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THE ADDITION OF DIAZOMETHANE AND PHENYL AZIDE TO ALIPHATIC α,β-UNSATURATED SULFONIC ACID DERIVATIVES

by
Pauline Kimm Chang

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in the
University of Michigan
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Committee in charge:

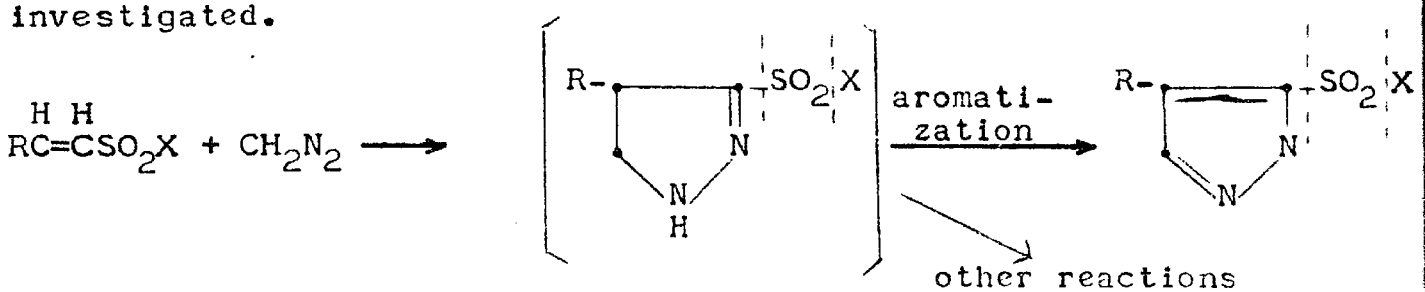
Assistant Professor Christian S. Rondestvedt, Jr., Chairman
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Abstract

THE ADDITION OF DIAZOMETHANE AND PHENYL AZIDE TO ALIPHATIC α,β-UNSATURATED SULFONIC ACID DERIVATIVES

by Pauline Kimm Chang

The ring-forming additions of diazomethane and phenyl azide to simple aliphatic α,β-unsaturated sulfonic acid derivatives were studied. Specifically, the effect of a β-alkyl substituent and the kind of sulfonyl derivative on the reactivity of the double bond, and the influence of the heterocyclic ring upon the chemistry of the sulfo group were investigated.



The α,β-unsaturated sulfonic acid derivatives studied in this work are ethylenesulfonyl chloride, propene-1-sulfonyl chloride, their corresponding N,N-diethyl amide and n-butyl ester, propene-2-sulfonyl chloride and α-bromoethylenesulfonyl chloride (the last with phenyl azide only). Their preparations involve mainly low-temperature dehydrochlorination of the corresponding 2-chloroalkanesulfonyl chlorides

with 2,6-lutidine or triethylamine.

Diazomethane reacts with α,β-unsaturated sulfonic acid derivatives to give the expected 3-sulfopyrazolines, the stabilities of which vary according to the sulfonyl group. The oily pyrazolines from diazomethane and the unsaturated sulfonamides and sulfonate esters (100% yield) were characterized by bromine aromatization to the corresponding pyrazoles. However, a pronounced tendency for concurrent cleavage by the hydrogen bromide liberated was observed. Pyrazoline-3-N,N-diethylsulfonamide gave 56% of pyrazole-3-N,N-diethylsulfonamide, 32% of 3-pyrazolidone hydrobromide and equivalent amounts of diethylamine hydrobromide and sulfate. 4-Methylpyrazole-3-N,N-diethylsulfonamide gave 59% of 4-methylpyrazole-3-N,N-diethylsulfonamide, a trace of 4-methyl-3-pyrazolidone and 18% of diethylamine hydrobromide and equivalent sulfate. A mechanism is proposed for the formation of the 3-pyrazolidone hydrobromides and diethylamine hydrobromide involving the cleavage at the sulfur-carbon bond prior to the aromatization, followed by decomposition of the unstable $SO_2N(C_2H_5)_2$ group to sulfur dioxide and diethylamine. The facile cleavage at the sulfur-carbon bond is ascribed to the nature of the pyrazoline ring. n-Butyl pyrazoline-3-sulfonate and n-butyl 4-methylpyrazoline-3-sulfonate undergo cleavage more readily at the ester link and give the corresponding 3-pyrazolesulfonic acids in 72% and 52% yield respectively. n-Butyl bromide, sulfate and a trace of pyrazole or 4-methylpyrazole were the other products. In contrast to

the cleavage of the pyrazolinesulfonamides, the cleavage of the sulfur-oxygen bond predominates due to the nature of the ester link and the unusual stability of the cleavage product, the 3-pyrazolesulfonic acid zwitter ion. The pyrazoline from ethylenesulfonyl chloride decomposes spontaneously into 3-pyrazolidone hydrochloride, which was isolated when excess diazomethane was present. In the absence of excess diazomethane, the pyrazolidone adds to a second mole of ethylenesulfonyl chloride in the Michael fashion to give 2-(2-proto-3-keto-1-pyrazolidinyl)-ethanesulfonate. The propenesulfonyl chlorides reacted with diazomethane but did not give pure adducts.

Neither α,β-unsaturated sulfonic acid derivatives containing a β-methyl nor n-butyl ethylenesulfonate gave adducts with phenyl azide. N,N-Diethyl ethylenesulfonamide gave the corresponding triazoline (45%) which is stable and did not aromatize to the triazole when treated with bromine. α-Bromoethylenesulfonyl chloride also gave the expected triazoline which aromatizes spontaneously to 1-phenyl-4-bromo-1,2,3-triazole (45%) with expulsion of the chlorosulfonyl group. The triazolines from ethylenesulfonyl chloride and propene-2-sulfonyl chloride were not isolable as such owing to their extreme reactivity. They add to a second mole of the chloride in the Michael fashion to yield 2-(1-proto-1-phenyl-1,2,3-triazol-3-yl)-ethanesulfonate and 1-(1-proto-1-phenyl-4-methyl-1,2,3-triazol-3-yl)-propane-2-sulfonate in 100% and 45% yield respectively.

The reactivity of the conjugated double bond has been shown to be greatest in the chlorides, next in the esters, and the least in the amides. Diazomethane is more reactive than phenyl azide in the addition to the double bond. A β-methyl group exerts an inhibiting effect on the addition reactions; the effect is greatest in the amides, next in the esters and least in the chlorides, and it is more pronounced with the phenyl azide additions than with diazomethane additions.

to

my late father,

Kiusic Kimm

ACKNOWLEDGEMENTS

The author wishes to express her deep appreciation to Professor Christian S. Rondestvedt, Jr., both for his suggestion and direction of this problem and for his sympathetic understanding and enthusiasm throughout this investigation.

The author also wishes to express her gratitude to Mr. and Mrs. C. Quackenbush and Mrs. M. M. Miller, without whose invaluable personal assistance, the completion of this work would have been impossible.

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TABLE OF CONTENTS

	page
INTRODUCTION	1
HISTORICAL	2
I. Addition of Diazomethane to Acetylenes and Olefins	2
II. Addition of Phenyl Azide to Acetylenes and Olefins	15
RESULTS AND DISCUSSION	24
I. Preparation of Aliphatic α,β-Unsaturated Sulfonic Acid Derivatives	24
II. Addition of Diazomethane	27
A. Diazomethane and α,β-Unsaturated Sulfonamides	27
1. N,N-Diethylethylenesulfonamide	27
2. N,N-Diethylpropene-1-sulfonamide	31
B. Diazomethane and α,β-Unsaturated Sulfonic Esters	33
1. n-Butyl ethylenesulfonate	33
2. n-Butyl propene-1-sulfonate	35
C. Diazomethane and α,β-Unsaturated Sulfonyl Chlorides	36
1. Ethylenesulfonyl chloride	36
2. Propene-1-sulfonyl chloride	39
3. Propene-2-sulfonyl chloride	39
D. Conclusions	40
III. Addition of Phenyl Azide	43
A. Phenyl Azide and α,β-Unsaturated Sulfonamides	43
1. N,N-Diethylethylenesulfonamide	43
2. N,N-Diethylpropene-1-sulfonamide	45
B. Phenyl Azide and α,β-Unsaturated Sulfonic Esters	47

page

C. Phenyl Azide and α,β-Unsaturated Sulfonyl Chlorides 47

1. α-Bromoethylenesulfonyl Chloride . . 47
2. Ethylenesulfonyl chloride 48
3. Propene-2-sulfonyl chloride 51
4. Propene-1-sulfonyl chloride 52

D. Conclusions 52

IV. Infrared Spectra Comparisons 54

EXPERIMENTAL 73

I. Syntheses of α,β-Unsaturated Sulfonic Acid Derivatives 73

A. Ethylenesulfonyl Chloride 73

Sodium 2-bromoethanesulfonate 73
2-Bromoethanesulfonyl chloride 74
2-Chloroethanesulfonyl chloride 74
Ethylenesulfonyl chloride 75

B. N,N-Diethylethylenesulfonamide 76

C. n-Butyl Ethylenesulfonate 76

D. Propene-1-sulfonyl Chloride 77

2-Chloropropane-1-sulfonyl chloride . . 77
Propene-1-sulfonyl chloride 78
Structure proof of propene-1-sulfonyl chloride by ozonization 78

E. N,N-Diethylpropene-1-sulfonamide 79

F. n-Butyl Propene-1-sulfonate 80

G. Propene-2-sulfonyl Chloride 81

Propylene sulfide 81
1-Chloropropane-2-sulfonyl chloride . . 81
Propene-2-sulfonyl chloride 82

II. Addition of Diazomethane 82

A. Diazomethane 82

Synthesis of N-nitroso-β-methylamino-isobutyl methyl ketone 82
Preparation of diazomethane from N-nitroso-β-methylaminoisobutyl methyl ketone 83

page

B. Diazomethane and N,N-Diethylethylene-sulfonamide 84

Formation of the adduct 84
Bromine dehydrogenation of the adduct . 84

C. Diazomethane and N,N-Diethylpropene-1-sulfonamide 87

Formation of the adduct 87
Bromine dehydrogenation of the adduct . 87

D. Diazomethane and Methyl Ethylene-sulfonate 89

Formation of the adduct 89
Attempted isolation of pyrazole from the adduct 90

E. Diazomethane and n-Butyl Ethylene-sulfonate 90

Formation of the adduct 90
Bromine dehydrogenation of the adduct . 90

F. Diazomethane and n-Butyl Propene-1-sulfonate 93

Formation of the adduct 93
Bromine dehydrogenation of the adduct . 94

G. Diazomethane and Ethylenesulfonyl Chloride 96

Reaction of diazomethane and ethylene-sulfonyl chloride 96
Reaction of 4-methyl-3-pyrazolidone and n-butyl ethylenesulfonate 99

H. Diazomethane and Propene-1-sulfonyl Chloride 99

I. Diazomethane and Propene-2-sulfonyl Chloride 102

III. Addition of Phenyl Azide 102

A. Preparation of Phenyl Azide 102

B. Phenyl Azide and N,N-Diethylethylene-sulfonamide 103

page

Formation of the adduct 103
Attempted dehydrogenation of N,N-diethyl-1-phenyl-1,2,3-triazoline-4-sulfonamide 103

C. Phenyl Azide and N,N-Diethylpropene-1-sulfonamide 105

D. Phenyl Azide and n-Butyl Ethylenesulfonate 106

E. Phenyl Azide and n-Butyl Propene-1-sulfonate 106

F. Phenyl Azide and Ethylenesulfonyl Chloride 107

Formation of the adduct 107
Addition of 1-phenyl-1,2,3-triazole to ethylenesulfonyl chloride 108
Reaction of 1-phenyl-1,2,3-triazole with acrylonitrile 108
Reaction of 1-phenyl-1,2,3-triazole with glacial acrylic acid 109
Reaction of 1-phenyl-1,2,3-triazole with methanesulfonyl chloride 109

G. Phenyl Azide and Propene-1-sulfonyl Chloride 109

H. Phenyl Azide and Propene-2-sulfonyl Chloride 110

I. Phenyl Azide with 1-Bromoethene-1-sulfonyl Chloride 110

IV. Syntheses of Model Compounds for Spectroscopic Comparisons 111

A. Pyrazole and Its Derivatives 111

Pyrazole 111
Pyrazole hydrochloride 112
Pyrazole picrate 112

B. 4-Pyrazolesulfonic Acid 112

C. Methyl 3-Pyrazolecarboxylate 113

D. 1-Phenyl-1,2,3-triazole and Its Derivatives 114

page

1-Phenyl-1,2,3-triazole-4-carboxylic acid 114
1-Phenyl-1,2,3-triazole 114
1-Phenyl-3-methyl-1,2,3-triazolium iodide 114
1-Phenyl-3-methyl-1,2,3-triazolium methanesulfonate 115
1-Phenyl-1,2,3-triazole hydrobromide . 116

F. 3-Pyrazolidone and Its Salts 116

3-Pyrazolidone 116
3-Pyrazolidone hydrochloride 117
3-Pyrazolidone hydrobromide 117

G. 4-Methyl-3-pyrazolidone and Its Salts . . 118

4-Methyl-3-pyrazolidone 118
4-Methyl-3-pyrazolidone hydrochloride . 118
4-Methyl-3-pyrazolidone hydrobromide . 118

SUMMARY 120

BIBLIOGRAPHY 123

LIST OF TABLES

page

1. Ultraviolet Absorption Characteristics of Aniline, Azobenzene and Some Derivatives of 1,2,3-Triazoles and Triazenes 46

LIST OF FIGURES

page

1. Infrared Spectra of Pyrazole, Pyrazole-3-N,N-diethylsulfonamide, 4-Methylpyrazole-3-N,N-diethylsulfonamide and Methyl pyrazole-4-carboxylate 57

2. Infrared Spectra of 1-Phenyl-1,2,3-triazoline-3-N,N-diethylsulfonamide (X), 3-Pyrazole-sulfonic Acid, 4-Methyl-3-pyrazolesulfonic Acid and 4-Pyrazolesulfonic Acid 58

3. Infrared Spectra of 1-Phenyl-1,2,3-triazole, 1-Phenyl-4-bromo-1,2,3-triazole, Propene-1-sulfonyl Chloride and Ethylenesulfonyl Chloride 59

4. Infrared Spectrum of 3-Pyrazolidone Hydrobromide. 60

5. Infrared Spectrum of 3-Pyrazolidone Hydrochloride 61

6. Infrared Spectrum of 4-Methyl-3-pyrazolidone Hydrobromide 62

7. Infrared Spectrum of 2-(1-Proto-5-keto-2-pyrazolidinyl)-ethanesulfonate (VIII) 63

8. Infrared Spectrum of 2-(1-Proto-4-methyl-5-keto-2-pyrazolidinyl)-ethanesulfonate (IX) . . . 64

9. Infrared Spectrum of 1-Phenyl-3-methyl-1,2,3-triazolium Iodide 65

10. Infrared Spectrum of 1-Phenyl-3-methyl-1,2,3-triazolium Methanesulfonate 66

11. Infrared Spectrum of 2-(1-Proto-1-phenyl-1,2,3-triazol-3-yl)-ethanesulfonate (XIV) 67

12. Infrared Spectrum of 1-(1-Proto-1-phenyl-4-methyl-1,2,3-triazol-3-yl)-propane-2-sulfonate 68

13. Infrared Spectrum of 1-Phenyl-1,2,3-triazoline Hydrobromide (XL) 69

14. Infrared Spectrum of V 70

page

15. Ultraviolet Spectra of (A) 1-Phenyl-1,2,3-triazole, (B) 1-Phenyl-4-bromo-1,2,3-triazole, (C) 1-Phenyl-1,2,3-triazole-4-carboxylic Acid, (D) 1-Phenyl-1,2,3-triazoline-4-N,N-diethyl-sulfonamide (X), (E) 1-Phenyl-1,2,3-triazoline Hydrobromide (XI) 71

16. Ultraviolet Spectra of (F) 2-(1-Proto-1-phenyl-1,2,3-triazol-3-yl)-ethane sulfonate,(XIV) (G) 1-Phenyl-3-methyl-1,2,3-triazolium Iodide . . 72

INTRODUCTION

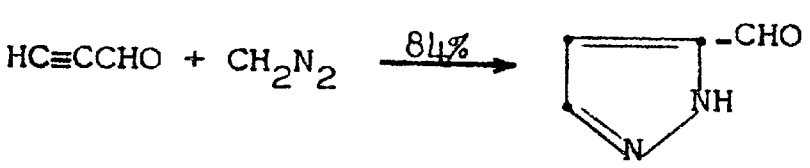
The addition of aliphatic diazo compounds and azides to carbon-carbon multiple bonds has been known since 1888[1]. From the former, one obtains pyrazole derivatives, whereas the latter yields derivatives of 1,2,3-triazole. It has been shown that addition takes place more readily where the double or triple bond is activated by the presence of a conjugated carbonyl, ester, nitro or cyano group, and that the terminal nitrogen of the diazo compound or the azide becomes attached to the carbon alpha to the activating group.

It appears, by analogy, that addition of diazo compounds or azides to α,β-unsaturated sulfonic acid derivatives should lead to the formation of derivatives of 3-sulfopyrazolines or 4-sulfo-1,2,3-triazolines respectively, and to the corresponding pyrazoles or triazoles upon aromatization. This dissertation is devoted to a study of the reaction between simple aliphatic α,β-unsaturated sulfonic acid derivatives and diazomethane or phenyl azide. The effect of the alkyl substituent on the double bond and the effect of the sulfonyl derivative group have been investigated. The influence of the heterocyclic ring upon the chemistry of the sulfo group has been studied.

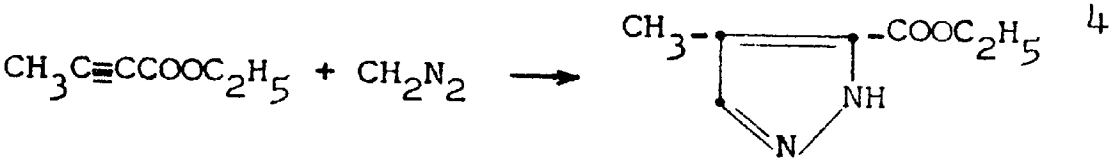
HISTORICAL

I. Addition of Diazomethane to Acetylenes and Olefins

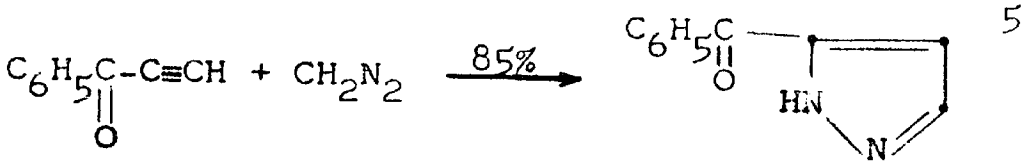
The addition of diazomethane to acetylene was discovered by v. Pechmann in 1898[2], who obtained a 50% yield of pyrazole by passing acetylene into an ethereal solution of diazomethane. Since then, various acetylenic compounds, especially those which contain an activating group such as an ester or a carbonyl have been shown to react with diazomethane to form substituted pyrazoles. In general, the carbon of the diazomethane adds to the carbon beta to the activating group, i.e.,



3



4



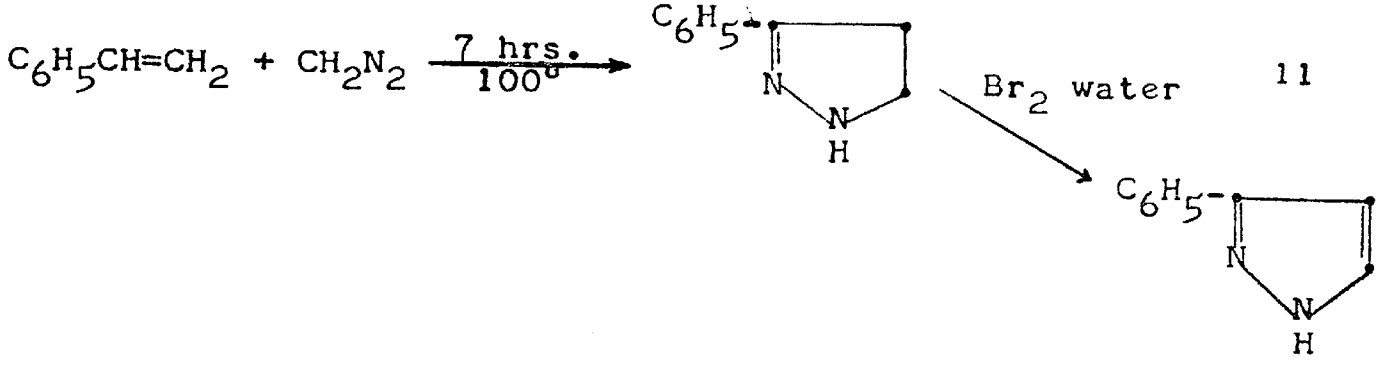
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However, v. Auwers and Ungemach found that this rule holds true only when the beta carbon does not hold an aryl group. When there is an aryl group on the beta carbon, a mixture of the isomers was obtained. Thus, methyl phenylpropiolate yields methyl 4-phenyl-3-pyrazolecarboxylate and methyl 3-phenyl-4-pyrazolecarboxylate in equal amounts when treated with diazomethane[3].

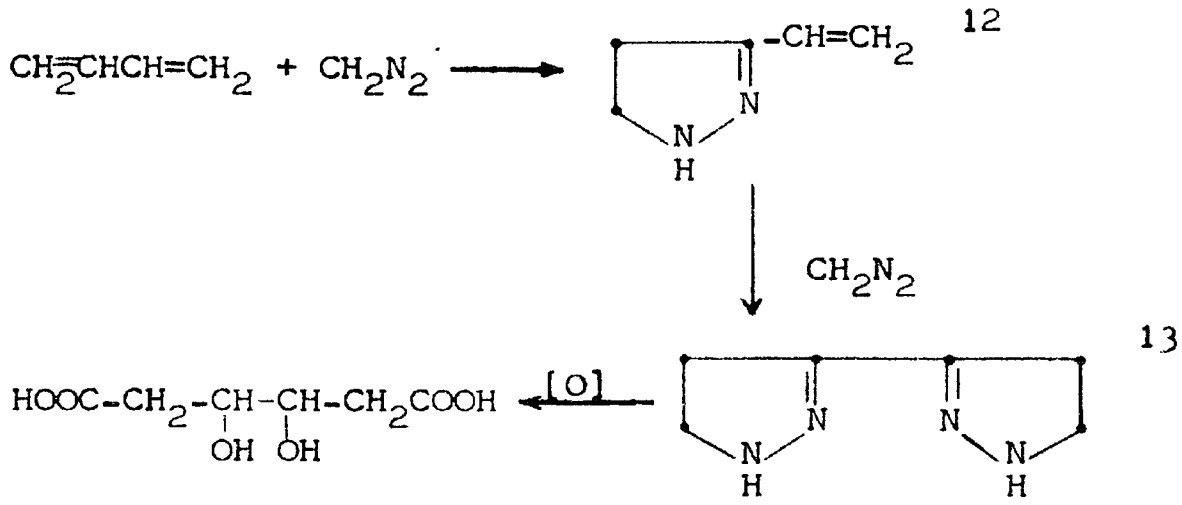
The reaction of diazomethane with symmetrical acetylenes usually takes place over a longer period. Diacetylene and diazomethane yield 3-ethynylpyrazole in 40-50% yield as the primary addition product; with excess diazomethane and prolonged standing (3 weeks), 3,3'-bipyrazolyl is also obtained[6]. Diazomethane adds to the acetal of acetylenedialdehyde in eight days to give 80% of the corresponding pyrazole[7].

When propargyl alcohol was allowed to react with diazomethane, the adduct was predominantly 3-hydroxymethylpyrazole (50%) with only a trace of the 4-isomer (2%). This indicates that the hydroxymethyl group has the same directive force as an ester group to a certain extent[8]. On the other hand, it is interesting to note that 2-butyne-1,4-diol[9] failed to react with diazomethane over a period of two weeks, which indicates that the hydroxymethyl group deactivates the triple bond.

Due to the greater availability and variety of olefins, the examples of addition of diazomethane to this class of compound are more numerous and varied. The reaction of diazomethane and ethylene was first carried out in cold ether by Azzarello in 1906[10]. Since then, other olefinic hydrocarbons have been reported to react with diazomethane under more vigorous conditions to yield pyrazolines with side chains:



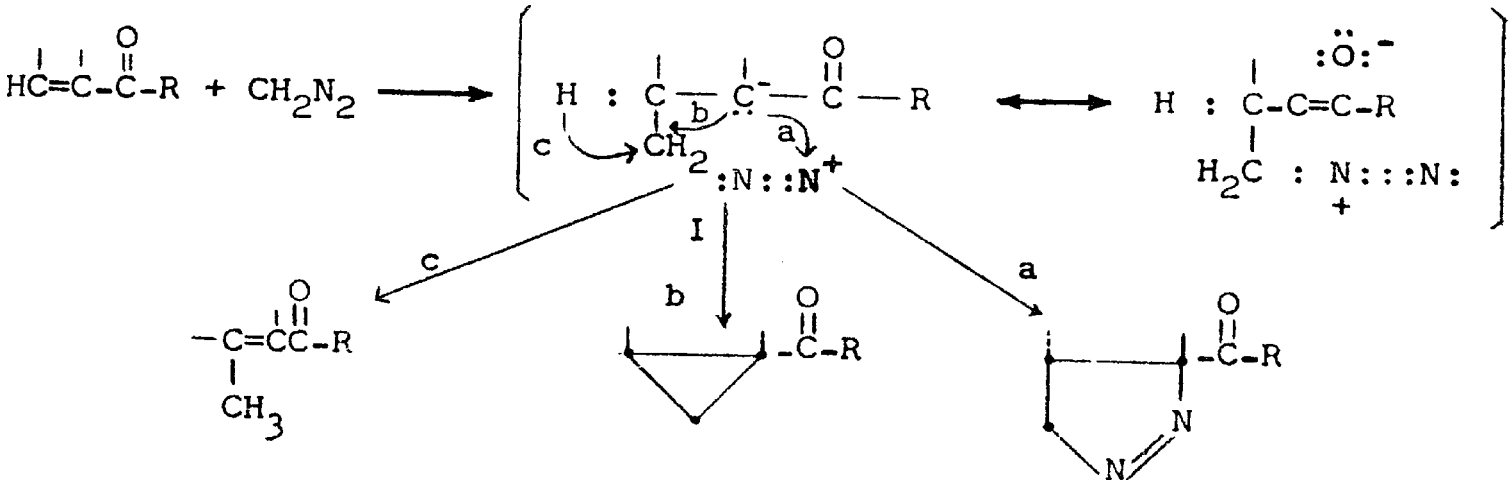
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In each of the above reactions, the last step served to eliminate beyond doubt the possible formation of the alternate pyrazolines. The reactions of diazomethane with 1,5-hexadiene[10] and allyl bromide[14] have also been reported. However, the structures of the adducts were not proven. It is of interest to mention here that vinyldiazomethane, which contains an ethylenic double bond and a diazo group in the same molecule undergoes intramolecular addition to yield pyrazole[15].

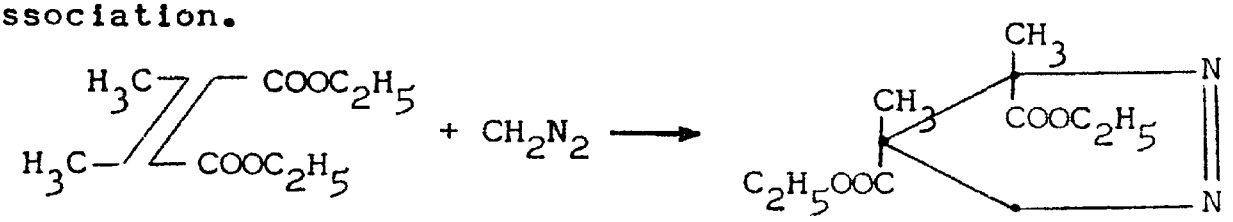
As a rule, Δ^1-pyrazolines, which contain the doubly bonded nitrogens, are formed first in the addition. Spontaneous rearrangement to the Δ^2-compound occurs if this results in the formation of a conjugated system[3,16]. When the rearrangement cannot yield such a system, it is frequently possible to isolate the Δ^1-compound, which may then be rearranged to the Δ^2-isomer by acid or heat. Since the Δ^2 structure has an imino-hydrogen, it can be distinguished from the Δ^1 structure by reaction with phenyl isocyanate, ethyl chlorocarbonate or similar reagents[16,17], although Δ^1-compound may rearrange into the Δ^2-compound during such transformations.

