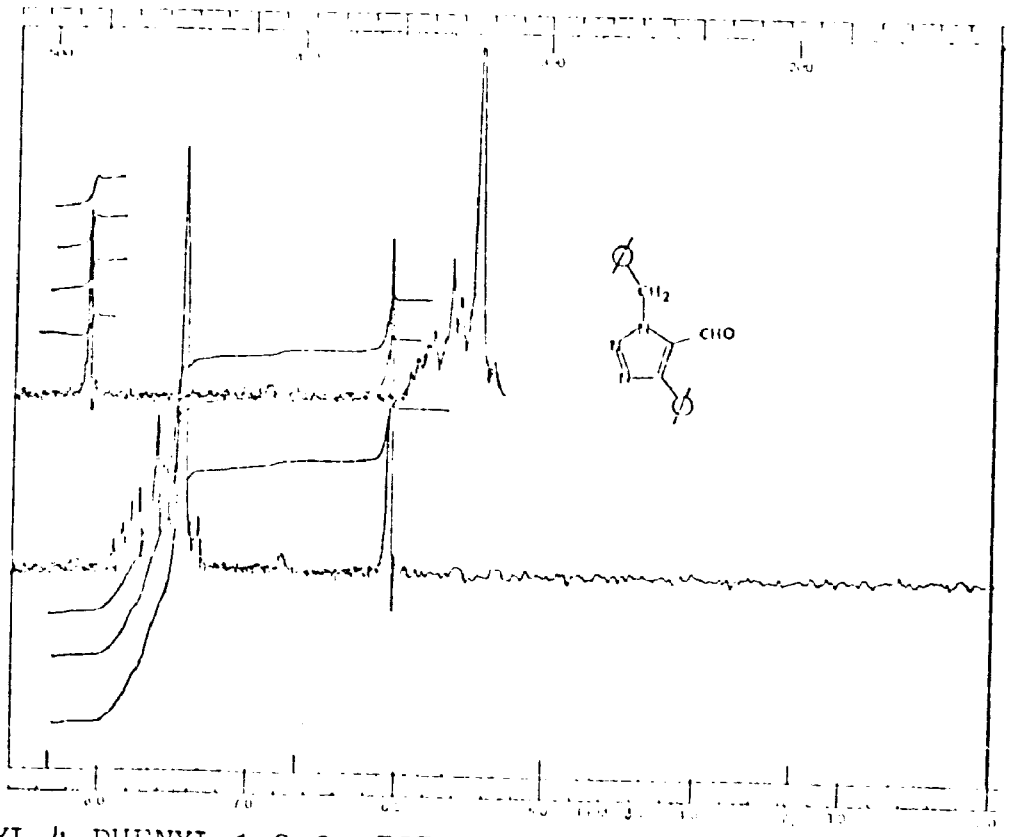
4-(2-HYDROXY-2-METHYLETHYL)-1-BENZYL-1,2,3-TRIAZOLE