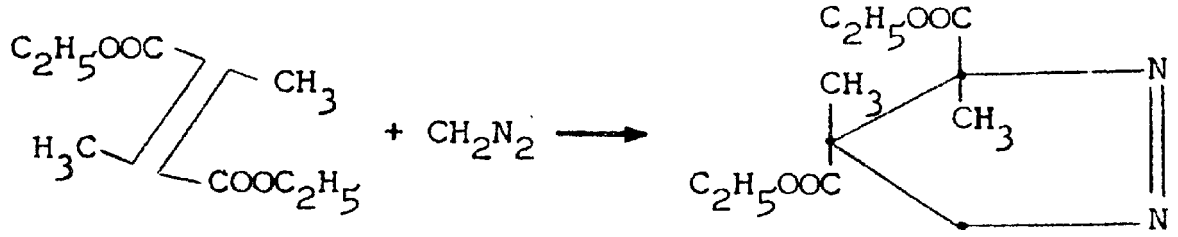
As in the additions of diazomethane to acetylenes described earlier, the diazo compound adds to olefins containing an activated double bond with more ease. Again, the carbon of diazomethane becomes attached to the position beta to the activating group. It is also well known that in many cases, depending on the substituents on the double bond, the addition of diazomethane to an olefin leads to the formation of its cyclopropane or methylated derivatives. Thus, the following mechanism has been suggested by Eistert to account for the formation of all three types of products[18]:



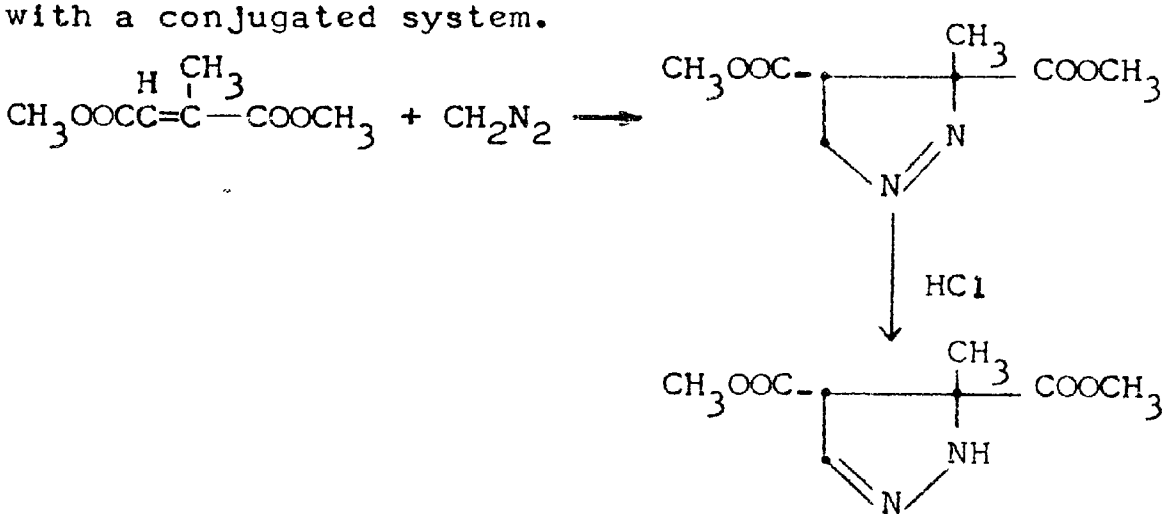
Evidence for the existence of a "resonance-stabilized" diazonium betaine intermediate such as I has been established by v. Pechmann in the reaction of diazomethane and benzoquinone[19]. The thermal decomposition of pyrazolines to cyclopropanes or the methylated olefins is believed to involve ring opening of the pyrazoline to I. However, in order to account for the stereospecificity of the addition reaction, as demonstrated in the following and other cases[16,17], one must assume that one of the nitrogens in I preserves the

configuration of the carbon next to the carbonyl by polar association.

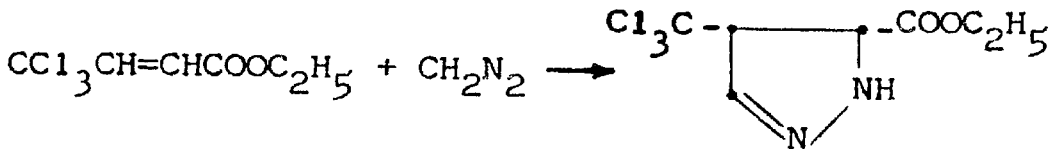




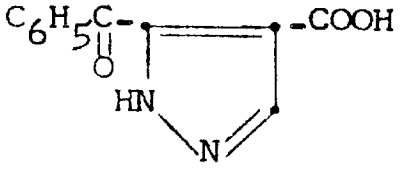
Examples of α,β-unsaturated esters reacting with diazomethane are numerous. Methyl acrylate and methyl crotonate yield methyl pyrazoline-3-carboxylate and methyl 4-methyl-pyrazoline-3-carboxylate respectively[20,21]. Cinnamic acid reacts with excess diazomethane to give 100% yield of methyl 4-phenylpyrazoline-3-carboxylate[22]. It is interesting to note that the pyrazoline obtained from dimethyl citraconate is chiefly dimethyl 3-methylpyrazoline-3,4-dicarboxylate, even though the isomeric 4-methylpyrazoline-3,4-dicarboxylic ester is the one capable of rearranging into a Δ^2-pyrazoline with a conjugated system.



Sometimes, however, the presence of two alkyl groups on the beta carbon inhibits the addition of diazomethane to the double bond. For example, β-methylcrotonic acid, β-methyl-α-bromocrotonic acid, as well as methyl β-ethoxy-crotonate[17,23] failed to react. It is also unexpected that β-chlorocrotonic esters do not react with diazomethane[17]. On the other hand, the presence of the group CCl_3 on the beta carbon of acrylic ester does not interfere with the usual mode of the diazomethane addition and one obtains the corresponding pyrazoline[17]:

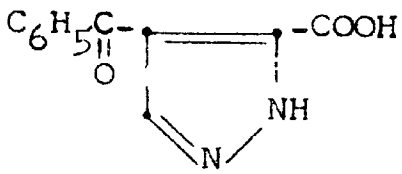


An interesting situation arises when diazomethane is added to α-bromobenzoylacrylic acid where both the alpha and beta carbon are connected to activating groups so that both II and III may be expected,



II

and



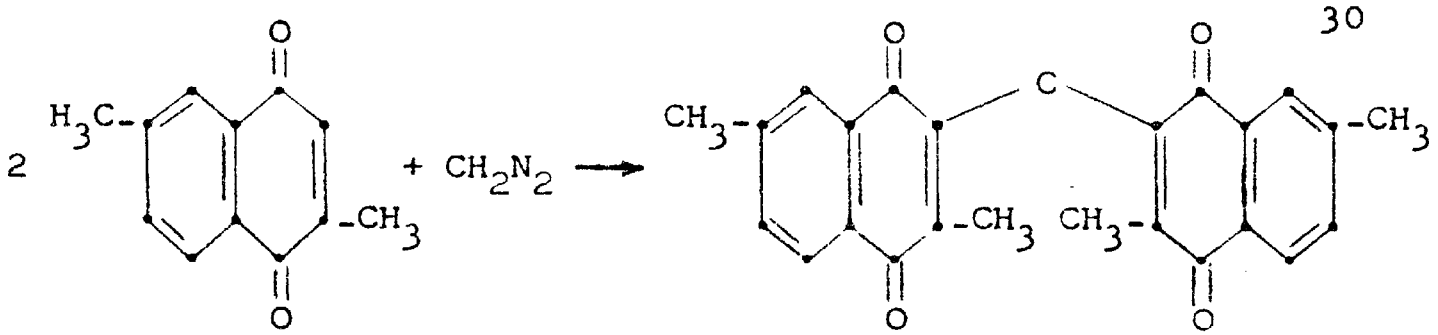
III

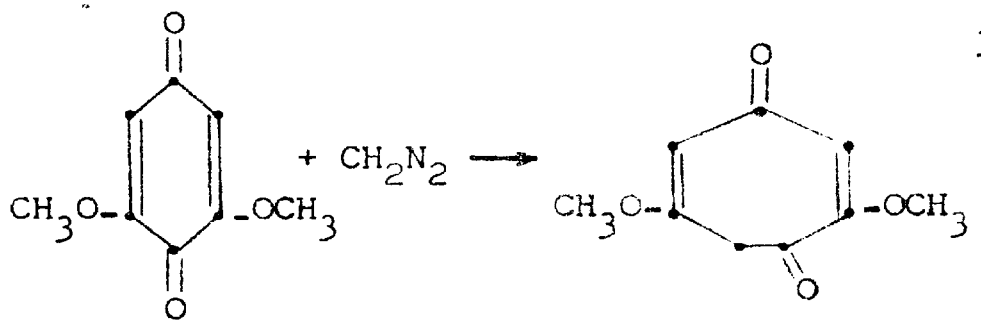
Although the author favored structure II, he did not prove it unequivocally[24]. Also, the author reported that the formation of the pyrazoline was not preceded by esterification at the acid group.

α,β-Unsaturated ketones react with diazomethane yielding pyrazolines, in general less smoothly than unsaturated

esters; the products are less stable. Mesityl oxide and diazomethane give 5-acetyl-4,4-dimethylpyrazoline which becomes oily when exposed to air; it can be distilled only in nitrogen[25]. Azzarello found that both benzalacetone and dibenzalacetone gave the corresponding pyrazolines, the latter consuming two moles of diazomethane to form the dipyrazolinyl ketone[26]. Benzalacetophenone gives a quantitative yield of 4-phenyl-5-benzoylpyrazoline when it is treated with diazomethane at -14°[27].

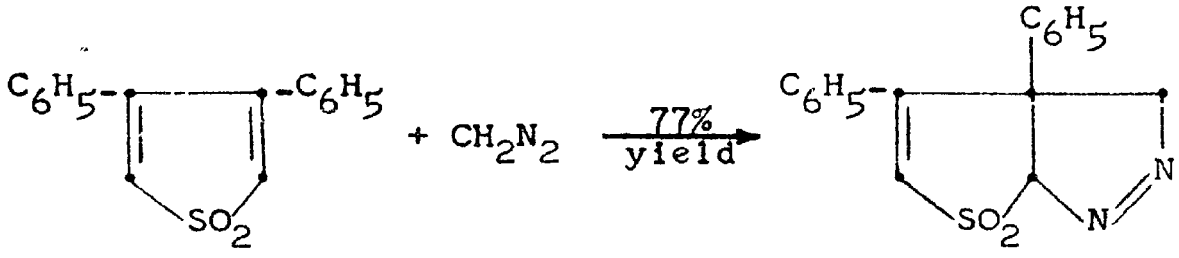
A number of 1,4-quinones also react with diazomethane to give pyrazolines. Among them are quinone[28], 1,4-naphthoquinone[25,19], and 2-diphenylmethyl-1,4-naphthoquinone[29]. However, some substituted 1,4-quinones, such as 2,6-dimethyl-1,4-naphthoquinone and 1,2-quinone, either failed to react or give other products[30]. Recently, it was reported that diazomethane reacts with 2,6-dimethoxyquinone to give a tropone[31]:

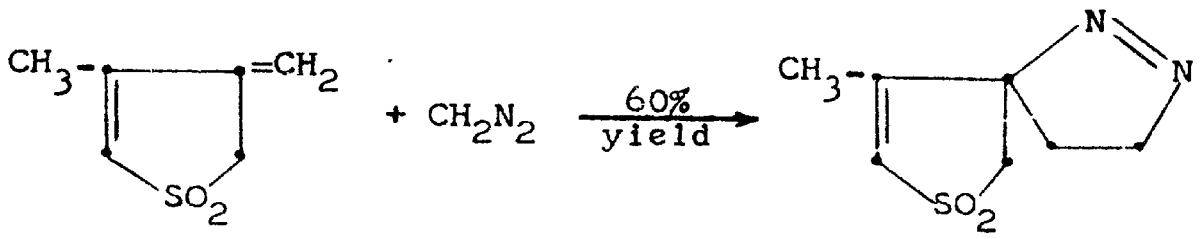




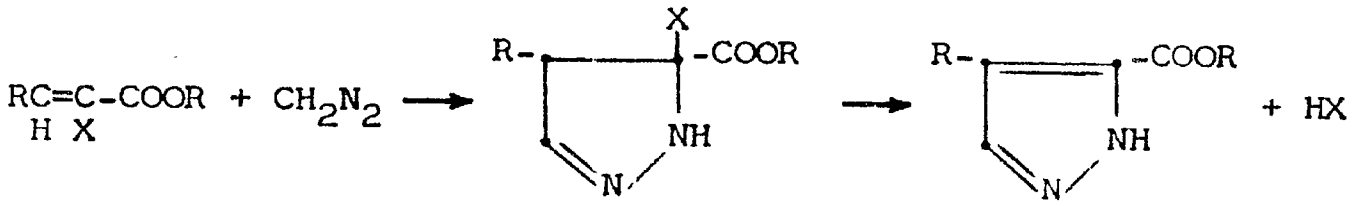
The reactions of diazomethane and α,β-unsaturated nitriles and nitro compounds have not been studied extensively. In most cases, the nitrile or nitro compound with α-hydrogen, such as acrylonitrile and ω-nitrostyrene give polymers when they are treated with diazomethane[4,32]. However, cinnamonitrile yields an unstable pyrazoline which loses a molecule of hydrogen cyanide to give 4-phenylpyrazole on distillation[4]. α-Methylacrylonitrile gave a pyrazoline which was not purified but yielded 1-methyl-1-cyanocyclopropane on distillation[33]. 1-Phenyl-2-nitropropene gives the corresponding pyrazoline as expected[32]. When there are two cyano groups or a cyano and an ester on the same end of the double bond, only a cyclopropane or a methylated derivative is obtained[34].

There has been virtually no report on the reaction of diazomethane and α,β-unsaturated sulfones, probably because no reaction occurs. Only a few cyclic sulfones containing a conjugated double bond system attached to the sulfonyl group are reported to react; diazomethane adds to the end double bond of the conjugated system. The double bond may sometimes be outside the ring and a spiro type derivative of pyrazoline is formed[35]:

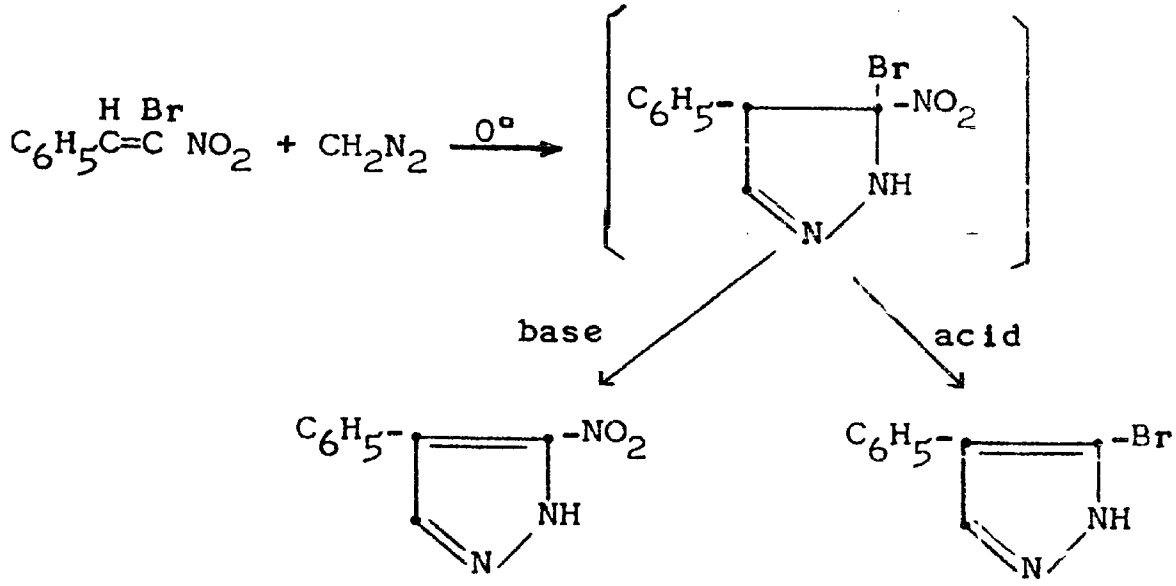




A number of α- or β-halo-α,β-unsaturated olefins and some α,β-unsaturated nitrile and nitro compounds yield pyrazolines which aromatize into pyrazoles by losing a molecule of hydrogen halide, hydrogen cyanide or nitrous acid either spontaneously or under mild conditions[4,36,37,38]. Typical examples of aromatization by way of dehydrohalogenation are given by α-chloro- and α-bromoacrylic acid[23], and α-chlorocrotonic acid[17]:



The same dehydrohalogenation is also observed with vinyl bromide when it is treated with diazomethane, thus providing an excellent method to synthesize pyrazole. In the case of cinnamonitrile, the 3-cyano-4-phenylpyrazoline derived from it gives 4-phenylpyrazole on distillation[4]. 1-Phenyl-2-nitropropene gives 3-nitro-3-methyl-4-phenylpyrazoline which aromatizes into 4-phenylpyrazole when heated at 100°, giving off oxides of nitrogen[32]. However, the most interesting example to illustrate this aromatization was reported by Parham and Bleasdale who studied the acid- and base-catalyzed decomposition of the pyrazoline from 1-bromo-1-nitro-2-phenylethylene[38]:

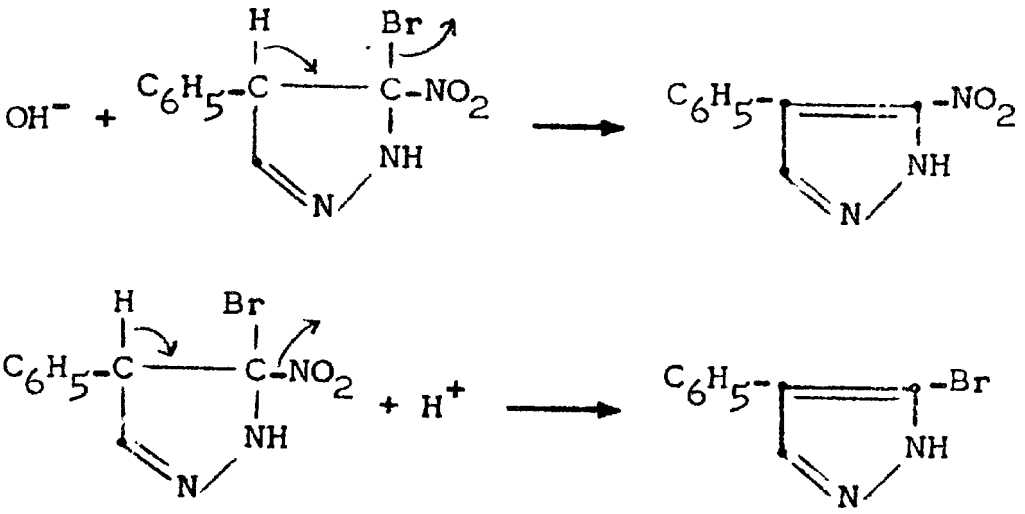


It was suggested that in basic media, aromatization proceeded by removal of a proton from C_4* followed by a shift of C_4 electrons into the ring and the simultaneous preferential elimination of the less basic bromide**; in acidic media, the aromatization may take place by an acid-catalyzed ionization of the nitro group facilitated by the coordination of a proton with subsequent or simultaneous expulsion of a proton at C_4. The greater solubility of nitroalkanes relative to bromoalkanes in sulfuric acid suggests that the nitro group is more suceptible to electrophilic attack by a proton than the bromine atom:

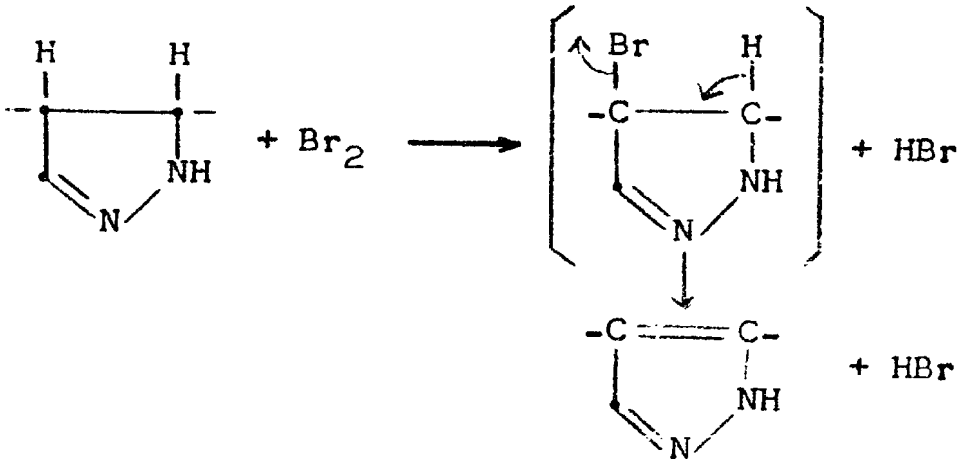
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*Parham suggested that, by analogy to picoline, the increased acidity of the hydrogen atom at C_4 is explained by "resonance stabilization" of the resulting ion ($^-C-C=N \longleftrightarrow -C=C-N^-$).

**Cf. Ingold et al., J. Chem. Soc., 1948, 2041.



The same mechanism could undoubtedly be applied to the well-known oxidation of pyrazolines to pyrazoles by bromine, one of the best and most commonly used methods for identification purposes[42]. This transformation probably involves a 4-bromo-pyrazoline* as the intermediate:

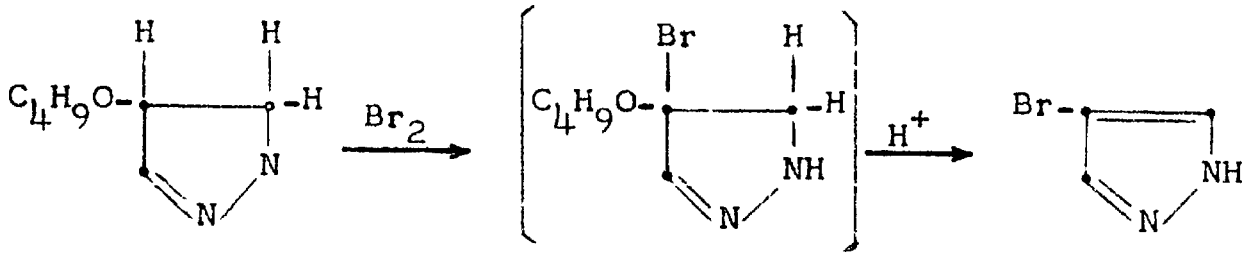


In most cases, one obtains the desired pyrazole without side reactions, but occasionally groups substituted on the pyrazoline may cleave off, a fact which may also be explained

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*See footnote (*), page 11.

by the same "preferential elimination" mechanism just discussed. For example, 4-butoxypyrazoline yields 4-bromopyrazole on treating with bromine[39]:



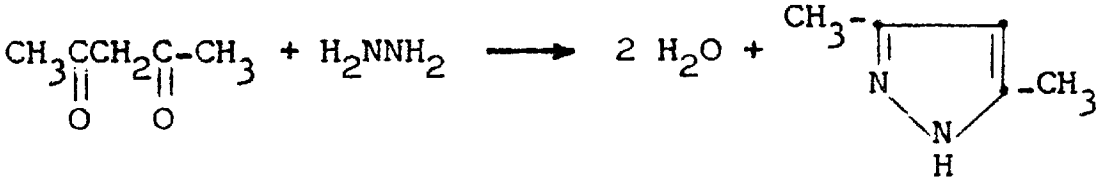
However, this is not the only way to interpret this reaction.

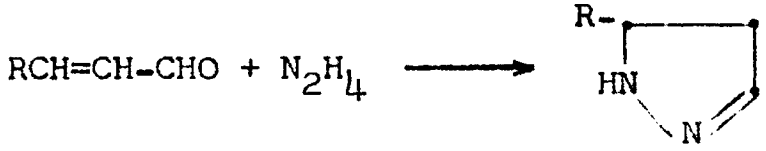
Pyrazoles and pyrazolines are weak bases which form salts with various acids. Frequently, the salts are titratable against base. Picrates are readily prepared and often serve as derivatives. The pyrazole ring is a stable aromatic unit which is not hydrogenated easily under ordinary conditions[38,40]. It can withstand direct sulfonation[41,42], nitration[42], and halogenation, the 4-position being the most susceptible. The ring can also survive alkaline permanganate oxidation. Polycarboxylic acids decarboxylate smoothly at their melting points[43]. Replacement reactions of the imino hydrogen with diazomethane[4,44], methyl iodide[43], formaldehyde[40], or Grignard reagents[45] yield pyrazolium derivatives. The reduction of pyrazole to pyrazolines[46] has been reported but usually is not successful.

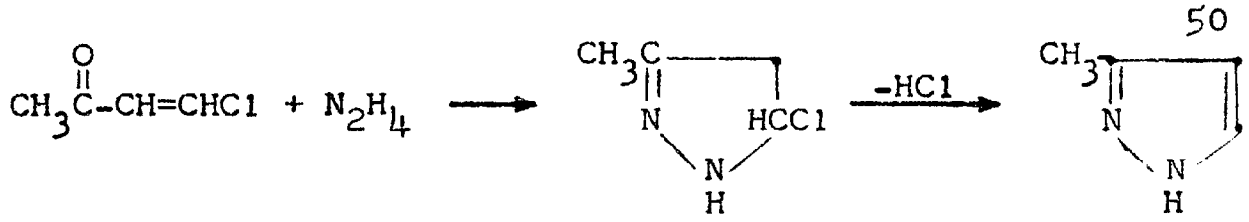
Pyrazolines are much less stable. Many are sensitive to oxygen or undergo thermal decomposition yielding cyclopropane derivatives or substituted olefins[16,17,23,33,35]. Therefore, they are customarily identified by oxidation to pyrazoles. As mentioned earlier, bromine dehydrogenation is

most commonly used on account of better yields and easy handling. Other oxidizing agents such as silver salts[46], potassium ferricyanide[47], chromic acid[48], and lead tetra-acetate[49] have been employed. The reactions involving the iminohydrogen in Δ^2-pyrazolines have already been mentioned earlier.

It should be noted that pyrazoles and pyrazolines can also be prepared by other methods, mainly by way of hydrazine derivatives[42]:





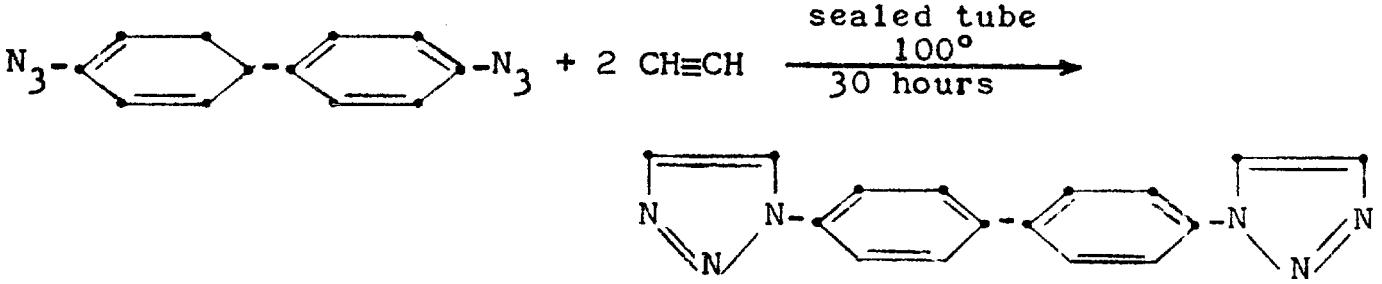


However, it is beyond the scope of this review to describe these reactions in detail and extensive reviews are available elsewhere[42].

The writer wishes to express her sincere appreciation to Professor R. C. Elderfield, who kindly permitted the use of the manuscript by T. L. Jacobs on the chapter of pyrazole and pyrazolines in the forthcoming "Heterocyclic Compounds" Volume V.

II. Addition of Phenyl Azide to Acetylenes and Olefins

The addition of phenyl azide to acetylene was first carried out by O. Dimroth and G. Fester[51] in 1910. The reaction required heating the reactants in a sealed tube at 100° for forty hours. Since then, similar reactions have been carried out using other aryl azides; 1-(2,4-dichlorophenyl)-1,2,3-triazole, 1-(2,5-dichlorophenyl)-1,2,3-triazole, as well as the 1,1'-bis-1,2,3-triazole derivative of biphenyl have been prepared[52].



Recently, diphenylacetylene (tolan) was found to give a 42% yield of 1,4,5-triphenyl-1,2,3-triazole when it was refluxed with phenyl azide in toluene[53].

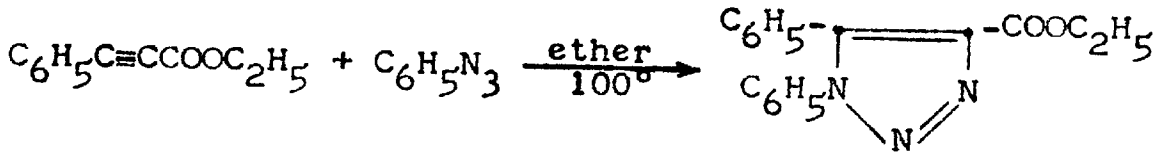
As an empirical approximation, azides may be regarded as analogs of aliphatic diazo compounds in which the carbon next to the nitrogen has been replaced by a nitrogen:

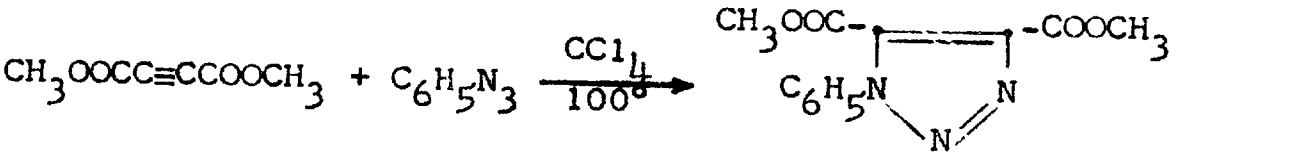
RCH=N=N and RN=N=N

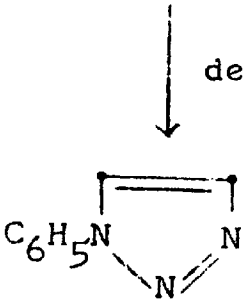
From the similarity of these formulas, it is expected that many of the addition reactions of aliphatic diazo compounds should be paralleled by the azides. It is, therefore, not surprising that when the triple bond is activated by an ester or carbonyl, the addition of aryl azides takes place

with considerably more ease, just as in the case of diazo compounds. Thus, in the formation of 4-formyl-1-phenyl-1,2,3-triazole from propiol aldehyde and phenyl azide, only six hours of refluxing in chloroform is required[3].