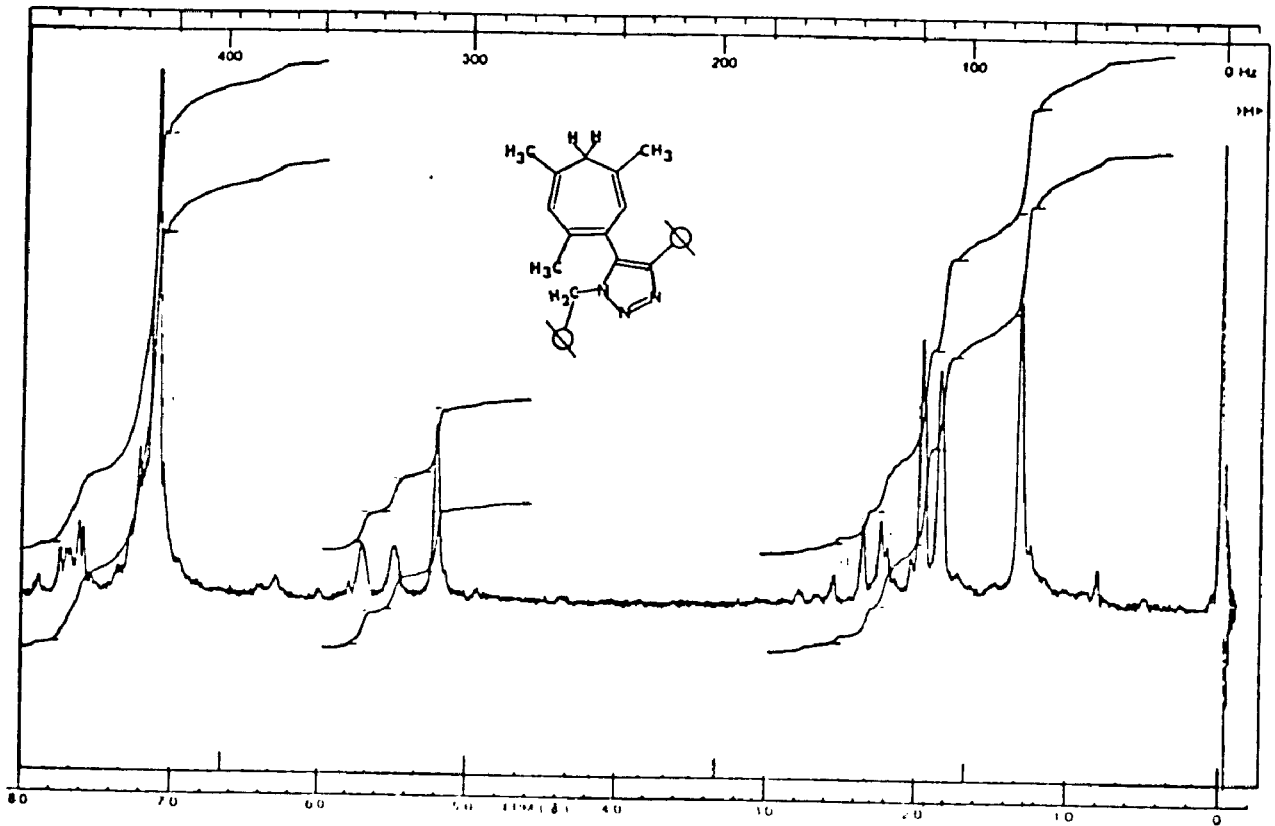
1-BENZYL-4-ISOPROPENYL-1,2,3-TRIAZOLE