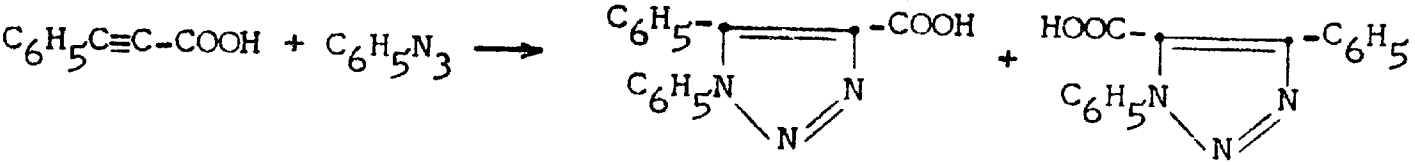
Ethyl phenylpropiolate and acetylenedicarboxylate esters react with phenyl azide to give the corresponding 1,2,3-triazoles with the terminal nitrogen of the azide adding to the alpha carbon[54]:







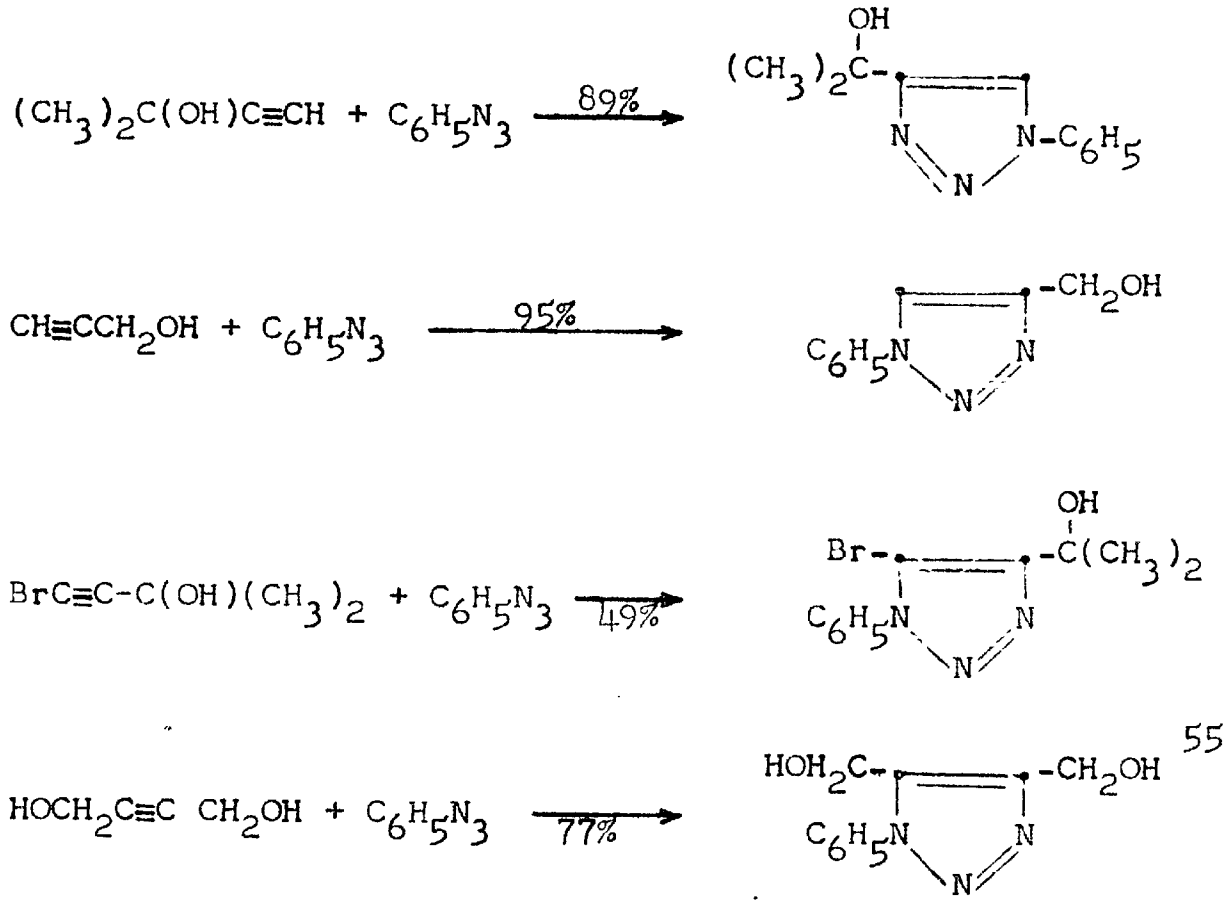
However, propiolic acid gives only a 15% yield of a mixture of the isomeric triazoles[53]:



The acetal of acetylenedialdehyde also yields the expected triazole, but the reactants have to be heated in a sealed tube at 100° for twenty-eight hours[7]. Besides phenyl azide,

p-xylyl azide has also been found to add to acetylenedicarboxylic esters to give 1-(p-xylyl)-1,2,3-triazole-4,5-dicarboxylic ester.

A number of ethynylcarbinols have recently been reported to form adducts with phenyl azide by refluxing the reactants in toluene from fifteen to twenty hours[53]. The azide usually adds to the acetylene so that the nitrogen attached to the phenyl group is also bound to the acetylenic carbon which bears a hydrogen.

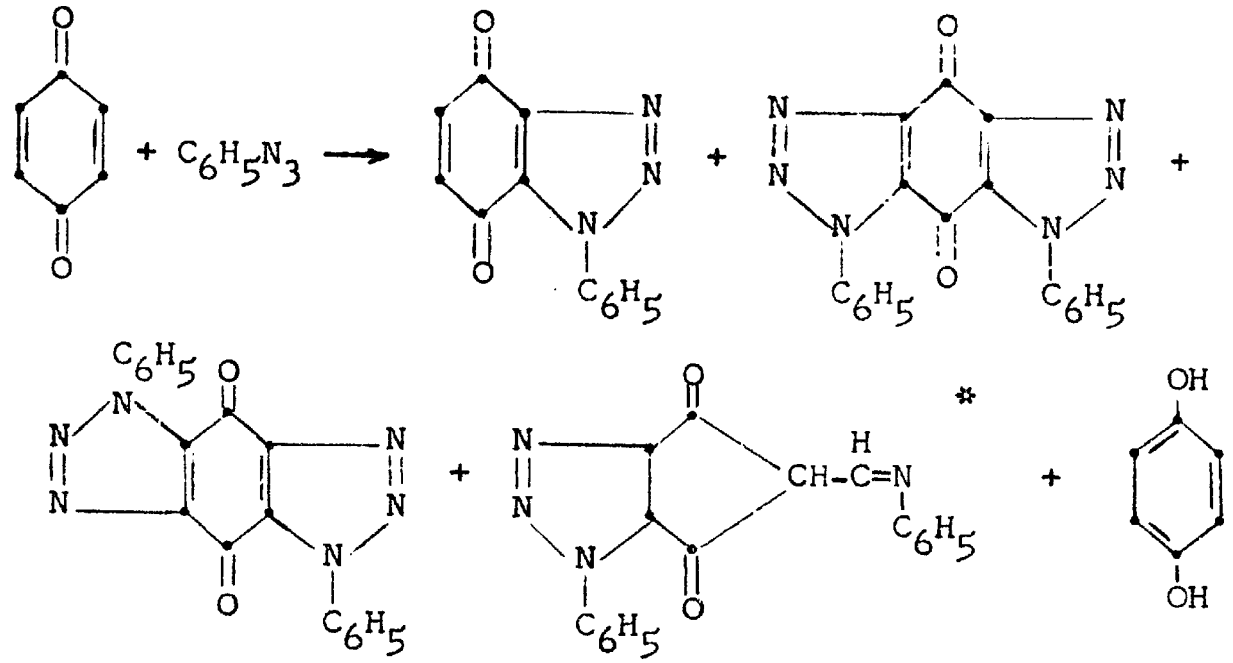


[55]

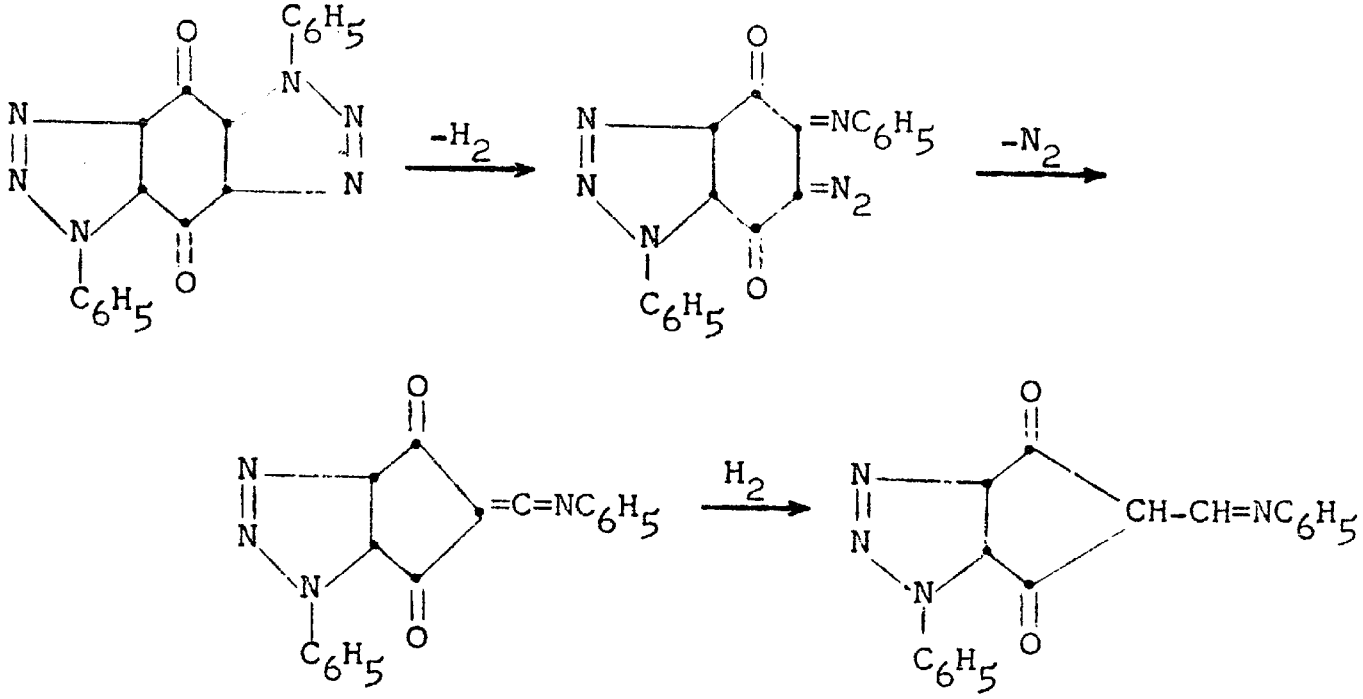
In the last reaction, it is interesting to note that the corresponding addition of diazomethane was not successful[9].

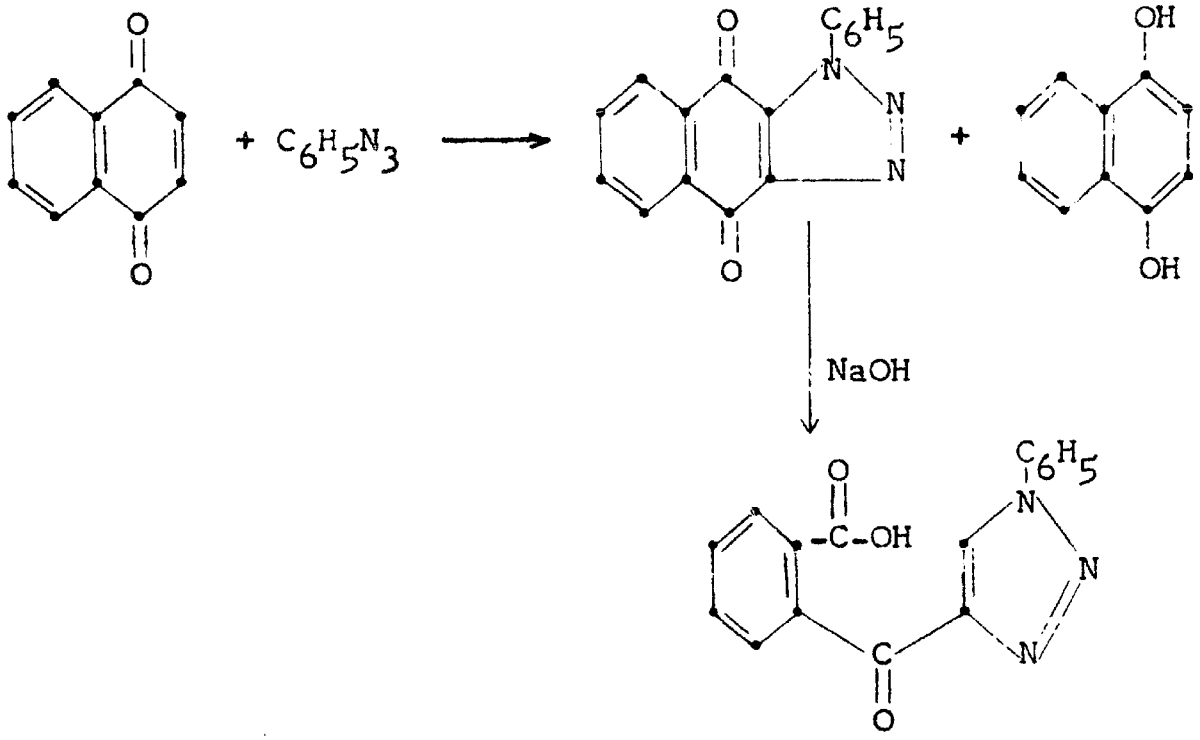
The reaction of aryl azides with olefinic compounds has not been explored extensively. Among unsaturated ketones,

quinone and 1,4-naphthoquinone react with phenyl azide to give the fused-ring 1,2,3-triazoles. The primary products are the corresponding triazolines; they are immediately oxidized to the triazoles by the presence of excess quinone or 1,4-naphthoquinone[56,57]:

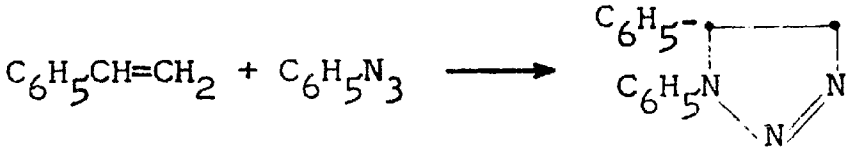


*This compound presumably is formed as follows:

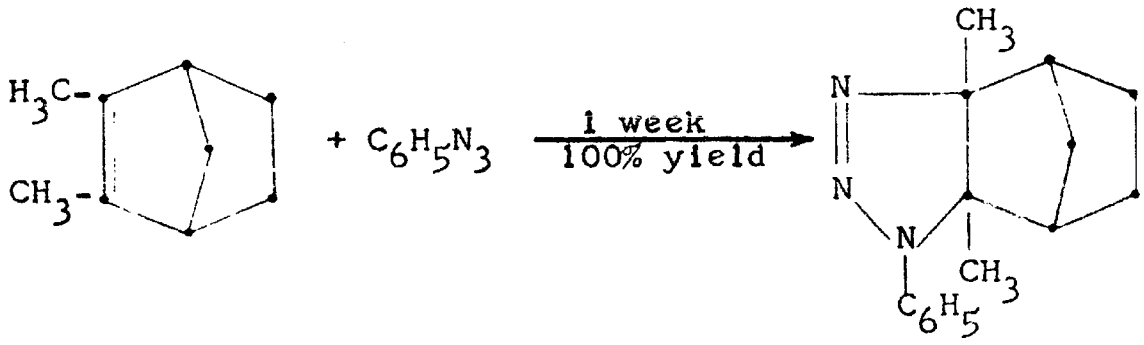


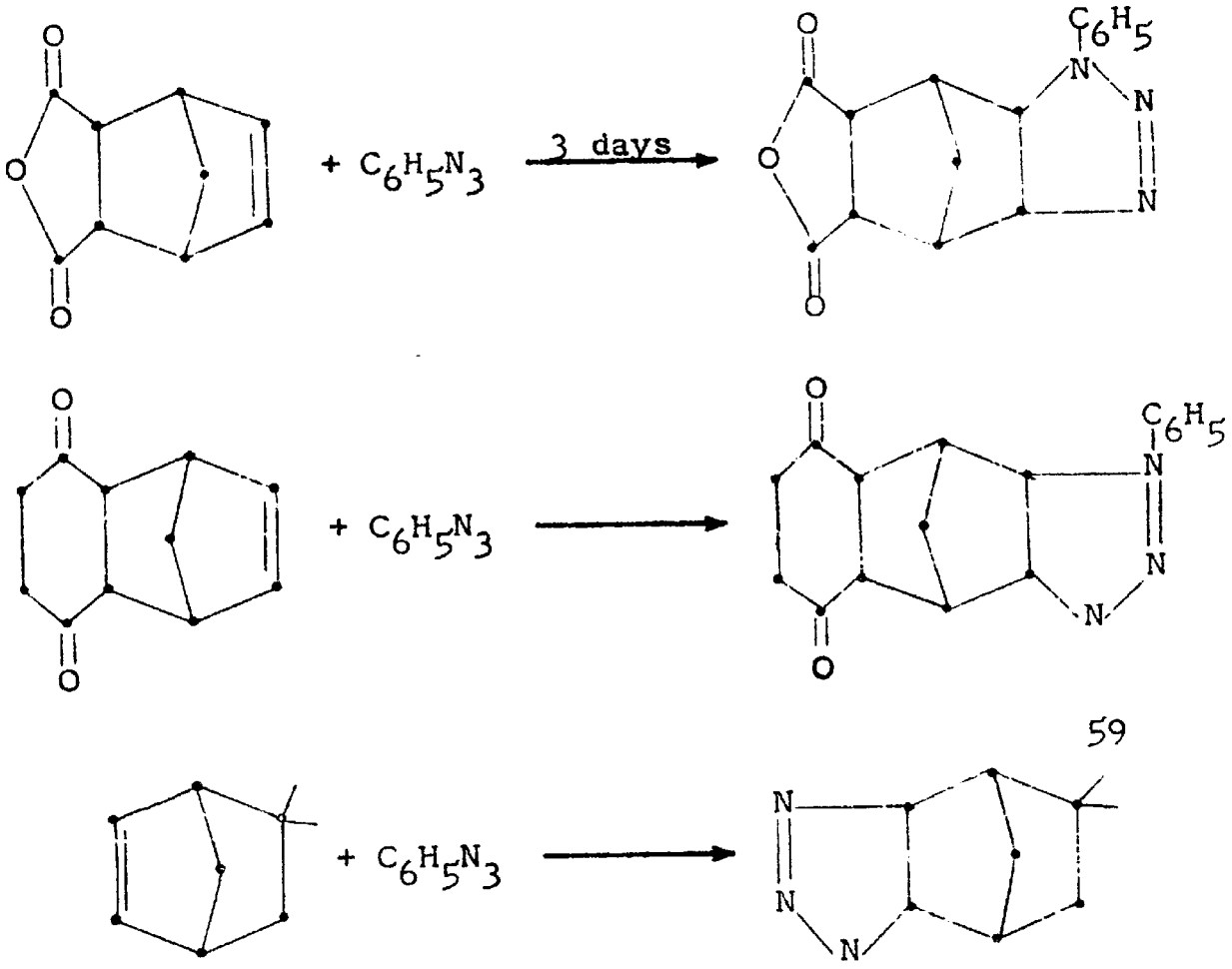


Wolffe reported that styrene, trimethylethylene and fumaric esters yield triazolines when they are treated with phenyl azide[56], but stilbene and cinnamic ester failed to react:



In 1933, Alder and Stein observed that several cyclic olefins and phenyl azide reacted to form 1,2,3-triazoline derivatives[58]:

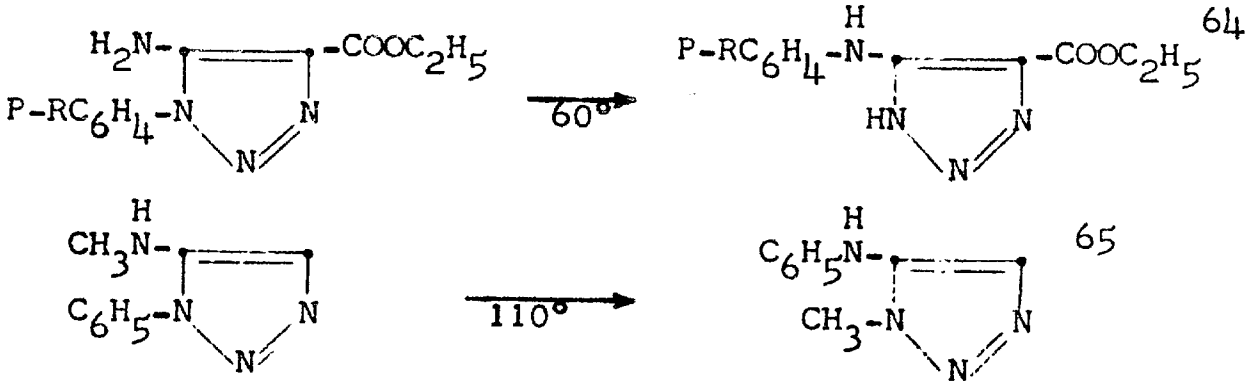




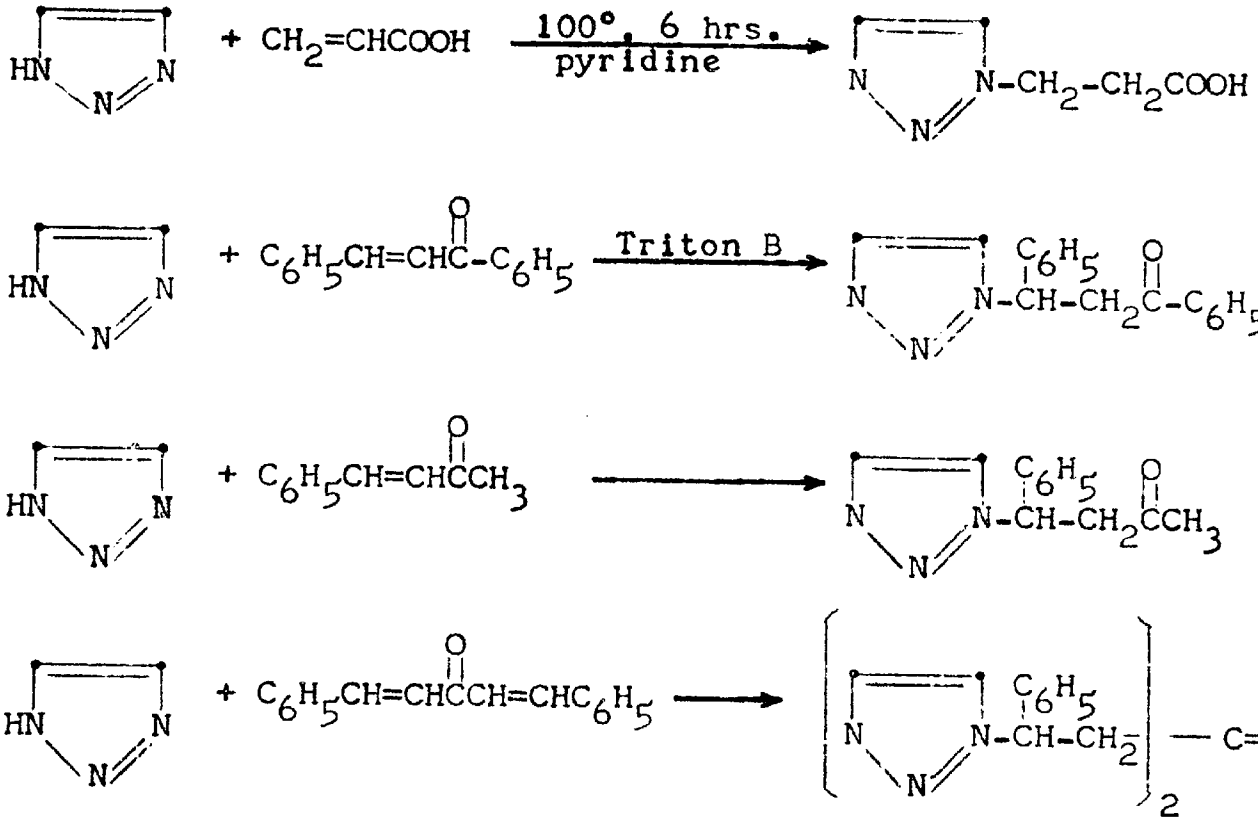
This addition of phenyl azide to olefinic linkage in strained cyclic compounds takes place so readily that it has now become a method for characterizing this class of olefins[59,60].

The triazole ring is a stable entity that can survive oxidation by alkaline permanganate and decarboxylation at high temperature[52,61,62]. It is not reduced by ordinary reducing agents such as sodium in methanol or zinc in acid[53]. More drastic conditions such as hydriodic acid mixed with red phosphorus produced only a resinous product[53]. Catalytic hydrogenation over Raney nickel gives a poor yield of mixed amines[53]. However, triazoles are readily methylated by methyl iodide at the 3-position to give 1,2,3-triazolium

quaternary salts[53,63]. 1-Aryl-5-amino-1,2,3-triazoles appear to rearrange to 5-arylamino-1,2,3-triazoles when heated alone or with acid:

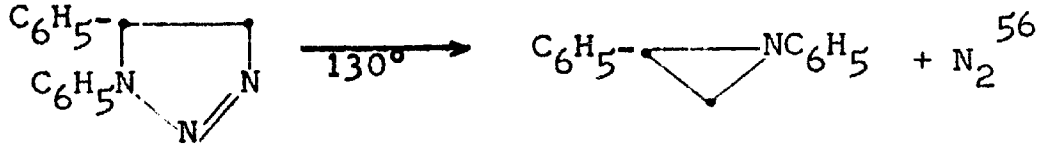


The parent 1,2,3-triazole and 1,2,3-triazoles with an unsubstituted imino group have been found to add in the Michael fashion to olefins containing an activated double bond[66]:



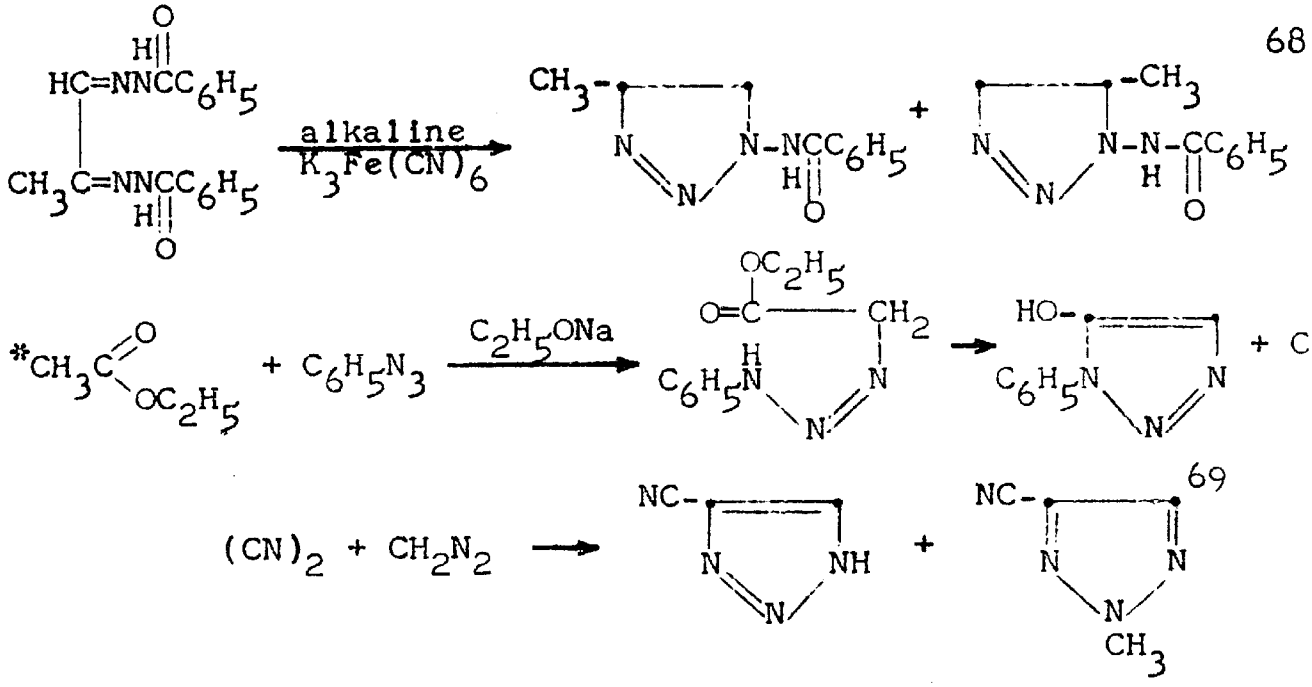
The chemistry of the triazoline ring has not been fully investigated. Aromatization of the triazolines formed

in the reaction of quinone and phenyl azide[56] indicates that oxidation of triazolines to triazoles should not be too difficult; however, the decomposition of triazolines with liberation of one mole of nitrogen seems to be predominating:



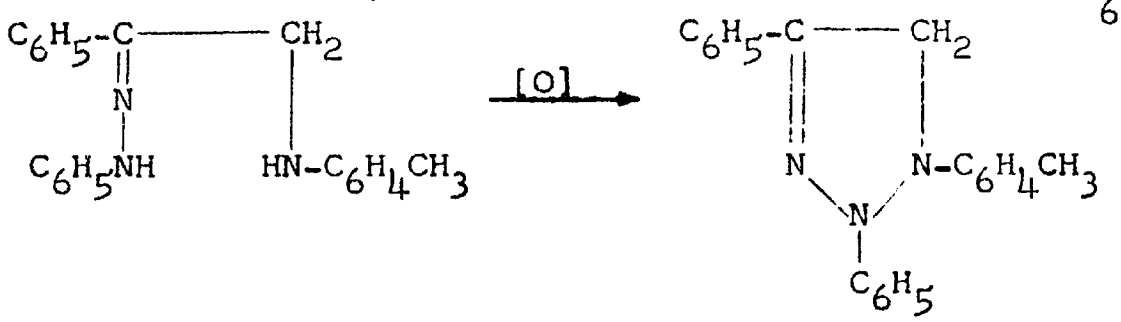
Unlike triazoles, triazolines have been reported to undergo hydrogenation and yield triazolidines when treated with sodium in alcohol[67].

There are many other methods of preparing triazole and triazolines. Since it is beyond the scope of this review to describe them in detail, only a few examples will be given here:



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*The formulation for this reaction given by Benson and Savell in "The Chemistry of the Vicinal Triazoles," Chem. Rev., 46, 16 (1950) is incorrect.



67

RESULTS AND DISCUSSION

I. Preparation of Aliphatic α,β-Unsaturated Sulfonic Acid Derivatives

In the present work, the reactions of diazomethane and phenyl azide with ethylenesulfonyl chloride, propene-1-sulfonyl chloride, propene-2-sulfonyl chloride and their corresponding diethylamides and n-butyl esters were investigated. Since most of these compounds had been either unknown or prepared in low yields prior to this dissertation, a considerable amount of effort was devoted to their preparation.

Ethylenesulfonyl chloride had been prepared previously by treating ammonium ethylenesulfonate with phosphorus pentachloride[70]. This salt was prepared from ethane-1,2-disulfonyl chloride by the method of Kohler[71] who hydrolyzed it to give a good yield of ethylenesulfonic acid, followed by conversion to the ammonium salt. However, the yield of the unsaturated sulfonyl chloride was low (32%) and the procedure tedious. A new method was then developed by Dr. C. S. Rondestvedt in this laboratory[72]. He found that β-chloroethanesulfonyl chloride (prepared from commercial sodium isothionate by the action of phosphorus pentachloride[73]) could be dehydrochlorinated to give ethylenesulfonyl chloride in 70% yield by the action of the highly hindered base, 2,6-lutidine, at -50°. The unsaturated sulfonyl chloride is a very strong lachrymator, reacts explosively with bases at room temperature and decomposes

on distillation under atmospheric pressure. Since the compound has a tendency to turn dark on standing, it was prepared in small quantities just prior to use to insure its purity.

A similar procedure gave the homolog, propene-1-sulfonyl chloride from 2-chloropropane-1-sulfonyl chloride. It was found that replacing 2,6-lutidine with a stronger base, triethylamine, and carrying out the dehydrochlorination at a slightly higher temperature than in the case of ethylenesulfonyl chloride was advantageous; the yield was as high as 80%. The propenesulfonyl chloride was proved to be α,β-unsaturated by ozonolysis to acetaldehyde and by infrared spectroscopy (see Experimental, page 79).

1-Propene-2-sulfonyl chloride had been prepared in low yield (31%) by Stewart and Cordts. They treated 1-chloropropane-2-sulfonyl chloride first with aqueous sodium carbonate to form sodium 1-propene-2-sulfonate, which was then converted to the chloride by action of excess phosphorus oxychloride[74]. It appeared to us that the low-temperature dehydrochlorination described above might be employed to advantage here and such was indeed the case; we were able to obtain a 50% yield of the desired sulfonyl chloride from 1-chloropropane-2-sulfonyl chloride in one step, using triethylamine as the dehydrochlorinating agent. Both the 1- and 2-propenesulfonyl chlorides are lachrymators but not as objectionable as ethylenesulfonyl chloride.

The preparation of the diethylamides of the foregoing unsaturated sulfonyl chlorides was found to be more

difficult than the corresponding N,N-diethyl-2-phenylethene-sulfonamide, the chief obstacle being the pronounced tendency of diethylamine to add to the double bond, besides the reaction with the sulfonyl group[73]. Fortunately, this difficulty could be overcome by carrying out the reaction at 70° so that the addition of the amine to the double bond was minimized without affecting the reactivity of the sulfonyl chloride group[72]. In this manner, N,N-diethylethylenesulfonamide was prepared from molar quantities of diethylamine, triethylamine and ethylenesulfonyl chloride in 42% yield (reported[72], 47%); the analogous preparation of N,N-diethyl-1-propene-1-sulfonamide proceeded in 46% yield. N,N-Disubstituted sulfonamides were chosen for this investigation for the obvious reason that their reaction with diazomethane would be restricted to the double bond.

The corresponding n-butyl esters of the unsaturated sulfonic acids were prepared by the method of Whitmore and Landau who treated 2-chloroethanesulfonyl chloride with one mole of the alcohol and two moles of pyridine[75]. Esterification and dehydrochlorination take place in one step to give the desired ester in 42% yield (reported[75], 61%). The n-butyl ester was selected for the addition reactions throughout this work primarily because of its higher yield over the other esters reported by Whitmore and Landau. Later, it became apparent that it also possessed the advantage of yielding products with higher molecular weights, and, hence, easier to isolate; this is particularly true when the reaction involves bond cleavage at the ester link.

An entirely similar procedure was employed to prepare the previously unknown n-butyl propene-1-sulfonate in 58% yield. The position of the double bond was assigned from infrared spectroscopy* and by analogy to the dehydrochlorination of 2-chloropropane-1-sulfonyl chloride.

II. Addition of Diazomethane

A. Diazomethane and α,β-Unsaturated Sulfonamides

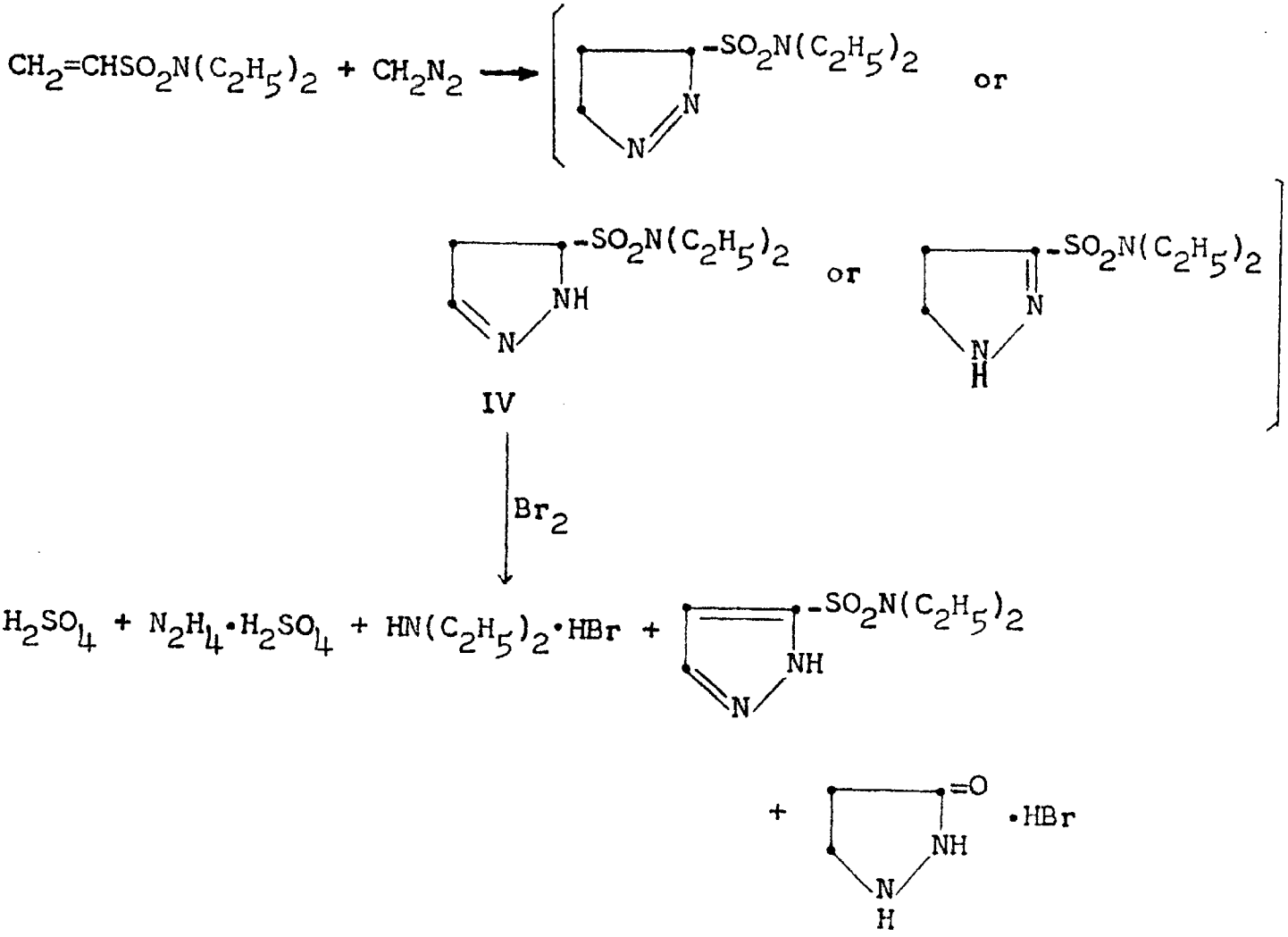
1. N,N-Diethylethylenesulfonamide.--Diazomethane was found to add to an equimolar amount of N,N-diethylethylenesulfonamide when an ethereal solution of these compound was allowed to stand at room temperature. The reaction was complete in twenty-four hours, giving 90% yield of a crude adduct. Since the oily adduct, expected to be the corresponding pyrazoline (IV), could not be purified by either recrystallization or distillation, it was characterized by bromine dehydrogenation to the pyrazole.

The crude adduct, when brominated in a chloroform solution at room temperature, gave a chloroform-insoluble precipitate, which, quite surprisingly, was found to be mainly 3-pyrazolidone hydrobromide (39%) contaminated with a trace of hydrazine sulfate. Their identities were proved by their mixed melting points with authentic samples. The chloroform filtrate and its water extracts gave 56% of

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*The infrared spectrum of n-butyl ethylenesulfonate showed a peak at 10.25 μ due to the terminal methylene group. This peak is absent in the spectrum of n-butyl propene-1-sulfonate.

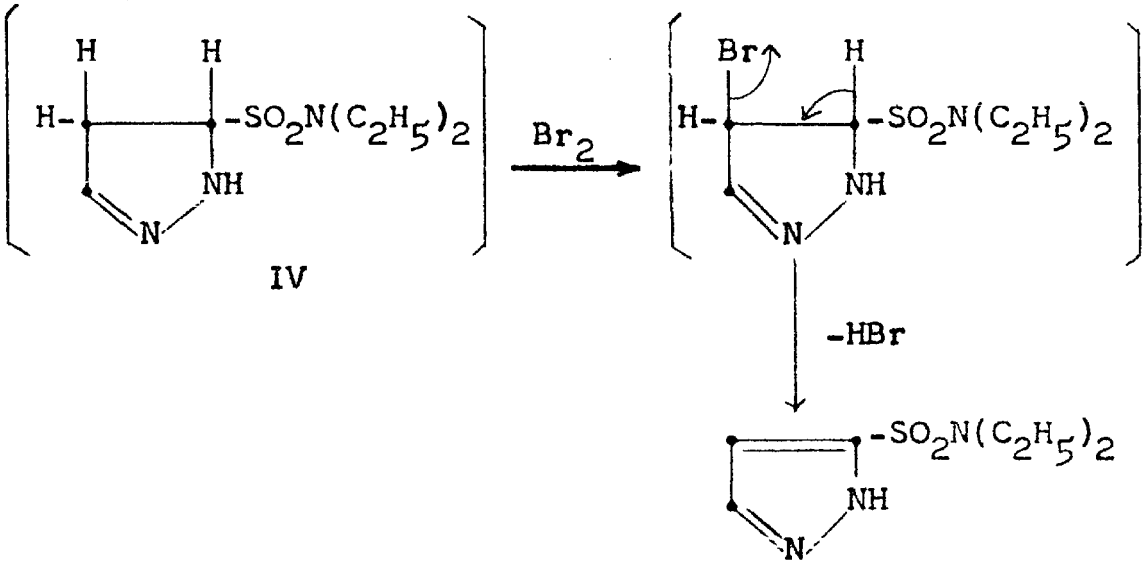
pyrazole-3-N,N-diethylsulfonamide and 20% of diethylamine hydrobromide respectively. Some sulfate was also isolated as barium sulfate from the aqueous extract:



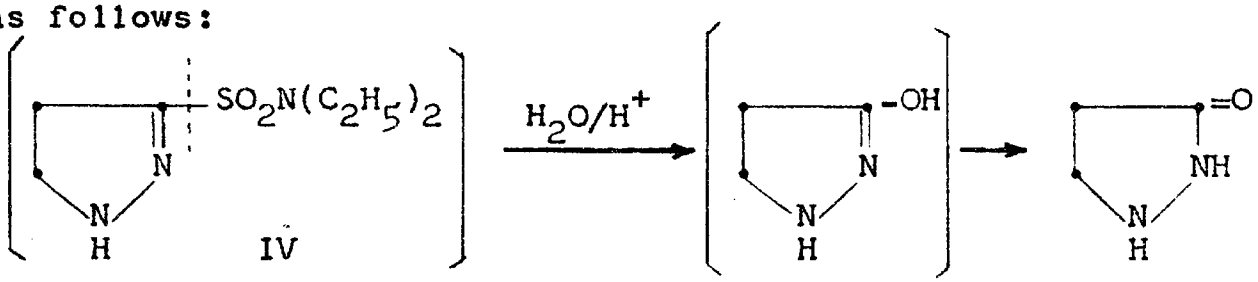
It appears that the unsaturated sulfonamide reacted with diazomethane normally to give IV, the carbon of the diazomethane attaching itself to the β-position*. When IV was treated with bromine, more than half of it was aromatized

*This was not proved unequivocally in this particular case; however, the above formulation is believed to be correct by analogy to the addition of diazomethane to n-butyl ethylenesulfonate, in which the sulfo position on the pyrazole ring was proven (p. 34) and by analogy to numerous examples of the addition of diazomethane to conjugated systems.

to the pyrazole as expected. The 4-position was probably brominated as discussed previously (see Historical, pages 11 and 12):



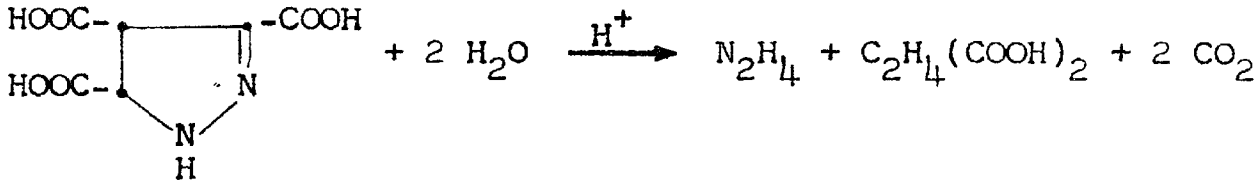
On the other hand, the isolation of 3-pyrazolidone hydrobromide indicates that there is a fairly pronounced tendency of IV to undergo transformation involving the 3-position as well, and the formation of the pyrazolidone may be explained as follows:



Although no attempt was made to support this formulation experimentally, the nature of this dissertation not being mechanistic, the isolation of diethylamine hydrobromide and barium sulfate in amounts almost equivalent to the pyrazolidone is in favor of it. It is well known that sulfonamides are very resistant to hydrolysis, heating with concentrated hydrochloric acid in a sealed tube at high temperature or prolonged

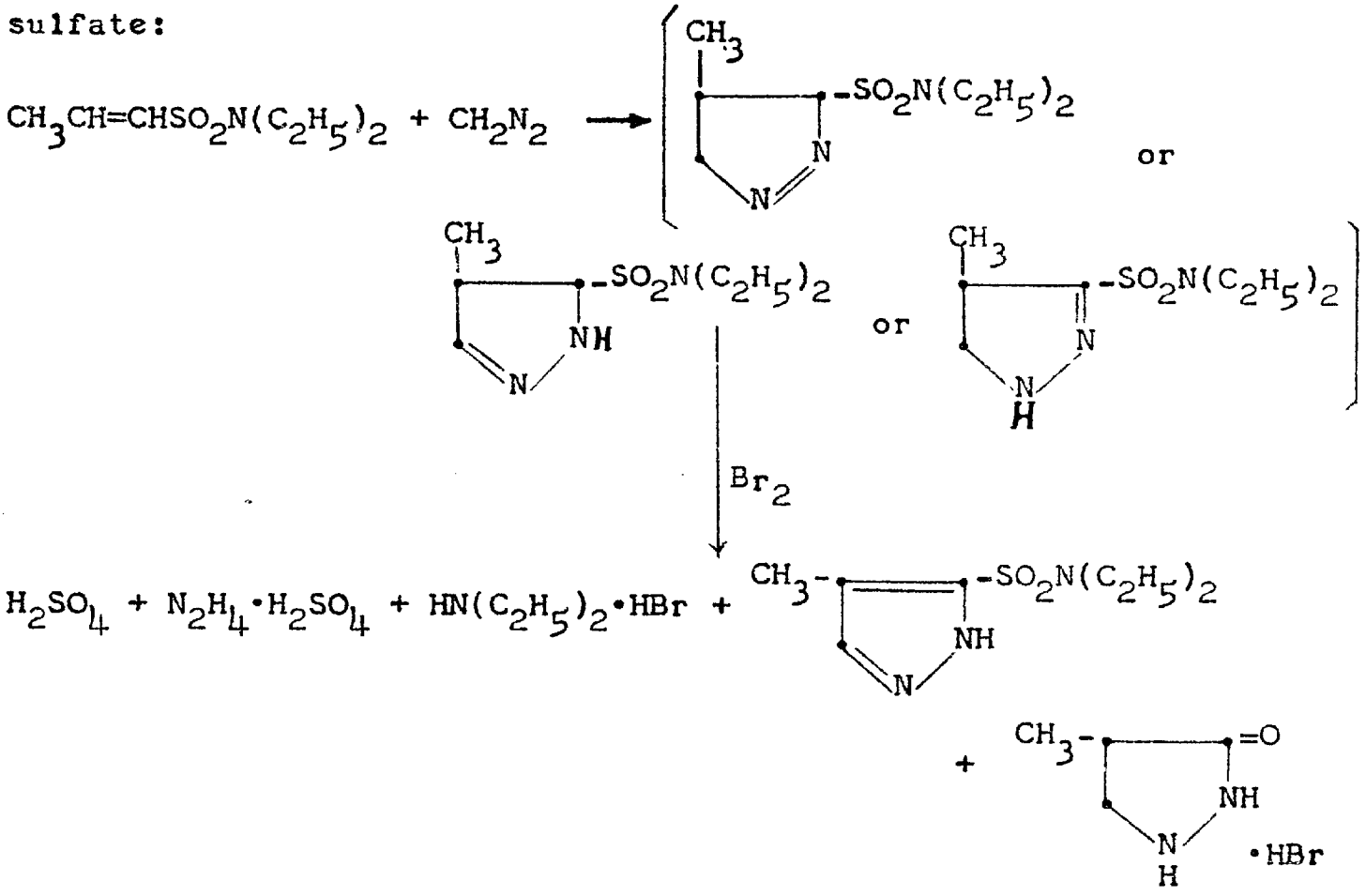
period of refluxing being required[76]. Yet, the mild conditions of bromination employed here brought about the hydrolysis of the sulfur-nitrogen bond. However, this is not so inconsistent if the above formulation is correct. One may reasonably assume that the formation of the pyrazolidone involves the cleavage of the carbon-sulfur bond first. Then the decomposition of the non-cyclic fragment into sulfur dioxide and diethylamine follows almost instantly; the former is oxidized by bromine to the sulfate and the latter forms a salt with the hydrogen bromide existing in the reaction mixture. The cleavage of the carbon-sulfur bond probably is facilitated by the nature of the heterocyclic ring.

The formation of hydrazine sulfate was unexpected at first. However, a survey of the literature revealed that as early as 1888, when Buchner first observed the reaction of diazoacetic ester with fumaric ester, he noted that the pyrazoline formed hydrazine and succinic acid when subjected to acid hydrolysis[1]:



Later, Franke also isolated a trace of hydrazine hydrochloride from 4,4-dimethyl-5-isopropylpyrazoline by heating the latter with hydrochloric acid[77]. Thus, the formation of hydrazine sulfate in our reaction is consistent with the known chemistry of the pyrazoline ring system.

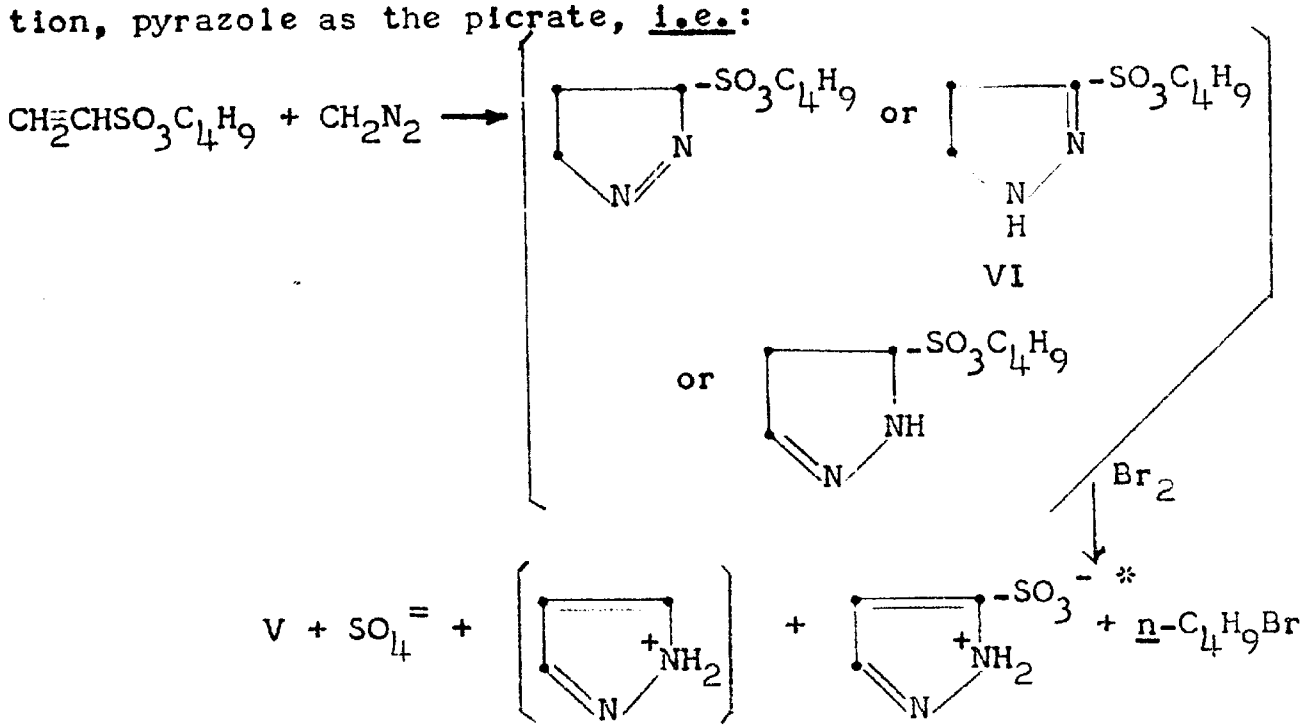
2. N,N-Diethylpropene-1-sulfonamide.--Diazomethane was found to add to an equimolar amount of N,N-diethylpropene-1-sulfonamide when an ethereal mixture of these compounds was allowed to stand at room temperature. The reaction was complete in four days, giving a crude adduct in 98% yield. Since the adduct was an oil which could not be purified, it was subjected to bromination in chloroform. There formed a trace of chloroform-insoluble hydrazine sulfate. The chloroform filtrate gave 59% of 4-methylpyrazole-3-N,N-diethylsulfonamide and from its water extract 18% of diethylamine hydrobromide and a trace of 4-methyl-3-pyrazolidone hydrobromide. Some sulfate was also isolated as barium sulfate:



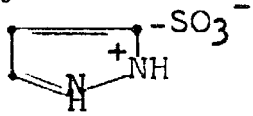
This reaction was analogous to the reaction of diazomethane and N,N-diethylethylenesulfonamide. The aromatization proceeded by bromination of the 4-position, followed by dehydrobromination to give 4-methylpyrazole-3-N,N-diethylsulfonamide. However, the reaction is different in two respects. The first is that the addition of diazomethane required four times longer because of the presence of the β-methyl. It is relevant to recall here that numerous examples of the inhibiting effect of a β-alkyl group on the addition of diazomethane to double bonds have been reported[17,23] (see Historical, page 7). The second is that the yield of 4-methyl-3-pyrazolidone hydrobromide is very low when compared with the yield of 3-pyrazolidone hydrobromide from the reaction of diazomethane and N,N-diethylethylenesulfonamide. It is not clear whether 4-methyl-3-pyrazolidone hydrobromide was actually formed in a much smaller amount or if a considerable amount of it escaped isolation because of its unfavorable physical properties such as its solubility in chloroform. As described previously, 3-pyrazolidone hydrobromide was isolated by virtue of its insolubility in chloroform, but 4-methyl-3-pyrazolidone hydrobromide had to be separated very tediously from the impure diethylamide hydrobromide (see Experimental, page 89). On the other hand, all attempts to isolate any different product parallel to the diethylamine hydrobromide and barium sulfate were not successful.

B. Diazomethane and α,β-Unsaturated Sulfonic Esters

1. n-Butyl ethylenesulfonate.--Diazomethane was found to react with an equimolar amount of n-butyl ethylenesulfonate at room temperature. The reaction was complete in three hours and a 99% yield of a crude adduct was obtained. Since it could not be purified by either recrystallization or distillation, it was characterized by bromine dehydrogenation. The crude adduct was dissolved in chloroform and the mixture brominated at room temperature. There separated a hygroscopic precipitate, which was found to be chiefly pyrazole-3-sulfonic acid (72%) and a trace of an unidentified high melting, methanol-insoluble substance (V). The chloroform filtrate, which had been extracted with water thoroughly, yielded n-butyl bromide. From the aqueous extract was isolated sulfuric acid as barium sulfate, and after basification, pyrazole as the picrate, i.e.:

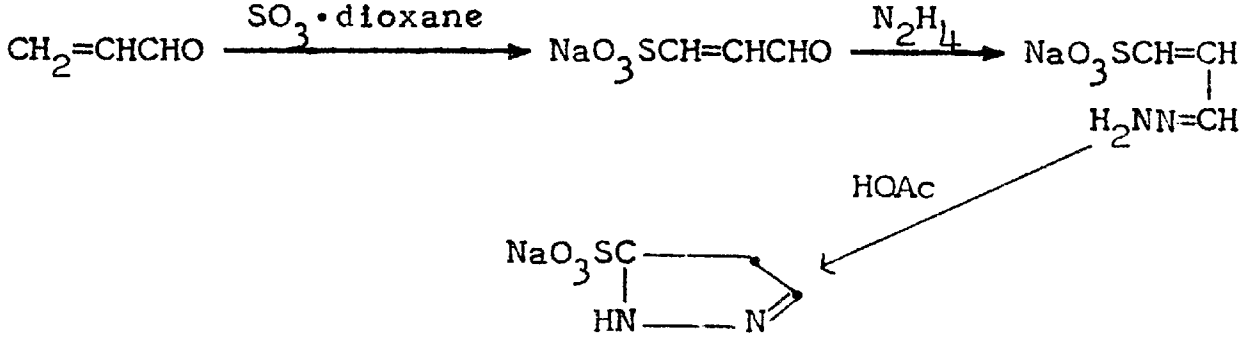


*It should be noted the location of the positive charge is assigned arbitrarily. The sulfonic acid could be represented just as well by



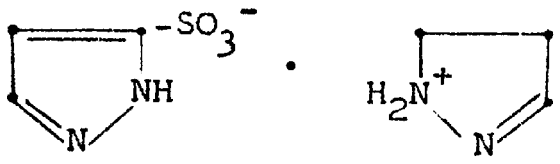
Apparently, the hydrogen bromide formed in the aromatization was sufficient to cause cleavage of the ester bond as evidenced by the isolation of the butyl bromide. The formation of pyrazole indicates that there is also a certain amount of cleavage at the carbon-sulfur bond.