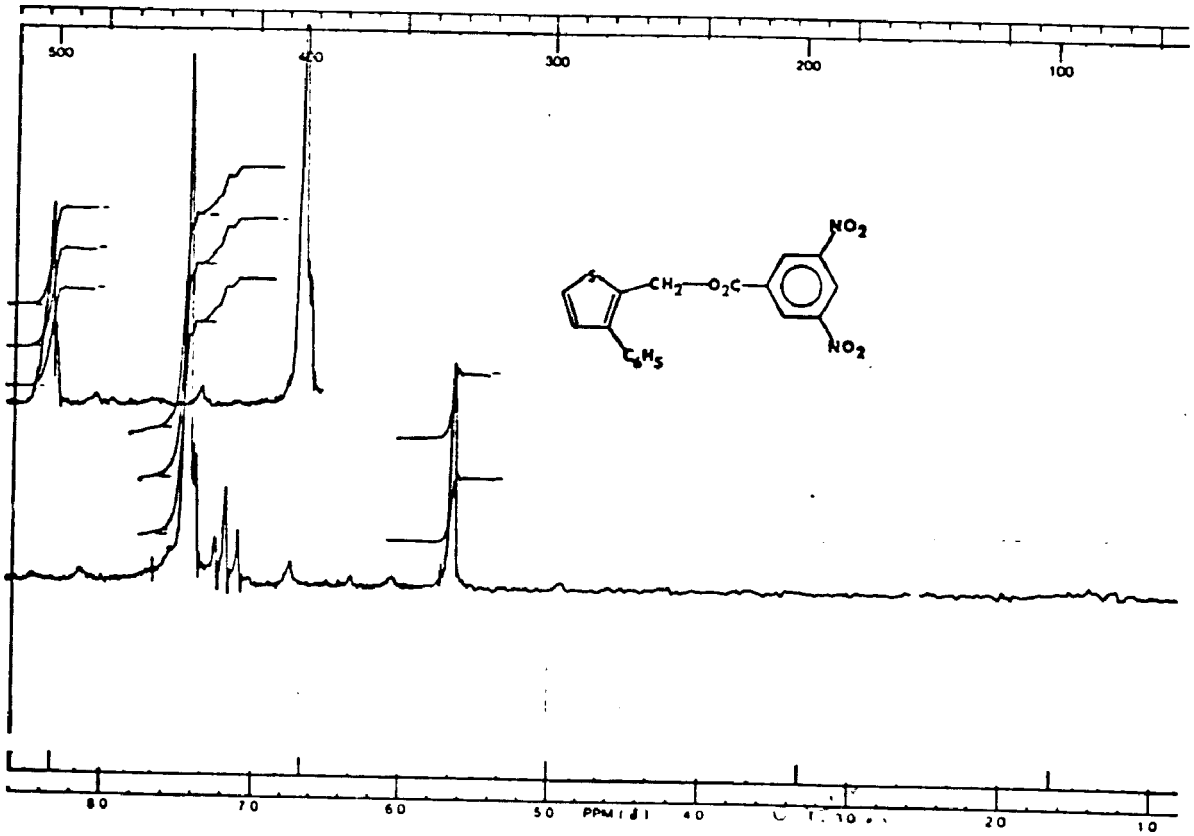
4-ACETYL-1-BENZYL-1,2,3-TRIAZOLE

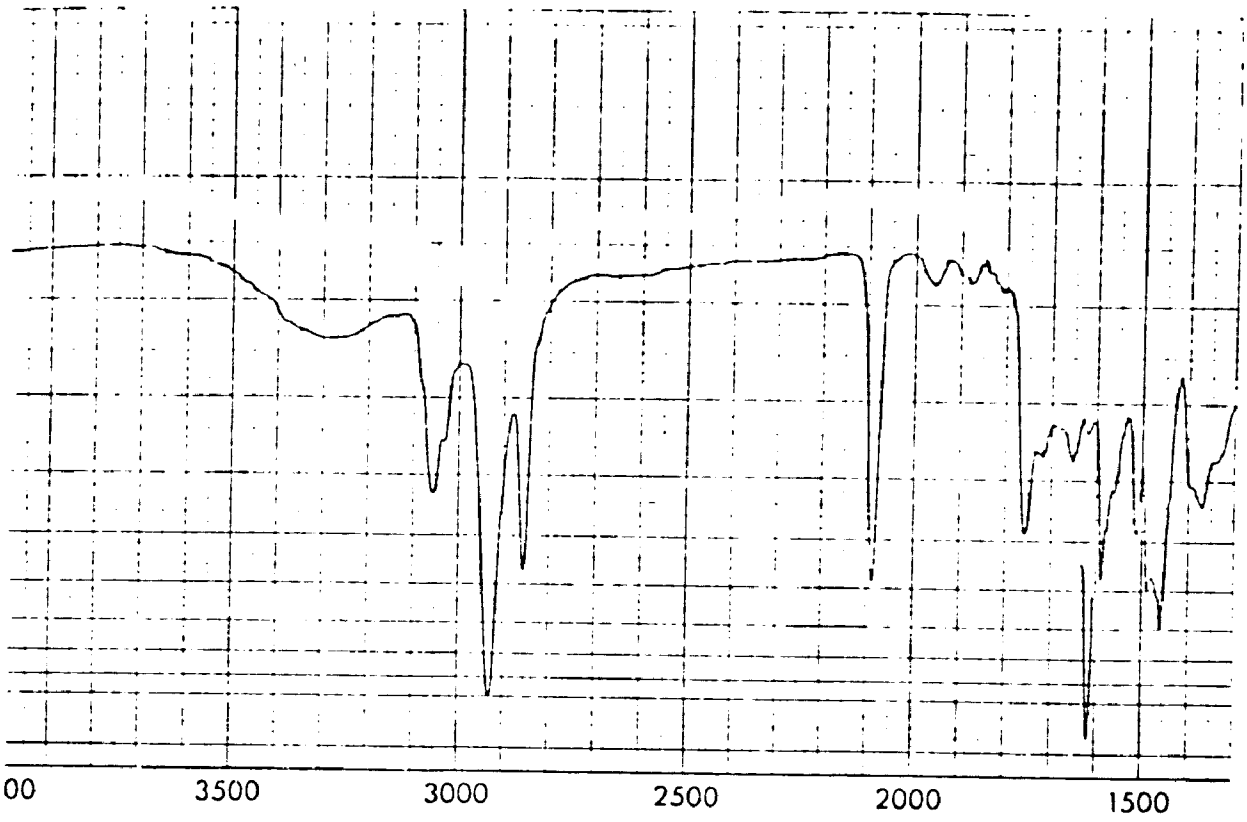