However, since the position of the sulfo group in the pyrazole ring had been assigned simply by analogy to known examples of diazomethane addition with α,β-unsaturated ketones, etc., it was thought desirable to prove the structure of the pyrazolesulfonic acid derived from VI more explicitly. It has been shown that direct nuclear substitution in pyrazole occurs preferentially at the 4-position[38,41,42,78]. Thus, pyrazole-4-sulfonic acid* was obtained by sulfonating pyrazole according to the procedure of Morgan and Ackerman[41]. As expected, this 4-pyrazolesulfonic acid was found to be definitely different from the pyrazolesulfonic acid from the bromination of VI, which, hence, must be 3-pyrazolesulfonic acid. An attempt had been made earlier to synthesize 3-pyrazolesulfonic acid by sulfonating acrolein[79] and then cyclizing[80] its hydrazone by action of glacial acetic acid; however, the cyclization step was not successful:



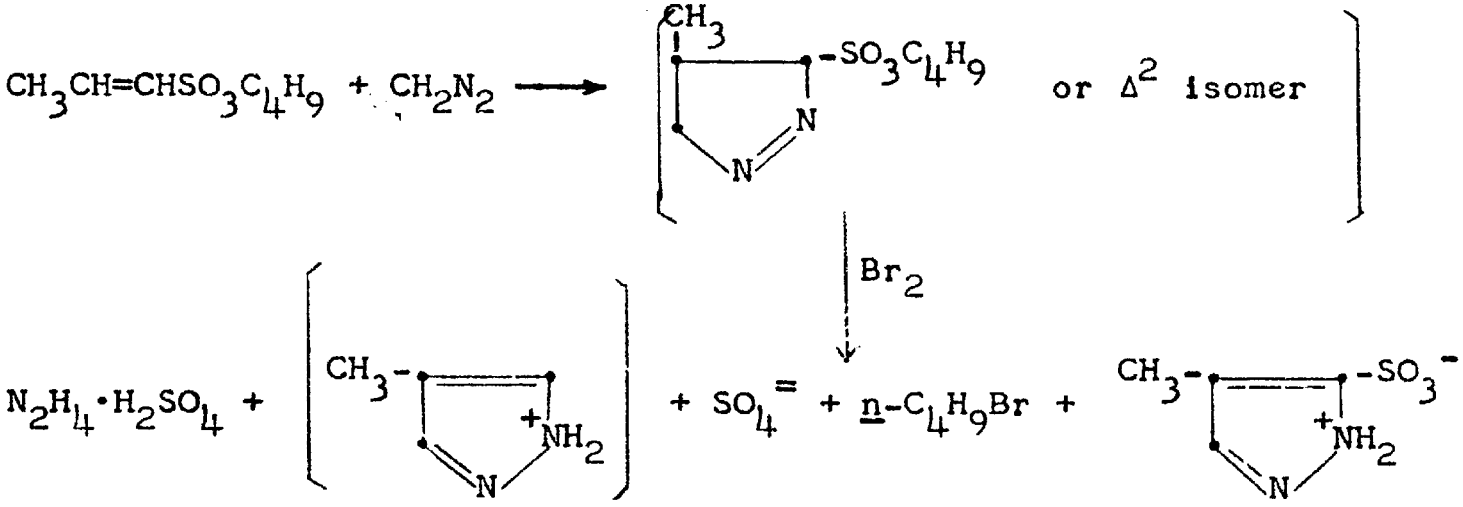
*Pyrazole-4-sulfonic acid is reported by Eppler, Z. Kr., 29, 233; however, no melting point was given. Our sample was found to decompose at 345°.

Unsuccessful attempts were made to identify V. From its analytical data, it appeared to possess the empirical formula $C_6H_{10}N_4O_3S$. One of the possible structural formulas could be:



However, no pyrazoline derivative or pyrazolesulfonic acid could be prepared from V by treatment with base or acid.

2. n-Butyl propene-1-sulfonate.--n-Butyl propene-1-sulfonate was found to consume an equimolar amount of diazomethane at room temperature. The reaction was complete in five hours and a quantitative yield of an oily adduct was obtained. Since it could not be purified by distillation or recrystallization, it was characterized by bromine dehydrogenation. When it was dissolved in chloroform and treated with an equivalent amount of bromine, there separated the expected chloroform-insoluble 4-methyl-3-pyrazolesulfonic acid in 52% yield. It was proved to be different from the known 3-methyl-4-pyrazolesulfonic[78] acid by comparing their melting points. The chloroform filtrate, which had been extracted with water thoroughly, yielded n-butyl bromide. From the aqueous extracts was isolated sulfuric acid as barium sulfate, and after basification, 4-methyl-3-pyrazole as the picrate:



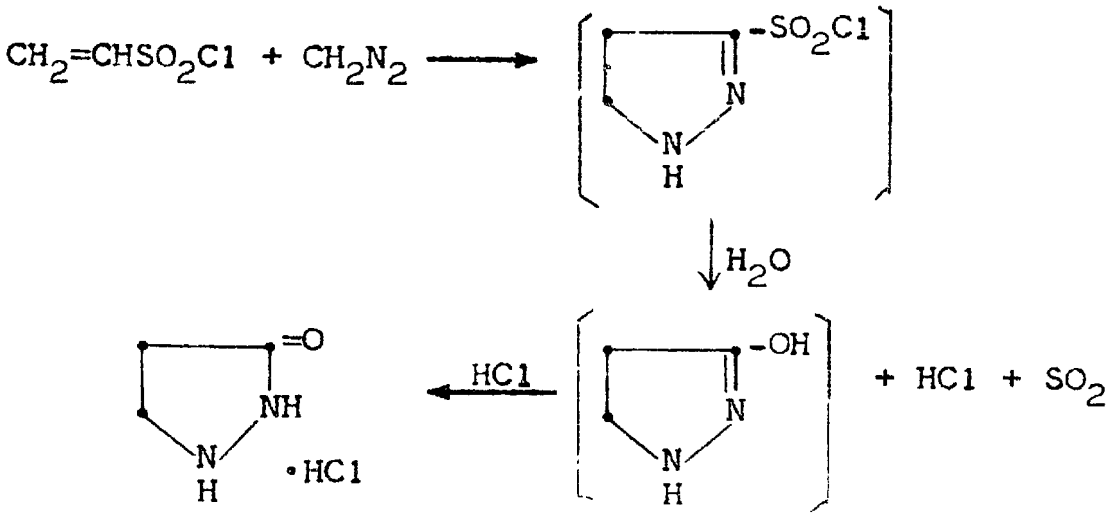
This reaction is closely analogous to the reaction of diazomethane and n-butyl ethylenesulfonate. The time required to complete the reaction was lengthened by the presence of the β-methyl group but the inhibiting effect here is not as pronounced as in the case of the unsaturated sulfonamides described in the previous section (see page 32).

C. Diazomethane and α,β-Unsaturated Sulfonyl Chlorides

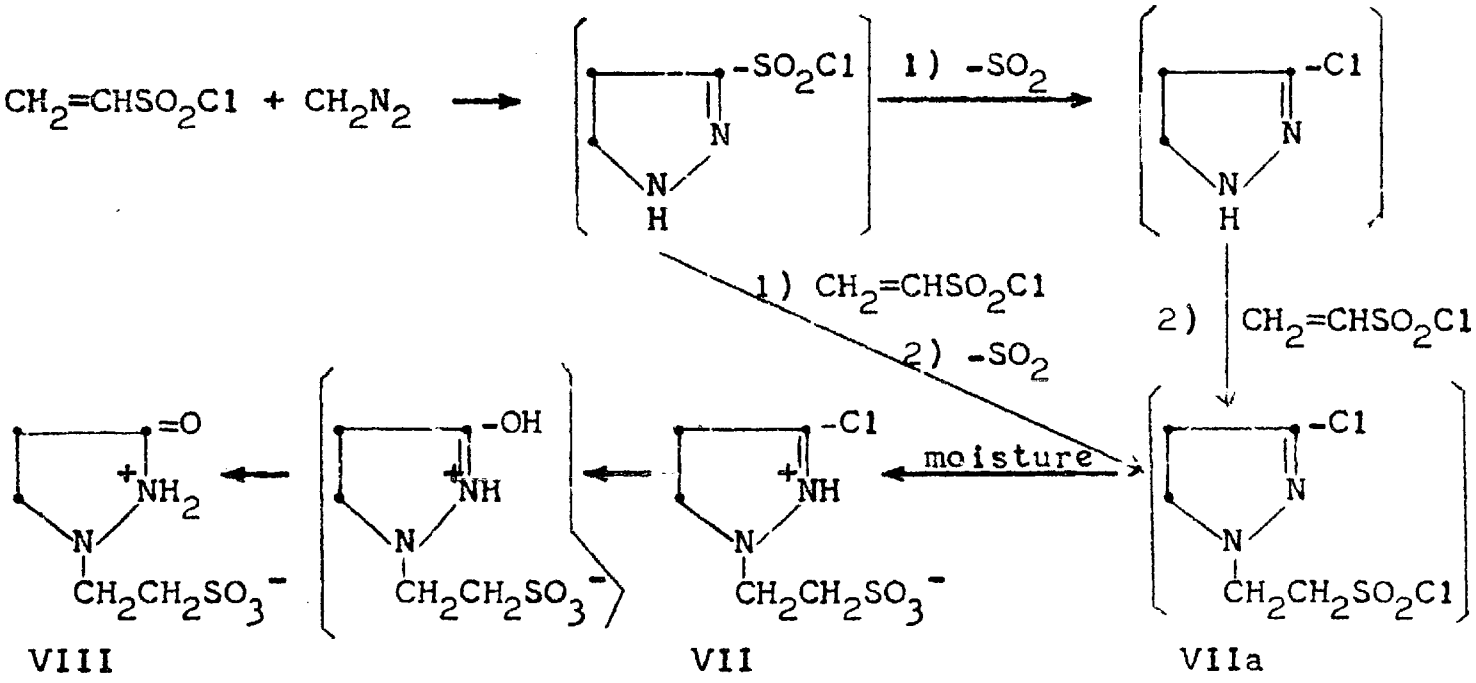
Arndt[81] has reported that sulfonyl chlorides do not react with diazomethane but he observed that at room temperature they catalyze the decomposition of diazomethane to a considerable extent, giving polymethylene and gaseous nitrogen. In this work, ethylenesulfonyl chloride, propene-1-sulfonyl chloride and propene-2-sulfonyl chloride were selected to react with diazomethane. It was expected that the reaction would be restricted to the double bond only.

1. Ethylenesulfonyl chloride.--Ethylenesulfonyl chloride was found to react with diazomethane instantaneously at room temperature, consuming approximately two moles of diazomethane per mole of double bond. There separated

immediately an ether-insoluble solid (50% by weight of starting materials) which became oily on contact with air and could not be purified. It gave a "neutral equivalent" of 690 and appeared to be polymeric. However, after several months standing in a loosely stoppered flask, a part of the oily adduct (20% by weight) turned into crystalline 3-pyrazolidone hydrochloride. It appears that at least a part of the ethylenesulfonyl chloride had reacted normally to yield the expected 3-pyrazolinesulfonyl chloride, which, on standing, was then converted to 3-pyrazolidone by the action of atmospheric moisture, as shown in the following scheme:



This unexpected result led us to further studies of this reaction by limiting the amount of diazomethane to one mole. However, in the absence of a large excess of diazomethane, an adduct (VII) corresponding to two moles of ethylene-sulfonyl chloride and one mole of diazomethane was formed as the major product. When VII was treated with water, compound VIII was obtained:

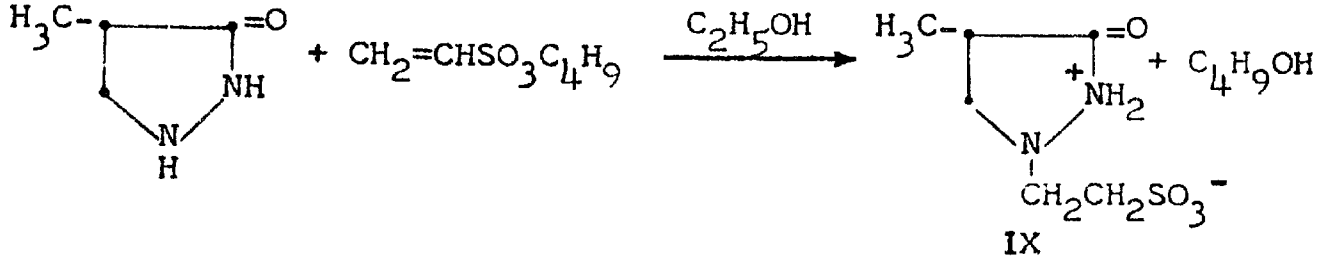


However, it must be noted that the above sequence is not necessarily the only possible representation. Step (1) and (2) might occur simultaneously. Also, some of VIII could be formed directly from VIIa by the action of moisture.

The structure of VII and VIII were assigned on the basis of analytical data and physical properties; both are very high melting, soluble in water and titratable against base to give the correct neutral equivalent. While VII is soluble in methanol, VIII is not. The aqueous solution of VII does not give a cold chloride test. If the above structures do represent the reaction (with the position of the side chain uncertain), a similar adduct should result from the addition reaction of a pyrazolidone and an ethylenesulfonic acid derivative in the Michael fashion. This was found indeed to be the case, for when 4-methyl-3-pyrazolidone*

*4-Methyl-3-pyrazolidone was used in place of 3-pyrazolidone because of its availability at that time.

reacted with n-butyl ethylenesulfonate a similar adduct, IX, with the expected physical properties and titratability was obtained. Its infrared spectrum* resembles that of VIII:



IX

2. Propene-1-sulfonyl chloride.--Propene-1-sulfonyl chloride was found to consume more than one mole of diazomethane per mole of double bond very rapidly at room temperature. There formed an ether-insoluble solid adduct (50% by weight of starting materials), which could not be purified and appeared to be polymeric (N.E. 590, analysis: $C_{11}H_{20}ClN_5O_2S$). Attempts to prepare derivatives from it were not successful (see Experimental, page 100). Attention was directed to the oil obtained after removal of the solvent from the filtrate, but no pure product was isolated.

3. Propene-2-sulfonyl chloride.--Propene-2-sulfonyl chloride was found to react with diazomethane very rapidly at room temperature. There formed a small amount of deposit which could not be purified. The reaction solution gave 73% yield of an orange oil (based on the weight of the starting materials). However, attempts to identify this oil were not successful.

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*Infrared spectral data are discussed more fully in Section IV, page 54.

D. Conclusions

In the addition of diazomethane to the α,β-unsaturated sulfonyl chlorides and their corresponding diethylamides and n-butyl esters, the double bond in the chlorides was most active, the esters next and the amides least as indicated by the time required to complete the reaction. The inhibiting effect of a β-methyl group is present in all these compounds but it is most pronounced in the amides, then the esters and almost negligible in the chlorides. The influence of the different sulfonyl derivatives on the relative reactivities of the conjugated double bond parallels that observed in the Diels-Alder reactions of these compounds[82].

The α,β-unsaturated sulfonamides react normally to give 3-pyrazolinesulfonamides. During the bromination of the impure pyrazoline, more than 50% of the pyrazoline aromatizes normally to the 3-pyrazolesulfonamide, but there is also a pronounced, concurrent cleavage of the sulfur-carbon bond by the resulting hydrogen bromide. The isolation of 3-pyrazolidone hydrobromide instead of a pyrazole unsubstituted at the 3-position indicates that the cleavage of the sulfur-carbon bond occurs before the pyrazoline aromatizes. Furthermore, because of the normal resistance of the sulfur-nitrogen bond in a sulfonamide to hydrolysis[76], it is thought that cleavage at the sulfur-carbon bond also precedes that of the sulfur-nitrogen bond in the amide. This would result in the formation of the 3-pyrazolidone and an unstable [$-SO_2N(C_2H_5)_2$] group, which decomposes into sulfur dioxide and diethylamine

as soon as it is formed. The carbon-sulfur bond here is probably much more susceptible to hydrolysis than a carbon-sulfur bond in an aliphatic sulfonamide due to the nature of the pyrazoline ring to which the carbon atom belongs.

The α,β-unsaturated sulfonate esters also react normally with diazomethane to give the expected 3-pyrazoline-sulfonate esters. During aromatization of the pyrazoline by bromination, a concurrent cleavage of the ester bond by hydrogen bromide was observed. This resulted in the isolation of the 3-pyrazolesulfonic acid zwitter ions as the major products without even a trace of the expected 3-pyrazole-sulfonate ester. In contrast to the cleavage of the pyrazolinesulfonamides just discussed, cleavage of the ester bond by hydrogen bromide undoubtedly occurs more readily. However, the cleavage may occur either before or after the aromatization. If the former is the case, then there would result a 3-pyrazolinesulfonic acid first, which then aromatizes to the 3-pyrazolesulfonic acid. If the latter is the case, then the 3-pyrazolesulfonate ester was formed first, and then followed by conversion to the 3-pyrazolesulfonic acid. There is no experimental evidence for choosing between the two but the second one seems to be preferable on the basis of the apparently greater difference of the energy contents between the pyrazolesulfonate ester and the pyrazole sulfonic acid zwitter ion. In any case, the greater ease of cleavage of the ester link and the unusual stability of the pyrazole-sulfonic acid zwitter seem to have decreased the cleavage of

the sulfur-carbon bond which is so pronounced in the case of the amides. Consequently, only a trace of pyrazole and 4-methylpyrazole were obtained. It is interesting to note that the sulfur-carbon bond cleavage here did not result in 3-pyrazolidones. Therefore, the 3-unsubstituted pyrazoles must have been formed by a "protonic" hydrolysis.

Among the α,β-unsaturated sulfonyl chlorides which were reacted with diazomethane, propene-1-sulfonyl chloride and propene-2-sulfonyl chloride did not give clear results. They do react with diazomethane but the adducts could not be purified nor identified by means of suitable derivatives. Analytical data on the impure adducts indicate that they were probably polymeric and there was also loss of sulfur. Ethylenesulfonyl chloride distinguishes itself from its homologues as well as the corresponding amides and esters by reacting with diazomethane to give unexpected products. With excess diazomethane 3-pyrazolidone was obtained, while with equimolar amounts 2-(2-proto-3-keto-1-pyrazolidinyl)-ethanesulfonate (VIII) was obtained*. It appears that probably a normal but unstable 3-pyrazolinesulfonyl chloride was formed, but due to the lability of the sulfonyl chloride group, it spontaneously loses the sulfur group to give 3-pyrazolidone. Furthermore, due to the unusual reactivity of the double bond in the ethylenesulfonyl chloride molecule, it is also capable of forming addition products with the

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*For a discussion of the nomenclature, cf. F. G. Bordwell, M. L. Peterson and C. S. Rondestvedt, Jr., J. Am. Chem. Soc., 76, 3946 (1954), footnote (7).

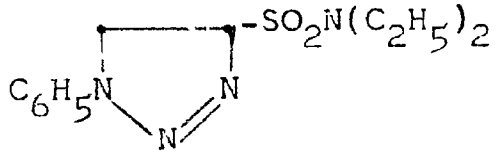
3-pyrazolidone or the 3-chlorosulfonylpyrazoline in the Michael fashion to give 2-(2-proto-3-keto-1-pyrazolidinyl)-ethanesulfonate (VIII). The isolation of 3-pyrazolidone hydrochloride parallels the isolation of 3-pyrazolidone hydrobromide from the reaction of N,N-diethylethylenesulfonamide and diazomethane.

III. Addition of Phenyl Azide

A. Phenyl Azide and α,β-Unsaturated Sulfonamides

1. N,N-Diethylethylehesulfonamide.--When phenyl azide was refluxed with N,N-diethylethylenesulfonamide in a benzene solution for sixteen hours, there formed the expected N,N-diethyl-1-phenyl-1,2,3-triazoline-4-sulfonamide in 30% yield. By analogy to the known examples of the addition reactions of phenyl azide to α,β-unsaturated compounds, it is believed that the terminal nitrogen of phenyl azide adds to the α-position:

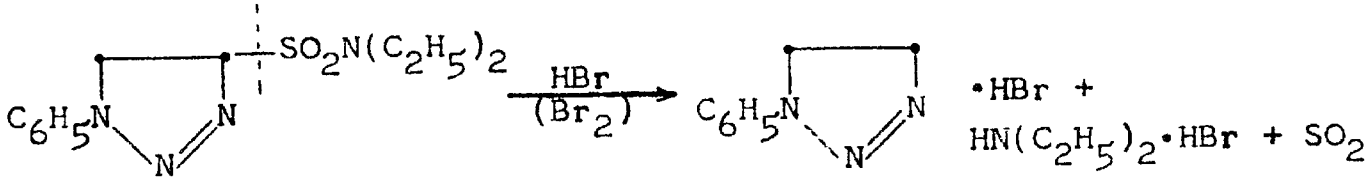
$$CH_2{=}CHSO_2N(C_2H_5)_2 + C_6H_5N_3 \longrightarrow$$



X

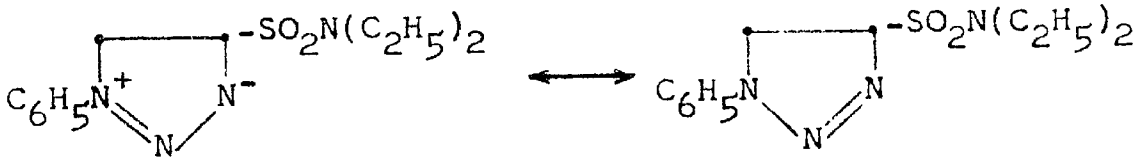
In order to establish more certainly that X is a triazoline, attempts were made to aromatize X. p-Quinone and N-bromosuccinimide were both found ineffective. Therefore, bromine dehydrogenation was employed. When a chloroform solution of X was treated with bromine, only a trace of chloroform-insoluble product was obtained (12%); the analytical data

suggested that it was 1-phenyl-1,2,3-triazoline hydrobromide. It was titratable against base, very high melting, soluble in water and different from an authentic sample of 1-phenyl-1,2,3-triazole hydrobromide. The chloroform filtrate, after it was thoroughly extracted with water, gave a considerable amount of tarry residue from which no isolable product was obtained. From the water extract was obtained 60% of diethylamine hydrobromide and a trace of sulfuric acid as barium sulfate:



X XI

A comparison of the ultraviolet spectra of X and XI with those of some known 1-phenyl-1,2,3-triazoles and triazene derivatives, as summarized in Table 1, seemed to indicate strongly that X and XI are truly triazolines and not triazoles. It is observed that 1-phenyl-1,2,3-triazoles all show one single maximum ranging from 2525 Å to 2430 Å and 4-phenyl-1,2,3-triazole at 2470 Å[83]. This indicates that the interaction of the phenyl group and aromatic triazole ring is responsible for this absorption. In compound X, however, due to the non-aromatic nature of the triazoline ring, and assuming one of its excited states to be Xa,



Xa X

there could be several types of compounds whose ultraviolet spectra may resemble the spectrum of X. In structure Xa, it resembles an azo compound as well as a 1-aryl-3-alkyl triazene and in structure X it may resemble an arylamine and an azo compound. This seems to be indeed the case, for compound X has a maximum at 3105 Å while the spectra of methylaminodiazobenzene and azobenzene have maxima at 3040 Å and 3130 Å respectively. It was also observed that X showed two other maxima at 2890 Å (shoulder) and 2253 Å, and aniline has maxima at 2875 Å and 2340 Å. In the case of XI, probably due to its salt state, the aniline structure seems to be predominating and maxima at 2848 Å and 2343 Å were observed (see Table 1, page 46, and Figure 15, page 71).

It could be seen that the identity of XI could be unequivocally established, if the free base 1-phenyl-1,2,3-triazoline could be synthesized independently. However, a search in the literature indicated that it is still an unknown compound inspite of its simplicity. Thus, the problem of its synthesis was not undertaken. It probably could be prepared from phenyl azide and ethylene under pressure.

2. N,N-Diethylpropene-1-sulfonamide.--When N,N-diethylpropene-1-sulfonamide was refluxed with phenyl azide in tetrahydrofuran for forty-eight hours, the mixture turned dark as a result of decomposition of the reactants. After solvent removal, about 50% of phenyl azide was recovered. No isolable product was obtained from the tarry residue, which appeared to be polymeric.

TABLE 1

ULTRAVIOLET ABSORPTION CHARACTERISTICS OF ANILINE, AZOBENZENE AND SOME DERIVATIVES OF 1,2,3-TRIAZOLES AND TRIAZENES

Compounds	Maximum wave length Å	$\varepsilon_{max} \times 10^{-3}$
1-Phenyl-1,2,3-triazole	2430	10.31*
1-Phenyl-4-bromo-1,2,3-triazole	2530	9.2
1-Phenyl-1,2,3-triazole-4-carboxylic acid	2472	11.9
4-Phenyl-1,2,3-triazole[83]	2470	15.8**
Aniline[84]	2875 2340	1.82** 9.12**
Azobenzene	3130	20.0
$C_6H_5N{=}N{-}N$ [85]	2895	16.0
$C_6H_5N{=}N{-}NHCH_3$[86]	3040 2761	7.58** 12.88
C_6H_5N (triazole) $-SO_2N(C_2H_5)_2$ (X)	3105 2890 (shoulder) 2253	8.45 6.28 10.80
C_6H_5N (triazole) ·HBr (XI)	2848 2340	0.50 5.08
C_6H_5N (triazole) $^{+}N{-}CH_2CH_2SO_3^{-}$	2525	8.77
$C_6H_5N^{+}$ (triazole) NCH_3 I^{-}	2516	8.41

*Ramart-Lucas and Hoch[86] report that 1-phenyl-1,2,3-triazole has a maximum at 2430 Å, $\varepsilon = 12.02 \times 10^3$.

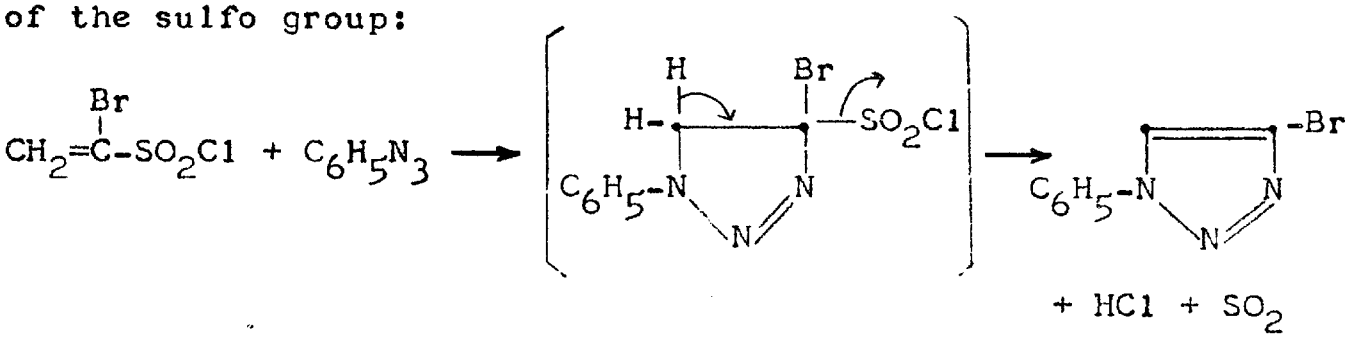
**These values were calculated or converted from the original data.

B. Phenyl Azide and α,β-Unsaturated Sulfonic Esters

When phenyl azide was refluxed with n-butyl ethylenesulfonate or n-butyl propene-1-sulfonate in a benzene solution for four hours, the mixture rapidly turned dark as a result of decomposition of the reactants. No identifiable product was isolated from either experiment, but about 50% of the phenyl azide was recovered.

C. Phenyl Azide and α,β-Unsaturated Sulfonyl Chlorides

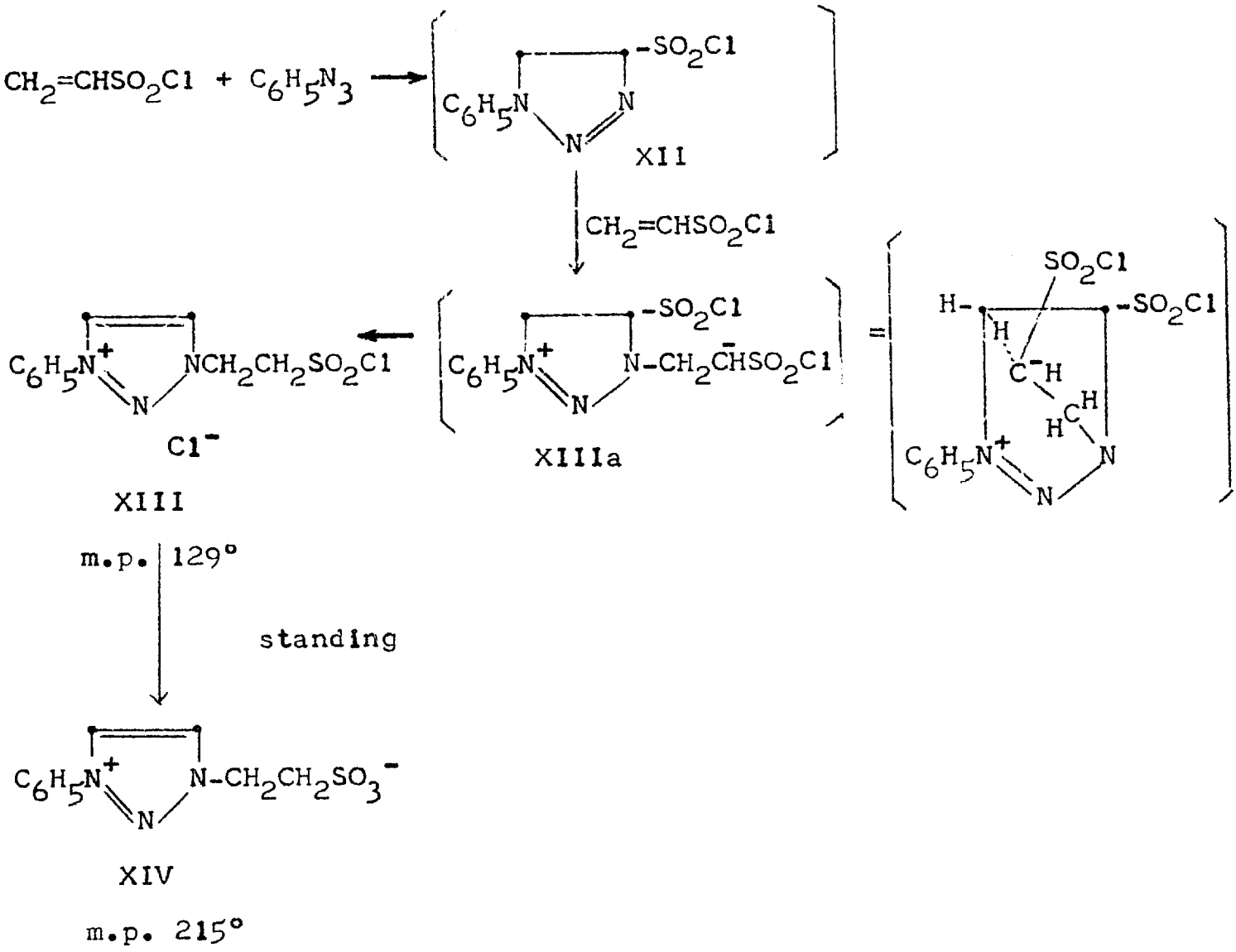
1. α-Bromoethylenesulfonyl Chloride.--α-Bromoethylenesulfonyl chloride reacted with an equimolar amount of phenyl azide to give 1-phenyl-4-bromo-1,2,3-triazole in 45% yield when the mixture was refluxed in chloroform for one hour. It appears that the primary adduct was the expected but unstable triazoline which immediately aromatized with expulsion of the sulfo group:



This formulation is in agreement with the previously discussed mechanism proposed by Parham for the acid-catalyzed aromatization of 3-bromo-3-nitro-4-phenylpyrazoline to 3-bromo-4-phenylpyrazole[38] (see Historical, page 11). He suggested that in an acid medium, the aromatization may take place with an electrophilic attack by a proton on the more susceptible nitro group, resulting in the simultaneous expulsion of the

nitro group and a proton from the 4-position. The greater susceptibility of the nitro group relative to bromine was suggested by the greater solubility of nitroalkanes relative to bromoalkanes in sulfuric acid. Thus, in the aromatization of the above 1-phenyl-4-bromo-1,2,3-triazoline-4-sulfonyl chloride, one may similarly assume that the sulfonyl chloride group is more susceptible to proton attack than the bromine since alkanesulfonyl chlorides were found to be more soluble in sulfuric acid than bromoalkanes.