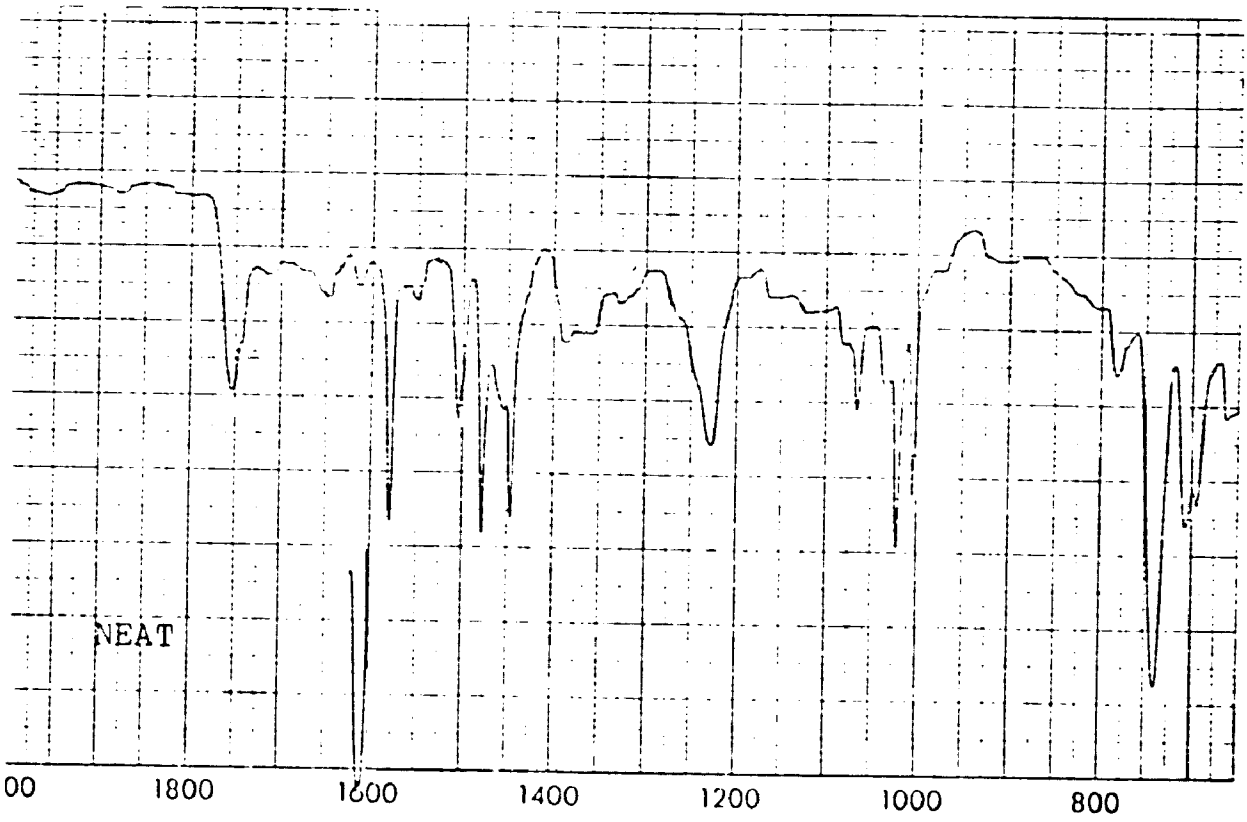
1-BENZYL-4-PHENYL-1,2,3,-TRIAZOLE-5-CARBOXALDEHYDE