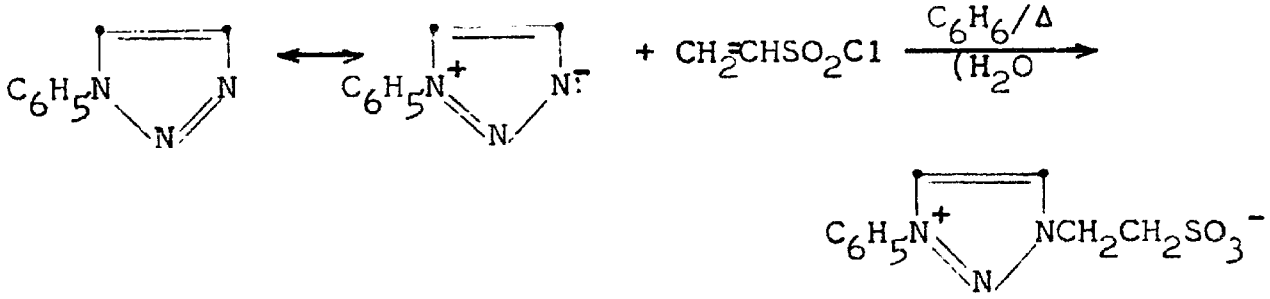
2. Ethylenesulfonyl chloride.--When a mixture of two moles of ethylenesulfonyl chloride and one mole of phenyl azide in benzene was allowed to stand at room temperature, a quantitative yield of a "two to one" solid adduct separated from the solution. The reaction was mildly exothermic and spontaneous; it was complete in five hours. The same adduct was obtained regardless whether one began with equimolar amounts of the chloride and phenyl azide, or one mole of the chloride with two moles of phenyl azide, or by adding the chloride slowly to the azide to keep the latter in excess at all times. The reaction may be represented as follows:



The structures of XIII and XIV were assigned by analysis and their physical properties. Judging from the melting point of the crude adduct, the primary adduct seems to be XIII. However, it is very unstable and changes into XIV during recrystallization, or simply on standing. XIII is titratable but its neutral equivalent varies according to its age. Its aqueous solution gives a chloride test with cold silver nitrate. XIV is high melting, soluble in water, not titratable (hence, quaternary nitrogen) and contains no

chlorine.

It appeared to us then if the structures of XIII and XIV were correct, we should be able to obtain the same product from 1-phenyl-1,2,3-triazole and ethylenesulfonyl chloride. Such was indeed the case; although the reactants had to be refluxed at 80° for six hours to give a quantitative yield of XIV:



However, this still left the position of the side chain unproven. Therefore, 1-phenyl-3-methyl-1,2,3-triazolium iodide* and the corresponding methanesulfonate were prepared to provide spectral comparisons. As expected, the infrared spectra of XIV and the model compounds were very similar (see Figures 9, 10 and 11, pages 65-67). The ultraviolet spectra of XIV and 1-phenyl-3-methyl-1,2,3-triazolium iodide show maxima at 2525 Å and 2516 Å respectively (Table 1, page 46). This spectral evidence indicates strongly that XIV is a 1-phenyl-3-alkyl-1,2,3-triazolium salt (see Fig. 16, page 72).

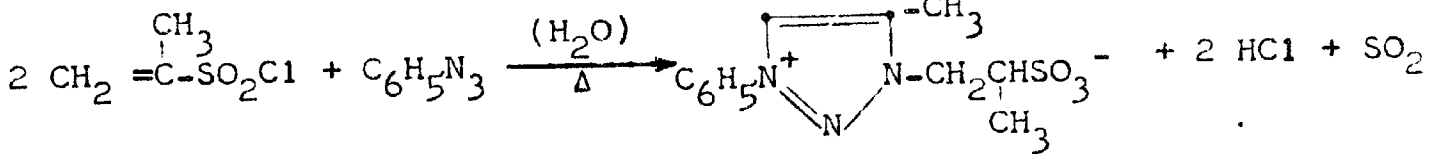
It could be thought that phenyl azide probably added to ethylenesulfonyl chloride in the normal fashion to give

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*This compound was prepared according to the method of Wiley and Moffat[63] who proved that 1-substituted 1,2,3-triazoles are alkylated at the 3-position.

XII. XII then added to the unusually active double bond of another molecule of ethylenesulfonyl chloride to give XIIIa, which instantly neutralizes its negative charge by a proton transfer from the 5-position resulting in a simultaneous aromatization by expulsion of the 4-chlorosulfonyl group to give XIII. Such a proton transfer is sterically possible. Another possible route involves the aromatization of XII to 1-phenyl-1,2,3-triazole which then adds to the second mole of ethylenesulfonyl chloride. This was abandoned on the basis of experimental evidence that 1-phenyl-1,2,3-triazole adds to ethylenesulfonyl chloride after six hours heating at 80° in contrast to the extraordinary ease of the other addition reaction. Furthermore, no 1-phenyl-1,2,3-triazole, a remarkably stable compound, was isolated from the reaction mixtures containing excess azide.

3. Propene-2-sulfonyl chloride.--Phenyl azide added to propene-2-sulfonyl chloride in a manner analogous to the addition of phenyl azide to ethylenesulfonyl chloride. However, the addition reaction had to be initiated by warming and only 45% of the adduct was obtained. It was assigned the structure 1-(1-proto-1-phenyl-4-methyl-1,2,3-triazol-3-yl)-propane-2-sulfonate:



Its infrared spectrum closely resembles that of 2-(1-proto-1,2,3-triazol-3-yl)-ethanesulfonate (Figures 11 and 12, pages

67 and 68). It is very high melting and soluble in water.

4. Propene-1-sulfonyl chloride.--When a solution of equimolar amounts of propene-1-sulfonyl chloride and phenyl azide in benzene was refluxed gently for three hours, it turned dark as a result of the decomposition of the reactants and about 50% of phenyl azide was recovered after solvent removal. The dark viscous residue did not yield an isolable product and appeared to be polymeric.

D. Conclusions

Among the α,β-unsaturated sulfonic acid derivatives whose reaction with phenyl azide were investigated, only N,N-diethylethylenesulfonamide, α-bromoethylenesulfonyl chloride, ethylenesulfonyl chloride and propene-2-sulfonyl chloride were found to give addition products. It should be noted that none of these compounds has a methyl group on the β-position. As expected, phenyl azide is less reactive than diazomethane in addition to α,β-unsaturated sulfonic acid derivatives. Consequently, the inhibiting effect of the β-methyl group is much more pronounced here as compared with the corresponding diazomethane addition and no adducts were obtained from the unsaturated sulfonyl derivatives containing a β-methyl group.

N,N-Diethylethylenesulfonamide reacted with phenyl azide to give the expected triazoline. However, the aromatization of the triazoline to the corresponding triazole was not successful, although it has been reported that certain

fused ring triazolines can be aromatized by the action of quinone[56,57]. It appears that the aromatization of a triazoline is very dependent on its stability which is in turn dependent on the nature of the substituents on the ring. Spontaneous aromatization was observed with the triazoline obtained from α-bromoethylenesulfonyl chloride and phenyl azide to yield 1-phenyl-4-bromo-1,2,3-triazole.

The reaction of ethylenesulfonyl chloride and propene-2-sulfonyl chloride is reminiscent of that of ethylenesulfonyl chloride and diazomethane. An adduct corresponding to two moles of the sulfonyl chloride and one mole of phenyl azide was obtained. As discussed earlier, the reaction probably involves the addition of the normally formed 1-phenyl-1,2,3-triazoline-4-sulfonyl chloride to a second molecule of ethylenesulfonyl chloride in the Michael fashion. However, this reaction, as well as the addition of 1-phenyl-1,2,3-triazole to ethylenesulfonyl chloride in an independent experiment, is extraordinary in that the addition occurs without the presence of an imino hydrogen. The electrons in the triazoline ring (XII) probably first pass to the triazolinium state as represented by XIIIa in order to have the 3-nitrogen capable of addition to the double bond. The possible steric condition for the proton transfer as represented in XIIIa seems to play an important role in explaining the unusual ease of this reaction. It appears that this addition is exclusive to the double bond of β-unsubstituted ethylenic sulfonyl chlorides, for attempts to extend the

addition of 1-phenyl-1,2,3-triazole to acrylonitrile and acrylic acid resulted in 95% recovery of starting materials. It should be noted that 1,2,3-triazoles with an unsubstituted imino hydrogen have been observed to add normally to a number of α,β-unsaturated sompounds in the presence of a basic catalyst[66].

IV. Infrared Spectra Comparisons

The infrared spectra of the compounds obtained in this investigation, expecially if they were previously unknown, were compared with closely related model compounds whenever possible. It is beyond the scope of this work to analyze each spectrum in detail and only brief comments will be made on the following key compounds:

Pyrazole-3-sulfonamides.--The infrared spectra of pyrazole-3-N,N-diethylsulfonamide and 4-methyl-3-N,N-diethylsulfonamide were compared with those of authentic pyrazole and methyl pyrazole-4-carboxylate. Mirone and Vampiri[87] reported that the spectrum of 3,5-dimethylpyrazole showed a strong peak at 6.28 μ due to the carbon-nitrogen double bond and weak peaks at 6.03 μ and 6.44 μ due to the carbon-carbon double bond. The spectrum also had a peak at 6.74 μ which they did not attribute to any structural unit. We observed that pyrazole itself showed a weak peak at 6.25 μ and 4-methylpyrazole-3-N,N-diethylsulfonamide showed a weak peak at 6.40 μ but all four had peaks in the 6.8 μ and 10.70 μ regions. It is believed that these "common" peaks probably

resulted from the vibrations of the "aromatic" pyrazole ring. The peaks due to the sulfonyl group in sulfonamides are at 7.50 μ and 8.70 μ (Figure 1, page 57)[88].

Pyrazole-3-sulfonic acids.--The infrared spectra of the pyrazole-3-sulfonic acids all have peaks in the 6.34 μ to 6.45 μ region owing to the vibrations of the "aromatic" pyrazole ring. It should be noted that the peaks have shifted toward the shorter wavelength when compared to those of the pyrazole-3-sulfonamides. They also have common peaks at 9.58-9.70 μ and 8.43 to 8.45 μ due to the sulfonate ion (see Figure 2, page 58).

Pyrazolidone derivatives.--The infrared spectra of 3-pyrazolidone hydrobromide and hydrochloride and 4-methyl-3-pyrazolidone hydrobromide obtained from the reactions are identical with those of the independently synthesized authentic samples. They all show the strong carbonyl peak characteristic of a cyclic amide at 5.8 μ[89]. The spectra are very similar to one another (Figures 4, 5, and 6, pages 60, 61 and 62).

The spectra of 2-(2-proto-3-keto-1-pyrazolidinyl)-ethanesulfonate (VIII) and 2-(2-proto-4-methyl-3-keto-1-pyrazolidinyl)-ethanesulfonate (IX) also show the strong carbonyl peak characteristic of a cyclic amide at 5.80 μ and 5.74 μ respectively. As expected, they also have the sharp peaks of the sulfonate group in the 8.5 μ and 9.7 μ region. Since these spectra were taken in Nujol, the weak

N-H peak which in the solid state normally occurs in the 2.9 μ - 3.1 μ region is masked by the Nujol peak.(Figures 7 and 8, pages 63 and 64)

1-Phenyl-1,2,3-triazoles.--The infrared spectrum of 4-bromo-1,2,3-triazole was compared with that of 1-phenyl-1,2,3-triazole. They both show strong peaks at 9.6 μ and 10.1 μ. Benson[83] has reported that 4-alkyl-1,2,3-triazoles have common peaks in the 8.8-9.2 μ and 9.8-10.3 μ region. (See spectra in Figure 3, page 59.)

1-Phenyl-3-alkyl-1,2,3-triazolium salts.--The infrared spectra of 1-phenyl-3-methyl-1,2,3-triazolium iodide, 1-phenyl-3-methyl-1,2,3-triazolium methanesulfonate, 2-(1-proto-1-phenyl-1,2,3-triazol-3-yl)-ethanesulfonate and (1-proto-1-phenyl-4-methyl-1,2,3-triazol-3-yl)-propane-2-sulfonate were very similar to one another. They all have a very strong peak at the 13.2 μ region, probably resulting from the vibration of the 1-phenyl-3-alkyl-1,2,3-triazolium skeleton. There is also a weak peak at the 6.30 μ region common to all. The sulfonate salts all show strong peaks at 8.25 μ and 9.64 μ due to the sulfonate group. (See Figures 9, 10, 11 and 12, pages 65-58.)

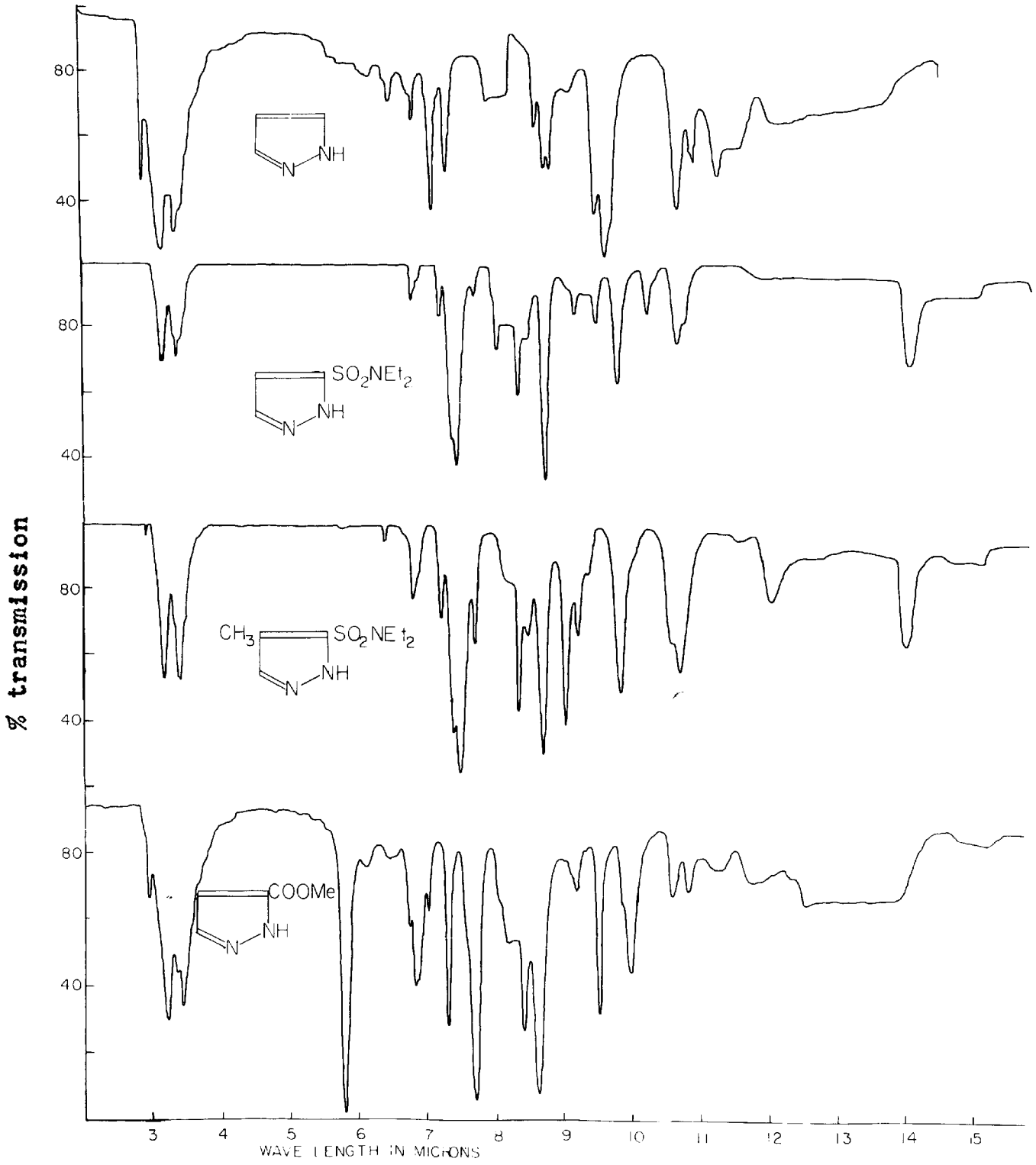


FIGURE 1

INFRARED SPECTRA OF PYRAZOLE, PYRAZOLE-3-N,N-DIETHYLSULFONAMIDE, 4-METHYLPYRAZOLE-3-N,N-DIETHYLSULFONAMIDE AND METHYL PYRAZOLE-4-CARBOXYLATE

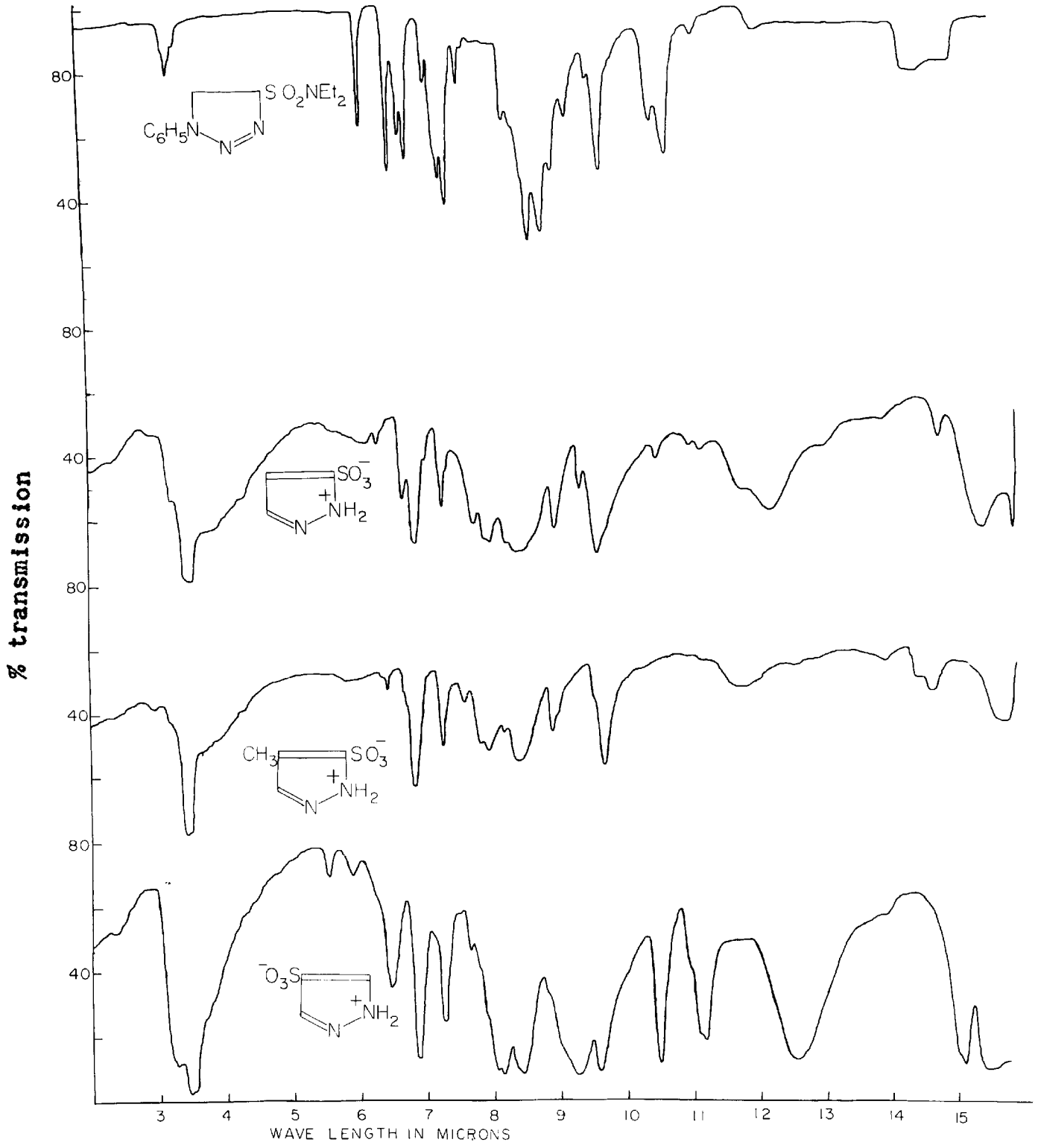


FIGURE 2

INFRARED SPECTRA OF 1-PHENYL-1,2,3-TRIAZOLINE-3-N,N-DIETHYL-SULFONAMIDE (X), 3-PYRAZOLESULFONIC ACID, 4-METHYL-3-PYRAZOLESULFONIC ACID AND 4-PYRAZOLESULFONIC ACID

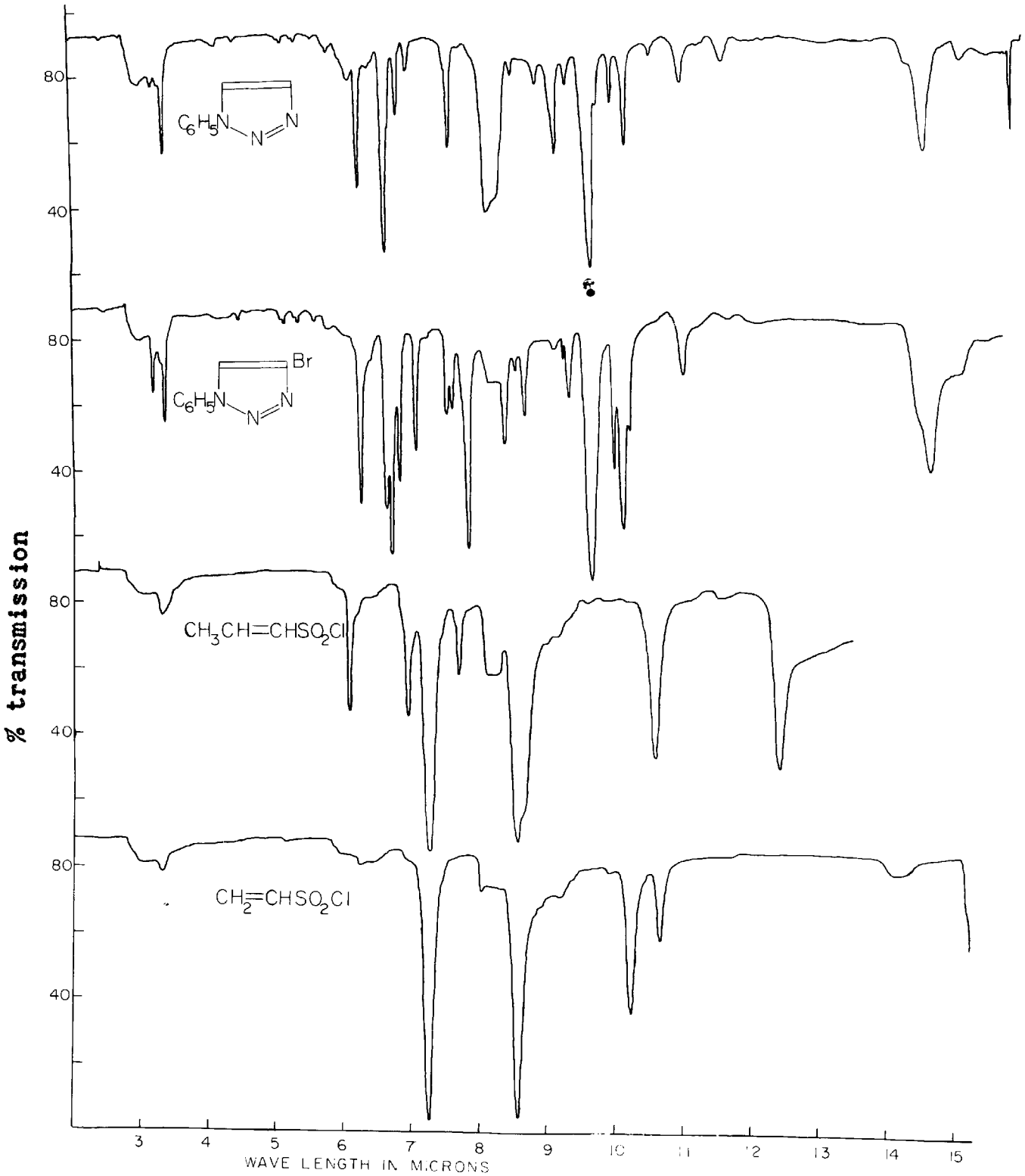


FIGURE 3

INFRARED SPECTRA OF 1-PHENYL-1,2,3-TRIAZOLE, 1-PHENYL-4-BROMO-1,2,3-TRIAZOLE, PROPENE-1-SULFONYL CHLORIDE AND ETHYLENESULFONYL CHLORIDE

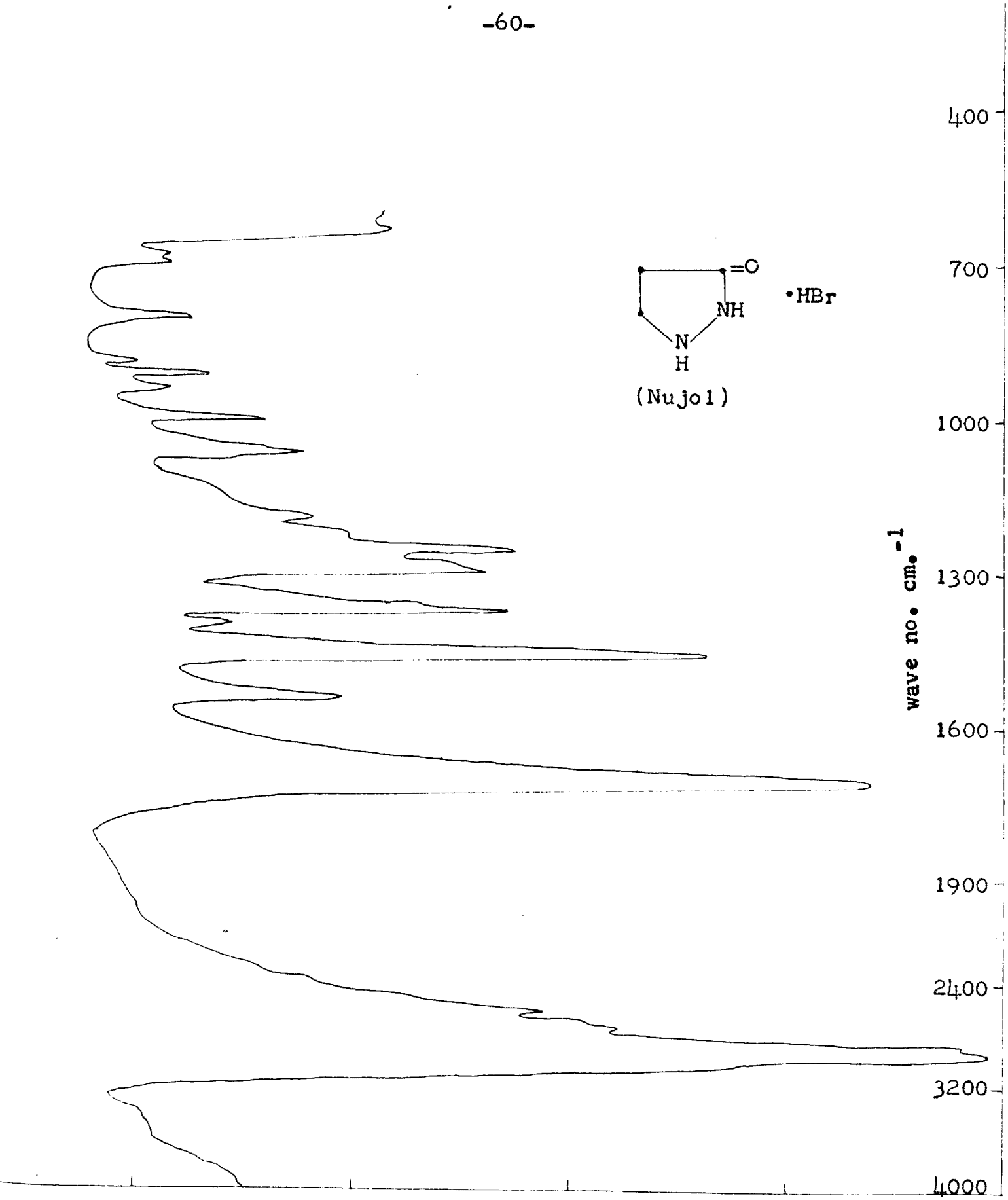


Fig. 4. INFRARED SPECTRUM OF 3-PYRAZOLIDONE HYDROBROMIDE

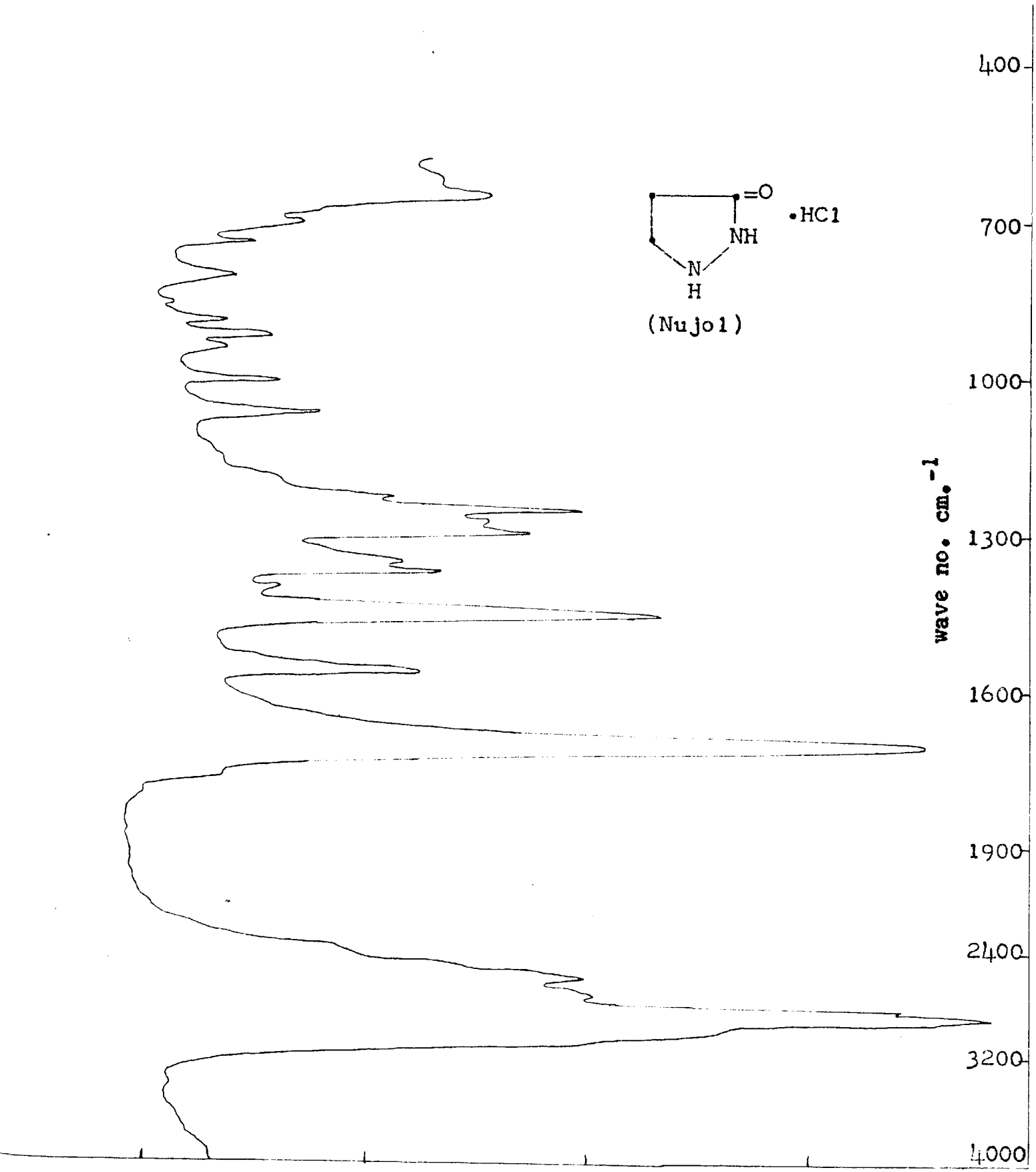


Fig. 5. INFRARED SPECTRUM OF 3-PYRAZOLIDONE HYDROCHLORIDE

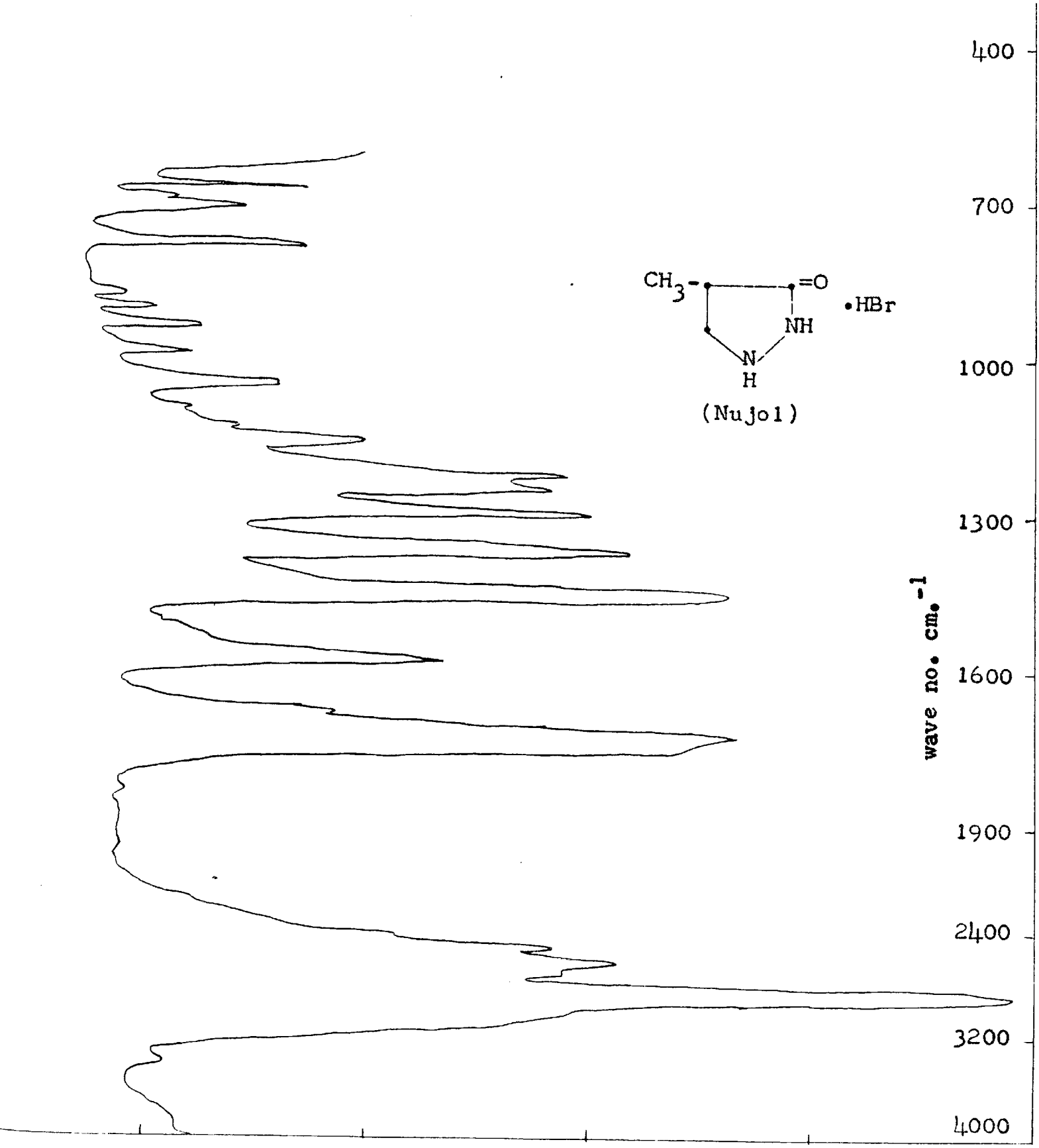


Fig. 6. INFRARED SPECTRUM OF 4-METHYL-3-PYRAZOLIDONE HYDROBROMIDE

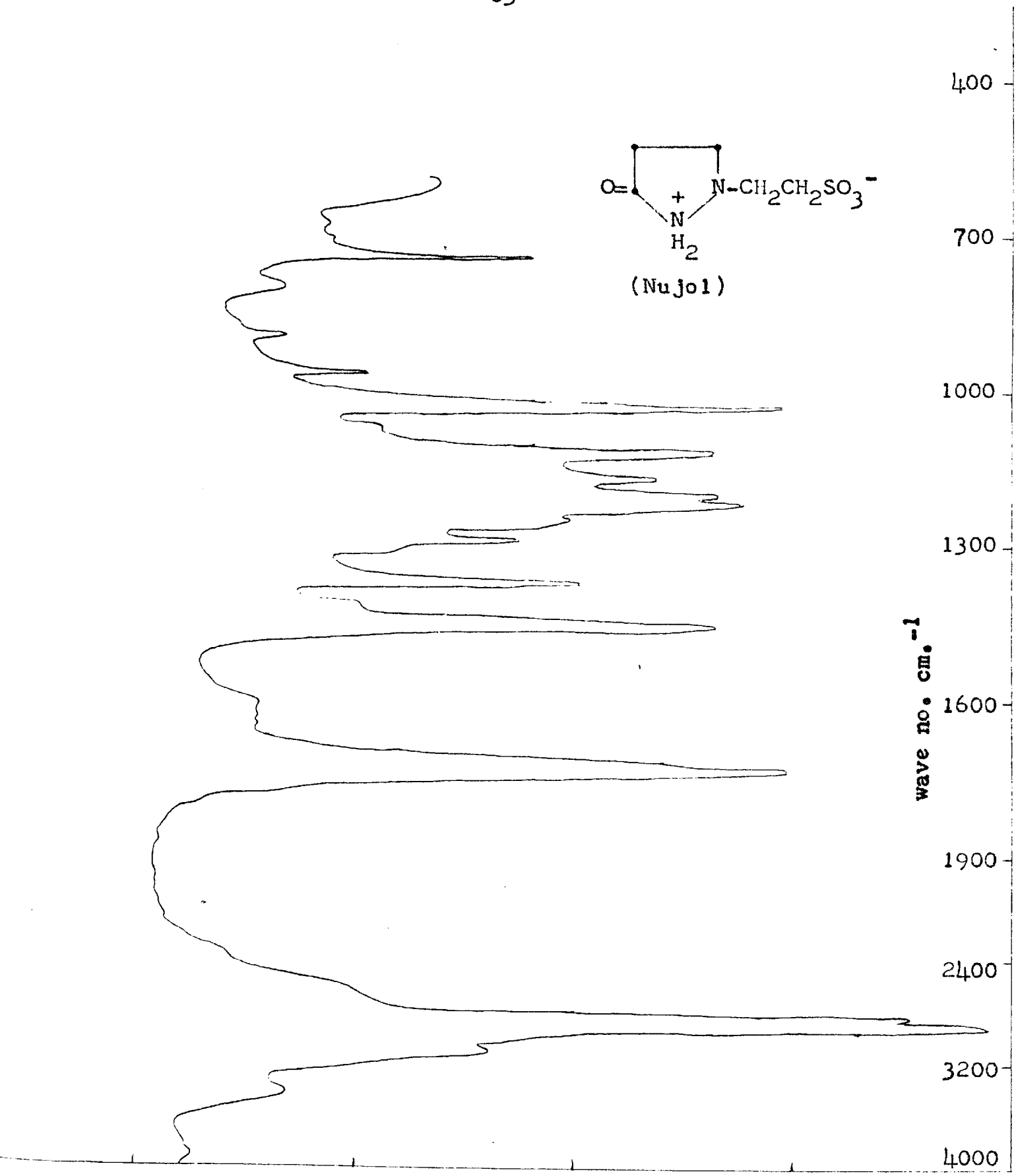


Fig. 7. INFRARED SPECTRUM OF 2-(1-PROTO-5-KETO-2-PYRAZOLIDINYL)-ETHANESULFONATE (VIII)

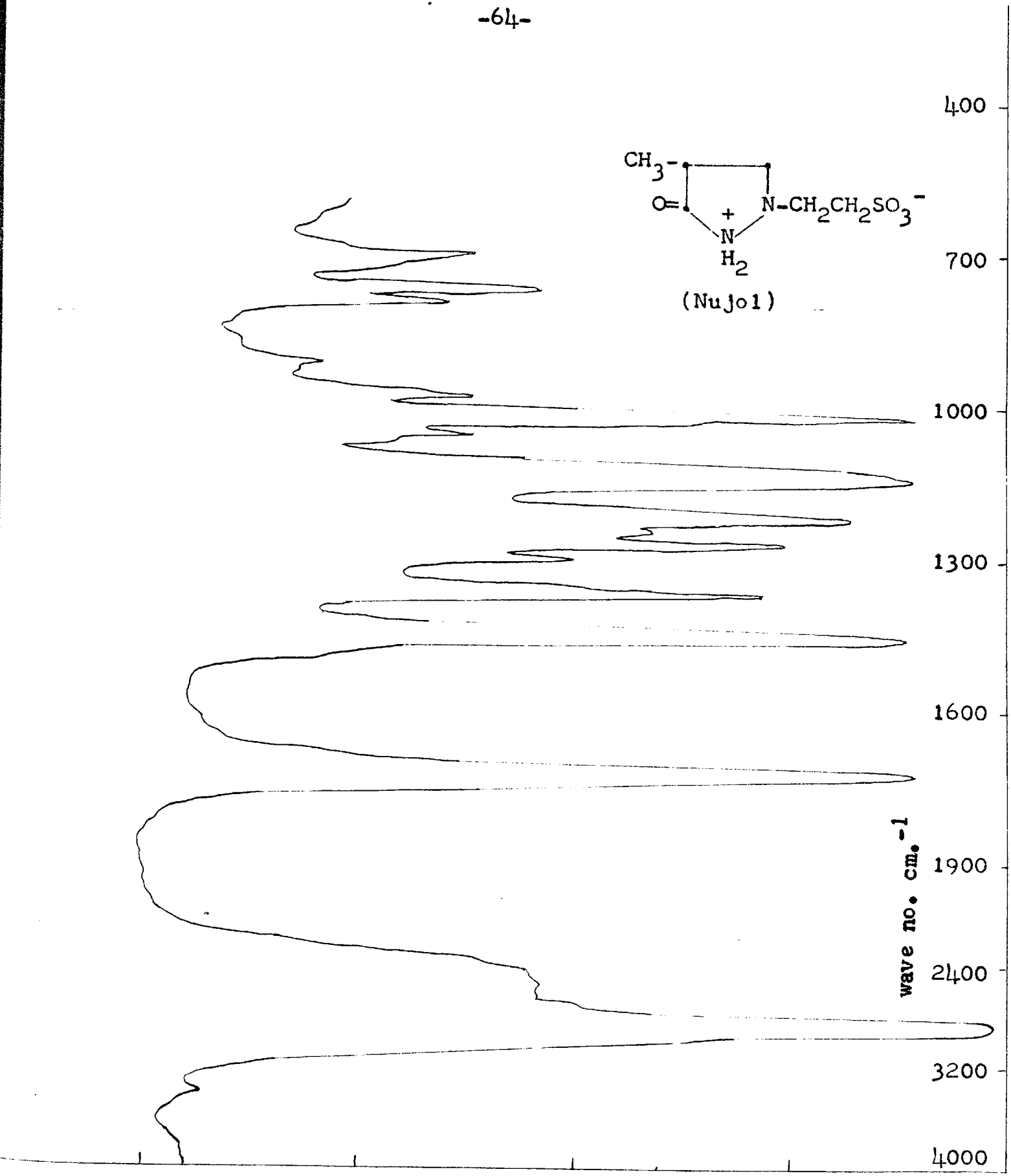


Fig. 8. INFRARED SPECTRUM OF 2-(1-PROTO-4-METHYL-5-KETO-2-PYRAZOLIDINYL)-ETHANESULFONATE

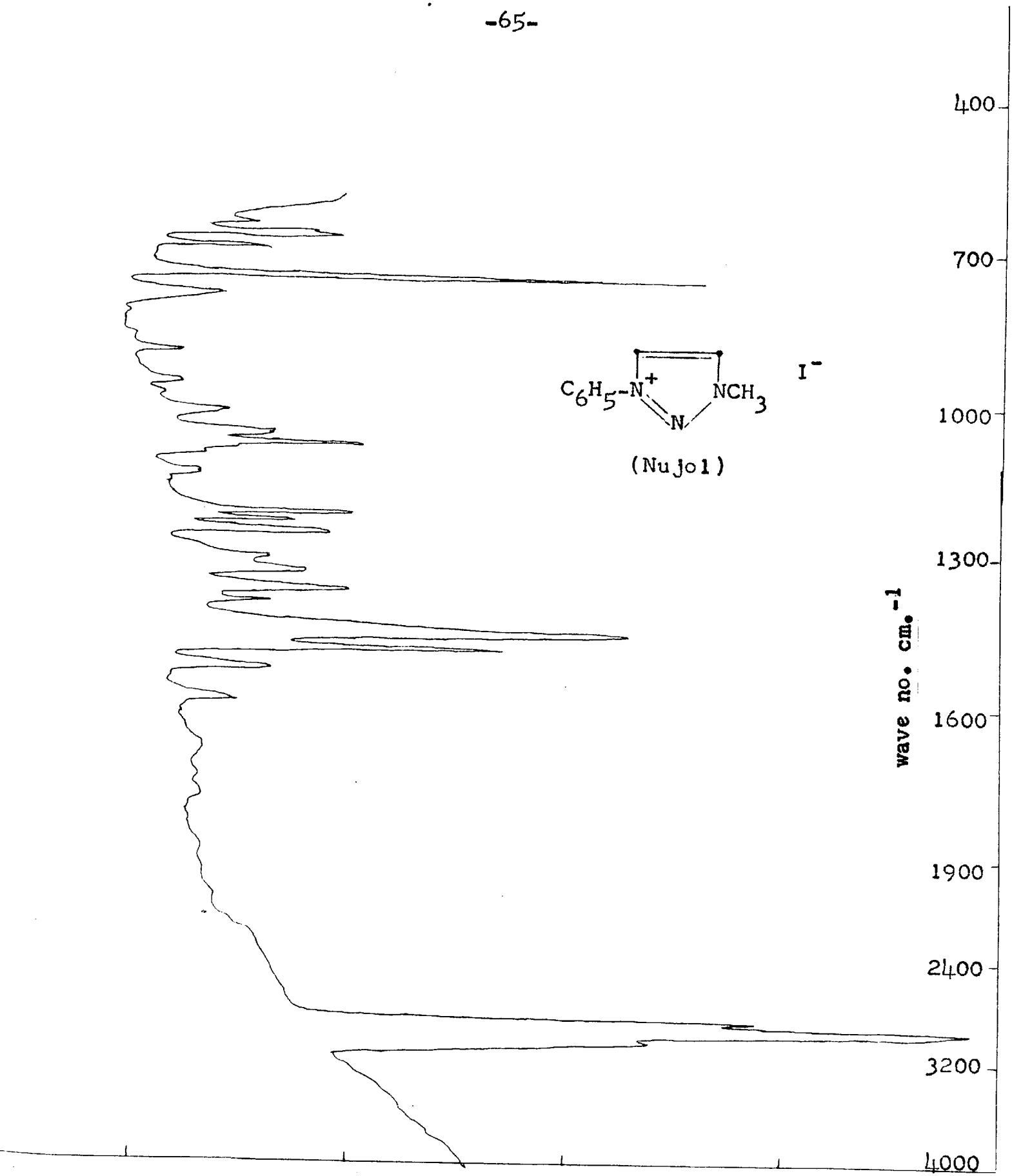


Fig. 9. INFRARED SPECTRUM OF 1-PHENYL-3-METHYL-1,2,3-TRIAZOLIUM IODIDE

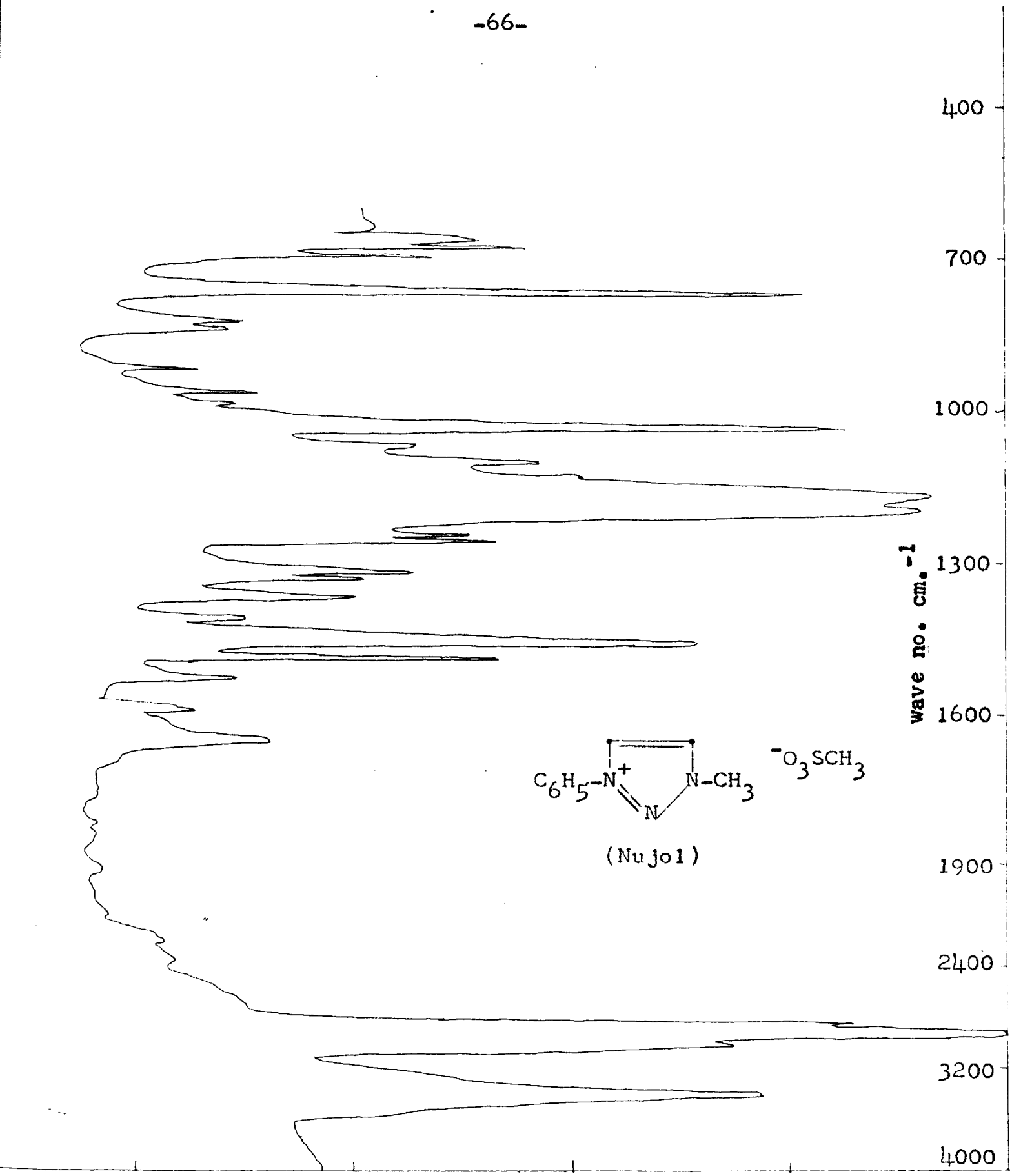


Fig. 10. INFRARED SPECTRUM OF 1-PHENYL-3-METHYL-1,2,3-TRIAZOLIUM METHANESULFONATE

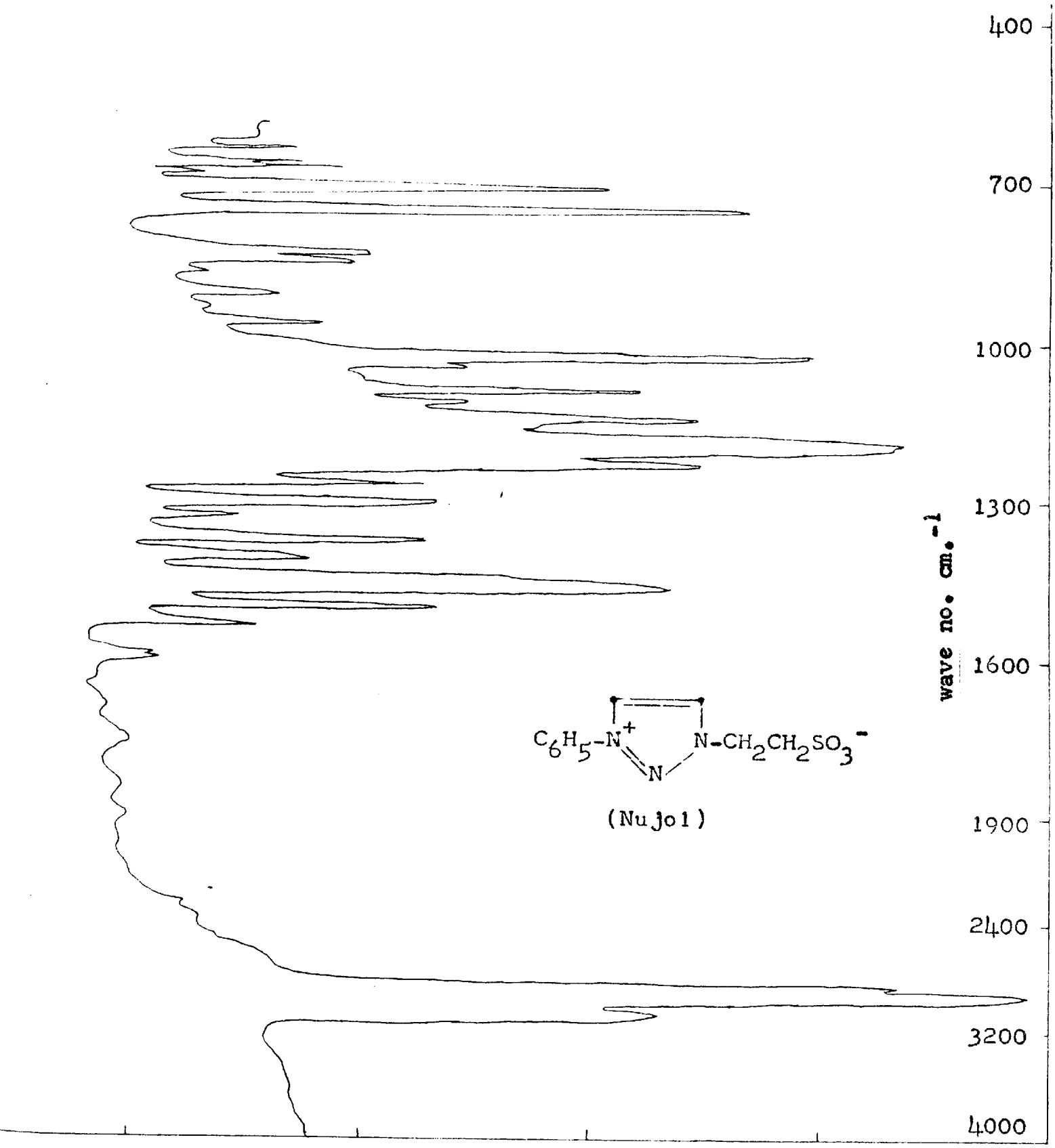


Fig. 11. INFRARED SPECTRUM OF 2-(1-PROTO-1-PHENYL-1,2,3-TRIAZOL-3-YL)-ETHANESULFONATE (XIV)