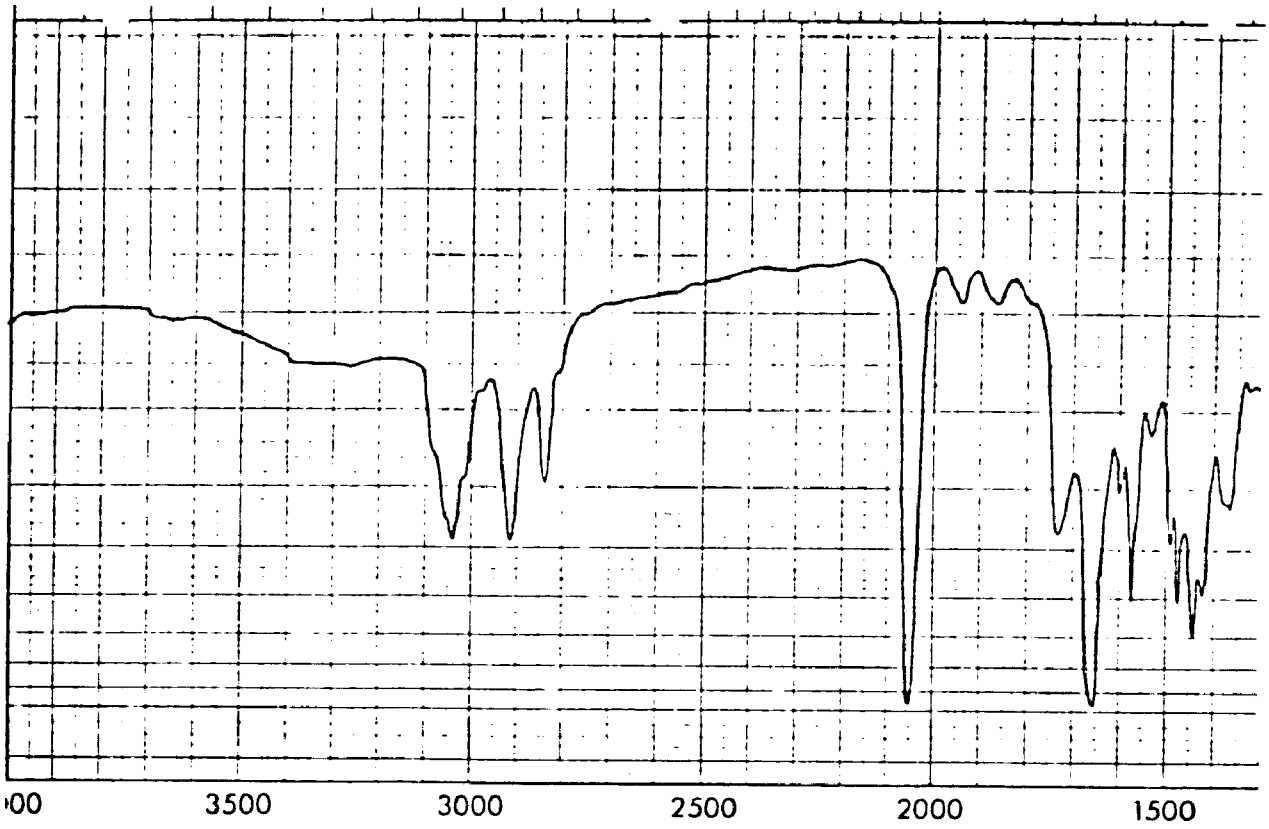
1,3,6-TRIMETHYL-4-(1-BENZYL-4-PHENYL-1,2,3-TRIAZOL-5-YL)-CYCLOHEPTATRIENE

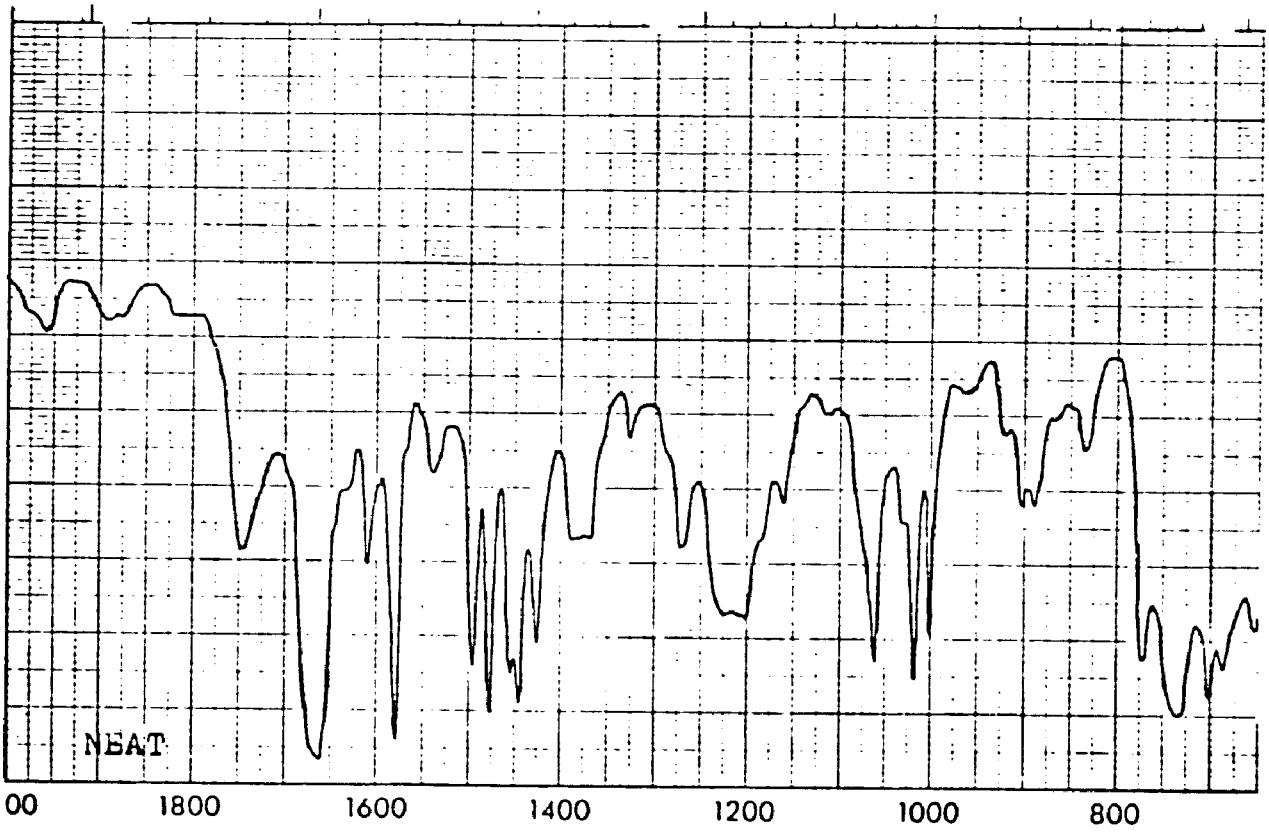






1-BENZYL-5-DIAZOMETHYL-4-PHENYL-1,2,3-TRIAZOLE





2-DIAZOMETHYL-3-PHENYLTHIOPHENE

REFERENCES

1. (a) P. Kropcho, J. Org. Chem., 27, 1089 (1962); (b) W. Kirmer, L. Horner, and H. Hoffmann, Justus Liebigs Ann. Chem., 614, 19 (1958); (c) Y. Ito, F. Saegusa, S. Kobayashi, K. Hirota, and T. Shimizu, Tetrahedron Lett., 6131 (1966).

2. (a) S. D. Saraf, Can. J. Chem., 47, 1173 (1969); (b) M. Saunders and R. W. Murray, Tetrahedron, 11, 1 (1960).

3. W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1971, p. 409.

4. (a) V. Franzen and H. Kuntze, Justus Liebigs Ann. Chem., 627, 15 (1959); (b) W. R. Bamford and T. S. Stevens, J. Chem. Soc., 4675 (1952).

5. E. M. Bruckmann and P. A. S. Smith, J. Org. Chem., 39, 1047 (1974).

6. N. Gjos and S. Gronowitz, Acta. Chem. Scand., 24, 99 (1970).

7. J. B. F. N. Engbert, G. van Bruggen, J. Strating, and H. Wynberg, Recueil Trav. Chim., 84, 1610 (1965).

8. F. Moulin, Helv. Chim. Acta., 35, 167 (1952).

9. (a) C. F. H. Allen and C. O. Edens, Org. Syn., 25, p. 92; (b) B. W. Howk and J. C. Sauer, J. Amer. Chem. Soc., 80, 4607 (1958).