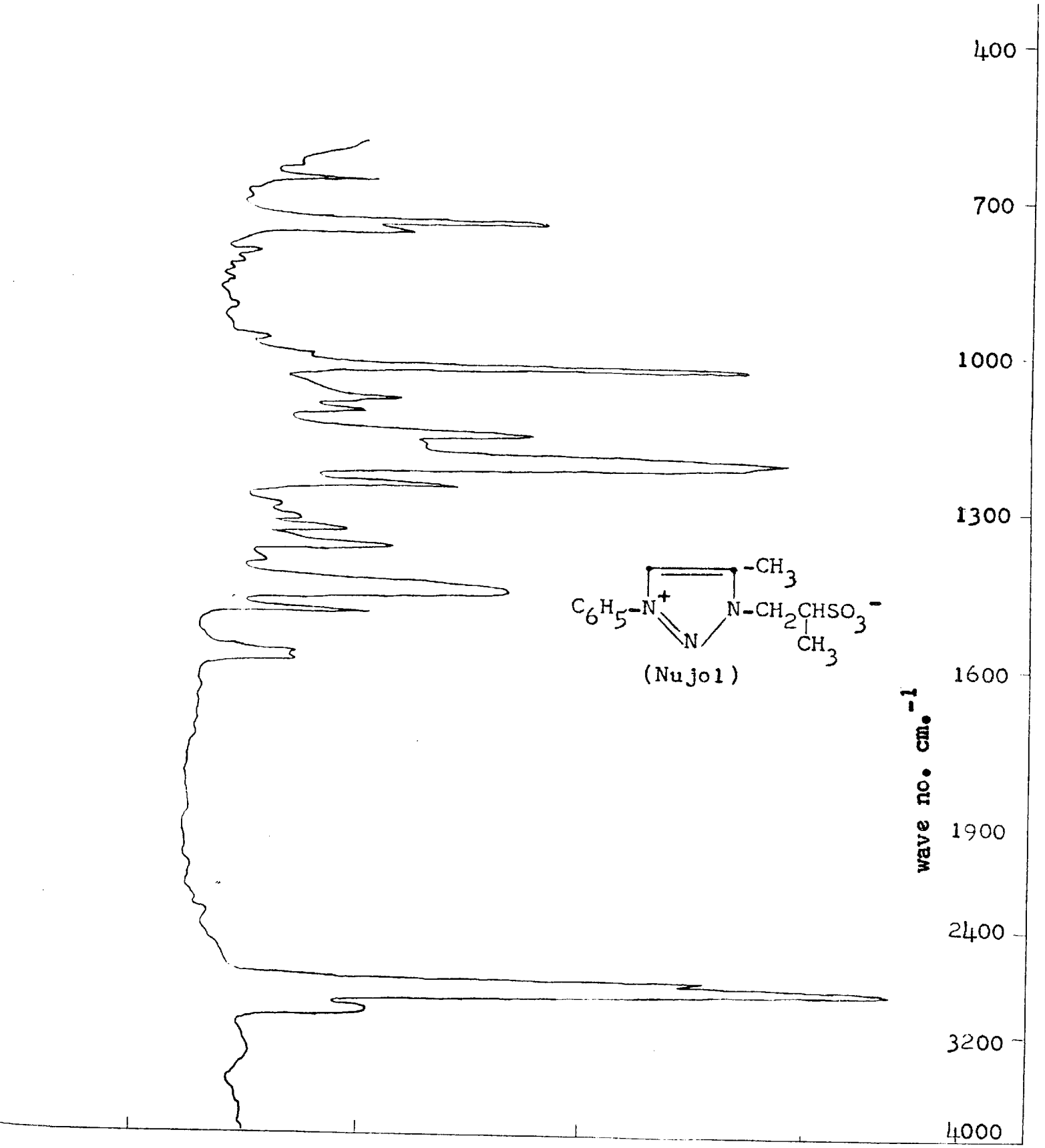


Fig. 12. INFRARED SPECTRUM OF 1-(1-PROTO-1-PHENYL-4-METHYL-1,2,3-TRIAZOL-3-YL)-PROPANE-2-SULFONATE

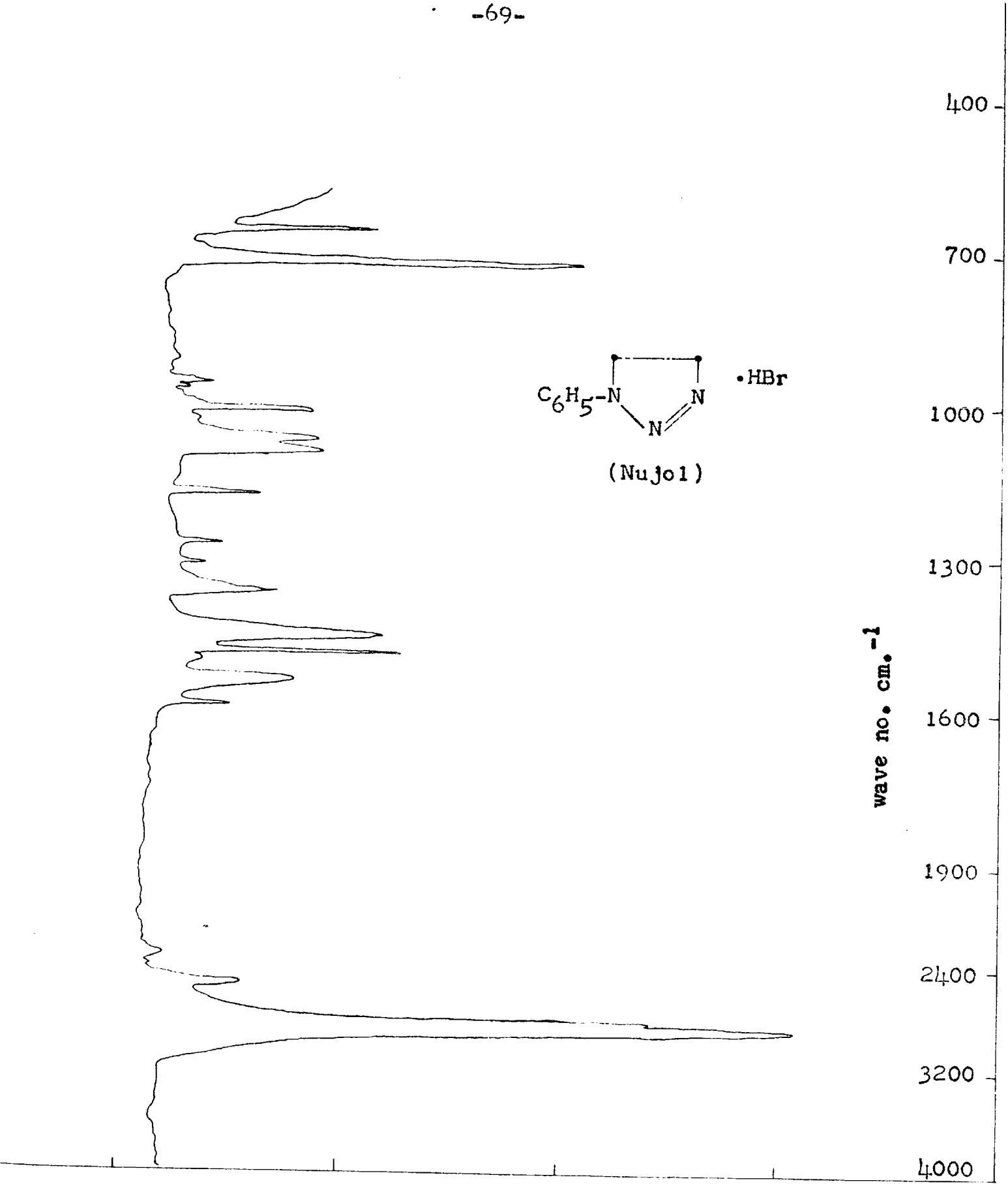


Fig. 13. INFRARED SPECTRUM OF 1-PHENYL-1,2,3-TRIAZOLINE HYDROBROMIDE (XI)

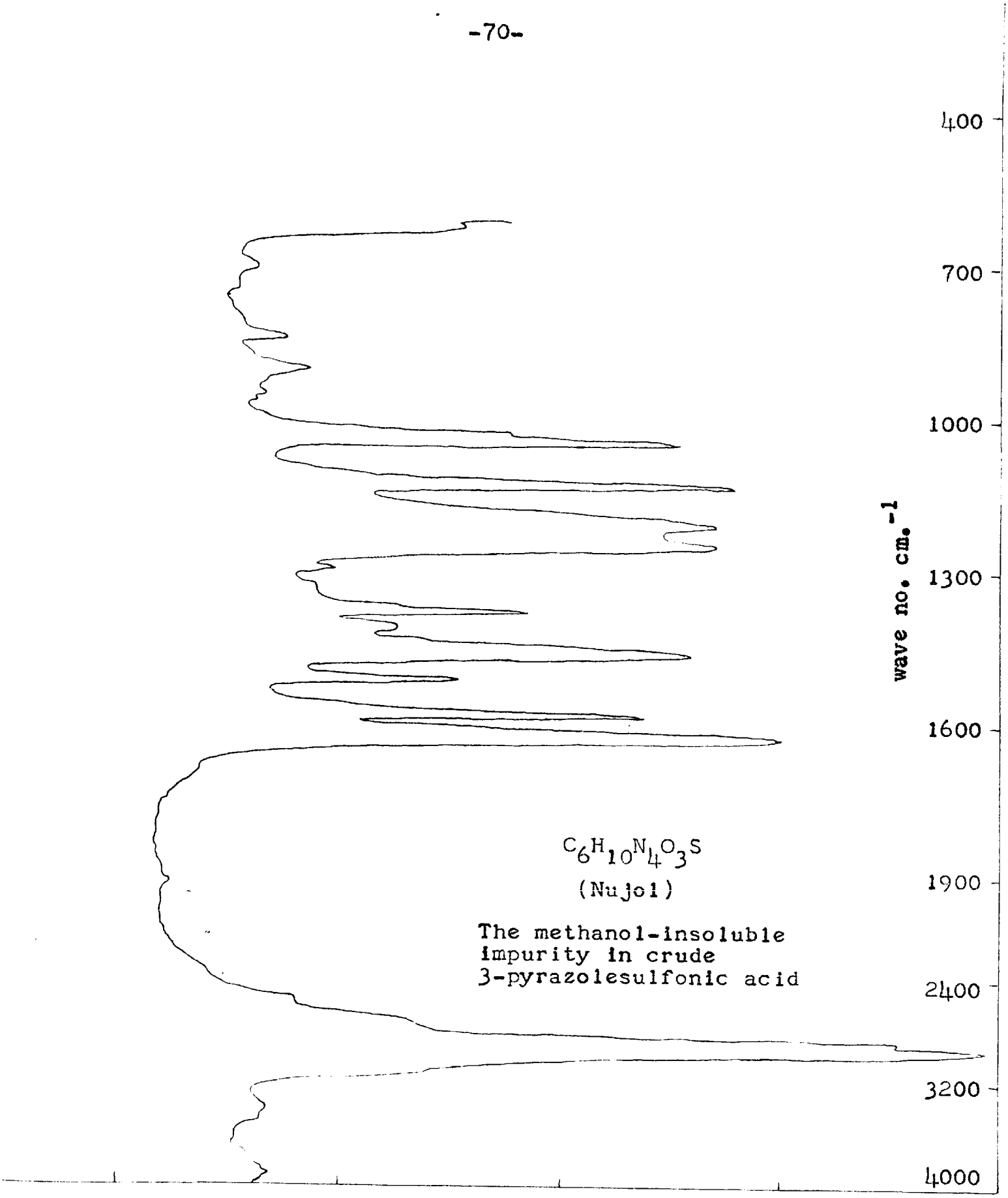


Fig. 14. INFRARED SPECTRUM OF V

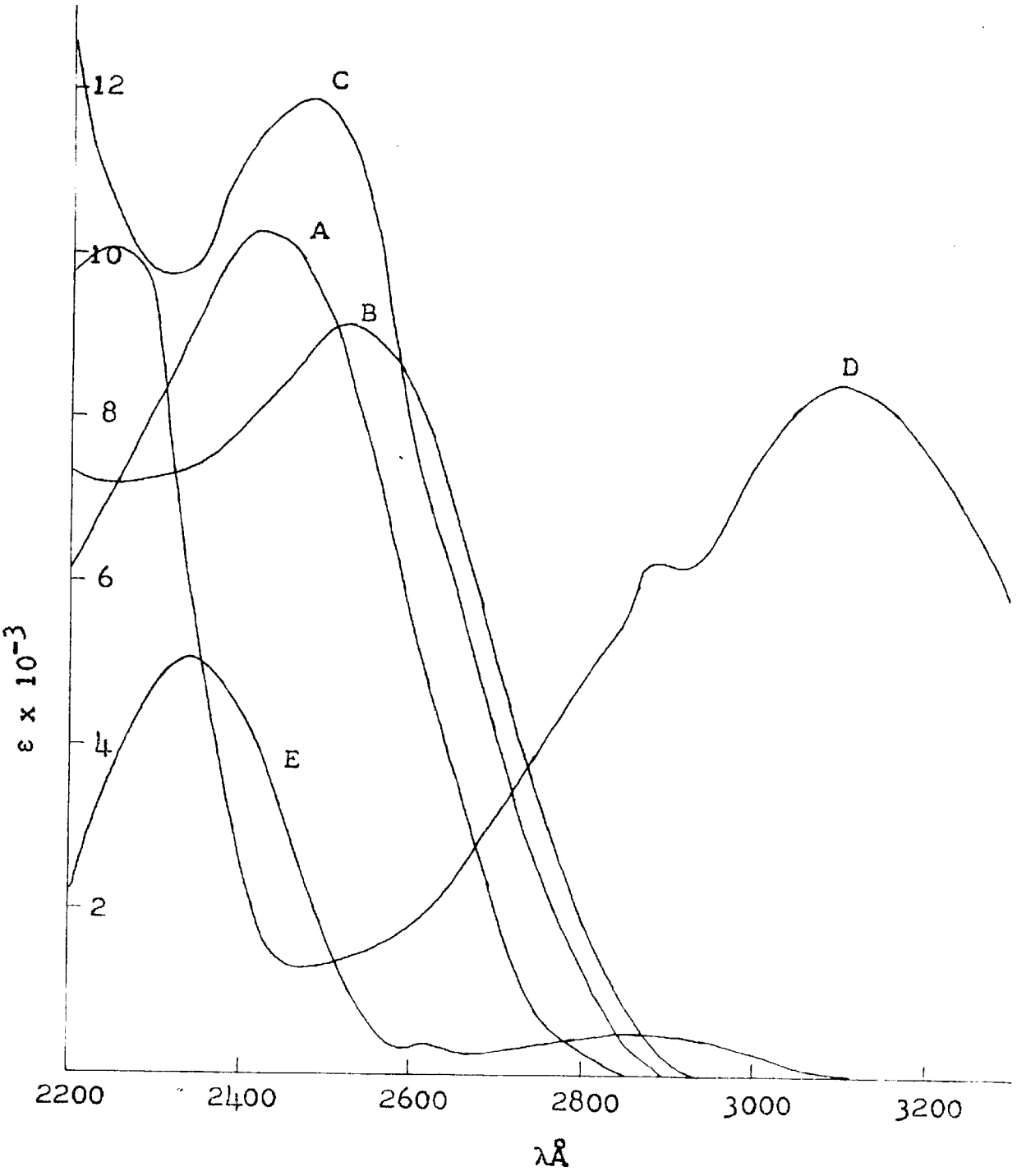


Fig. 15. ULTRAVIOLET SPECTRA OF (A) 1-PHENYL-1,2,3-TRIAZOLE, (B) 1-PHENYL-4-BROMO-1,2,3-TRIAZOLE, (C) 1-PHENYL-1,2,3-TRIAZOLE-4-CARBOXYLIC ACID, (D) 1-PHENYL-1,2,3-TRIAZOLINE-4-N,N,-DIETHYLSULFONAMIDE (X), (E) 1-PHENYL-1,2,3-TRIAZOLINE HYDROBROMIDE (XI)

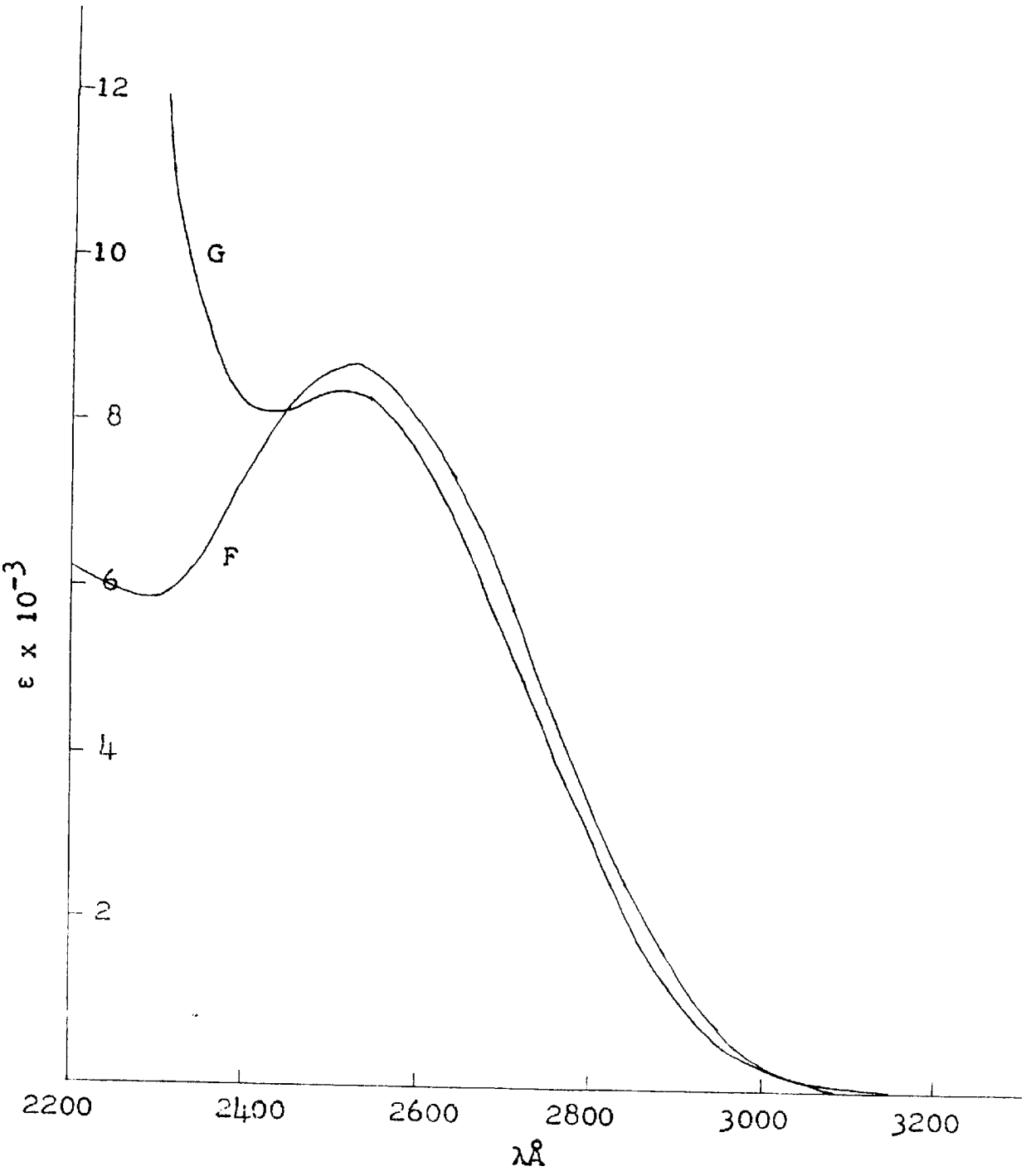


Fig. 16. ULTRAVIOLET SPECTRA OF (F) 2-(1-PROTO-1-PHENYL-1,2,3-TRIAZOL-3-YL)-ETHANESULFONATE (XIV), (G) 1-PHENYL-3-METHYL-1,2,3-TRIAZOLIUM IODIDE

EXPERIMENTAL*

1. Syntheses of α,β-Unsaturated Sulfonic Acid Derivatives

A. Ethylenesulfonyl Chloride

Sodium 2-bromoethanesulfonate[90].--In a 5-l. round-bottomed flask, fitted with a reflux condenser, a mechanical stirrer and a separatory funnel, there were placed 615 g. (3.3 moles) of ethylene dibromide, 1250 ml. of 95% alcohol and 450 ml. of water. The stirrer was started and the mixture heated to boiling. To the well-stirred boiling mixture a solution of 125 g. (1 mole) of anhydrous sodium sulfite in 450 ml. of water was added through the separatory funnel over a period of about two hours. The solution was boiled under a reflux condenser for two hours after all the sulfite had been added. The condenser was then set for distillation, and the alcohol and the ethylene bromide were distilled. The remaining water solution was poured into a large evaporating dish and evaporated to dryness on the water bath. The sodium 2-bromoethanesulfonate was extracted from sodium bromide and unchanged sodium sulfite with 2 l. of boiling 95% alcohol. On cooling the solution, most of the salt crystallized; the mother liquor was used for a second extraction of the residue. The yield was 150 g. (71%) (reported[90], 78-90%).

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*Melting points in this section are uncorrected. Analyses were done by Anna Griffin in this laboratory, Spang Microanalytical Laboratory and Geller Microanalytical Laboratories.

2-Bromoethanesulfonyl chloride[91].--In a 2-l. round-bottomed flask fitted with a calcium chloride tube there were thoroughly mixed 150 g. (0.71 mole) of sodium 2-bromoethanesulfonate and 150 g. (0.72 mole) of phosphorus pentachloride. The reaction proceeded quietly and the contents of the flask became semi-fluid. After the reaction seemed to have stopped, the mixture was heated on a steam-bath for about three hours to insure complete reaction. It was then cooled thoroughly in an ice-salt mixture and treated with about 750 ml. of ice water to dissolve the salts and decompose any excess phosphorus pentachloride. The oily layer, consisting of the sulfonyl chloride and considerable phosphorus oxychloride, was separated and distilled under reduced pressure. The yield of the chloride was 100 g. (64%), b.p. 93°/7 mm. (reported[91], 64-71%, b.p. 119-121°/25 mm.).

2-Chloroethanesulfonyl chloride.--2-Chloroethanesulfonyl chloride was prepared essentially by the procedure of Goldberg[73]. It was found more convenient to reflux the reaction mixture with stirring, then to distill off the bulk of phosphorus oxychloride until the pot temperature reached 135°. Powdered phosphorus pentachloride (450 g., 2.16 moles) was cautiously added to 150 g. (1.04 moles) of sodium isothionate* and the mixture, which developed much heat and rapidly became liquid, was transferred to a 500 ml. three-necked flask fitted with a reflux condenser, a mechanical

*This compound was kindly supplied in generous quantity by the Wyandotte Chemical Corporation.

stirrer and a thermometer. After the mixture had been refluxed at 120-125° for six hours with stirring, the condenser was then set for distillation under a water pump. About 90 ml. of phosphorus oxychloride was collected. The remaining liquid product was cooled and stirred in 1000 ml. of ice-water until all the phosphorus oxychloride was decomposed. The oil was separated, taken up in benzene, and dried over calcium chloride. The oil remaining after evaporation of the solvent was distilled; the yield of the sulfonyl chloride was 136 g. (84%), b.p. 51-54°/1 mm. (reported[73], 62.5%, b.p. 77-79°/4 mm.).

Ethylenesulfonyl chloride[72].--A solution of 16.2 g. (0.1 mole) of 2-chloroethane-1-sulfonyl chloride in 100 ml. of anhydrous ether placed in a 300 ml. three-necked flask fitted with a stirrer, a drying tube and a dropping funnel was cooled to -40° and a solution of 12.7 g. (0.12 mole) of 2,6-lutidine (Reilly) in 20 ml. of ether was added at such a rate that the temperature did not exceed -30° (20 min.). The mixture was stirred while it warmed up to room temperature. After cooling to 0°, 40 ml. of ice-cold 1% sulfuric acid was added with stirring. The layers were separated, and the ether layer was washed again with cold acid, then with water and saturated sodium chloride solution. After drying with sodium sulfate, the mixture was distilled. The yield of the sulfonyl chloride was 7.8 g. (62%), b.p. 25-27°/0.2 mm. (reported[72], 72.2%, b.p. 34-36°/0.2 mm.). Ethylenesulfonyl chloride is a strong lachrymator.

In earlier runs, when 2,6-lutidine from an open bottle of unknown origin was used in the dehydrochlorination, the yield varied from 15% to 36%.

B. N,N-Diethylethylenesulfonamide[72]

A solution of 6.3 g. (0.05 mole) of ethylenesulfonyl chloride in 40 ml. of anhydrous ether was cooled to -70°. A mixture of 3.7 g. (0.05 mole) of diethylamine and 5.1 g. (0.05 mole) of triethylamine in 25 ml. of anhydrous ether was added below -50° with stirring. After warming to room temperature, the mixture was poured into ice-water, the organic layer was extracted thoroughly with dilute ice-cold 1% hydrochloric acid, and the acid extracts were extracted once with chloroform. The combined organic layer was washed with water and dried with sodium sulfate. The sulfonamide was distilled after removal of solvent; 3.4 g. (42%), b.p. 67-69°/0.5 mm., $n_D^{24.6}$ 1.4603 (reported[72], 47%, b.p. 80-82°/1 mm., $n_D^{24.3}$ 1.4602).

C. n-Butyl Ethylenesulfonate

n-Butyl ethylenesulfonate was prepared essentially by the procedure of Whitmore and Landau[75] except that anhydrous ether was used in place of methylene dichloride as the solvent.

A solution of 17 g. (0.22 mole) of n-butyl alcohol and 32 g. (0.20 mole) of 2-chloroethanesulfonyl chloride in 200 ml. of anhydrous ether was cooled to 0°. Dry pyridine, 34.8 g. (0.44 mole), was added slowly with efficient stirring.

The temperature was kept below 10° during the addition, which required from two to three hours. The reaction mixture was then allowed to come slowly to room temperature. Dilute hydrochloric acid (2%, 200 ml.) was added and the ether layer, after washing with ice-cold water, was dried over sodium sulfate, and the ester was recovered and vacuum distilled. The yield was 14.2 g. (42%), b.p. 75-77°/1.3 mm. (reported[75], 61%, b.p. 115-117°/15 mm.).

Methyl ethylenesulfonate was prepared in the same manner. However, subsequent reactions were carried out with the n-butyl ester since it was prepared in higher yields than other esters[75].

D. Propene-1-sulfonyl Chloride

2-Chloropropane-1-sulfonyl chloride.--The procedure for preparing 2-chloroethanesulfonyl chloride was followed in this preparation. Powdered phosphorus pentachloride (450 g., 2.16 moles) was cautiously added to 160 g. (1.02 moles) of sodium 2-hydroxypropanesulfonate*, and the mixture, which developed much heat and rapidly became liquid, was transferred to a 500 ml. three-necked flask, fitted with a reflux condenser, a mechanical stirrer and a thermometer. After the mixture was refluxed at 120-125° with stirring for six hours, the condenser was then set for distillation under a water pump, and about 140 ml. of phosphorus oxychloride was collected. The remaining liquid product was cooled and

*This compound was kindly supplied in generous quantity by the Wyandotte Chemical Corporation.

stirred in 1000 ml. of ice-water until all the phosphorus oxychloride had been decomposed (1/2 hour). The oil was separated, taken up in benzene, and dried over calcium chloride. The oil remaining after evaporation of the solvent was distilled; the yield of the sulfonyl chloride was 70 g. (40%), b.p. 55°/1.5 mm.

Propene-1-sulfonyl chloride[72].--A solution of 15.5 g. (0.087 mole) of 2-chloropropane-1-sulfonyl chloride in 50 ml. of ether was cooled to -40° and 8.85 g. (0.087 mole) of triethylamine in 25 ml. of ether was added slowly below -25°. The mixture was stirred at -25° for two hours and then in an ice bath for one hour. To the mixture was then added 50 ml. of ice-cold 1% sulfuric acid and the layers were separated. The ether layer was washed with water and saturated sodium chloride solution and then dried over sodium sulfate. The residue after evaporation of the ether was vacuum distilled; 9.4 g. (80%), b.p. 32-34°/0.3 mm., $n_D^{24.5}$ 1.4775. The sulfonyl chloride is a lachrymator, but not as objectionable as ethylenesulfonyl chloride.

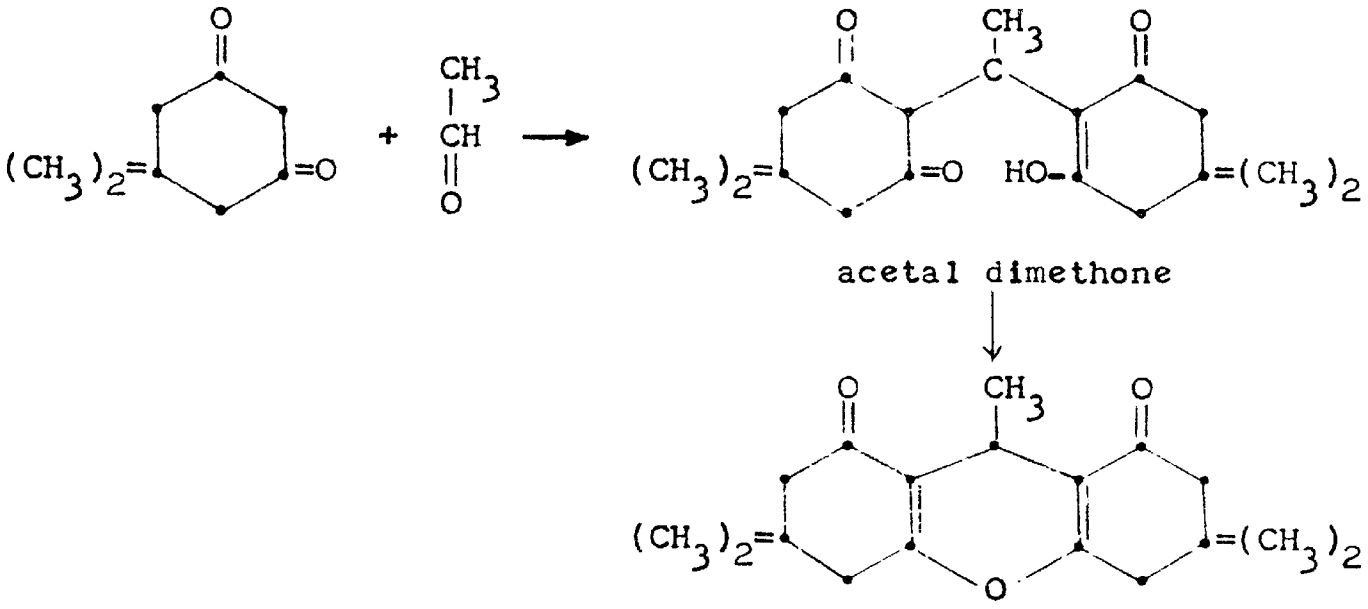
Anal. Calcd. for $C_3H_5ClO_2S$: Cl, 25.22.

Found: Cl, 25.40 (saponification followed by Volhard titration method).

Structure proof of propene-1-sulfonyl chloride by ozonization.--A solution of 2 g. of the sulfonyl chloride in 60 ml. of ethyl acetate was placed in an ozonization tube immersed in a Dry Ice and acetone bath and ozonized for 1-1/2 hrs. until the solution turned blue. The ozonide solution

was then added through a dropping funnel to a boiling mixture of 0.7 g. of zinc dust, traces of hydroquinone and silver nitrate in 100 ml. of water. The mixture was refluxed for 1/2 hr. and distilled.

To 10 ml. of the aqueous layer of the distillate was added a little dimedone and the mixture was heated at 50° until the dimedone derivative precipitated.



The acetaldimethone was recrystallized from alcohol, m.p. 138-139°. There was also some of the anhydride, m.p. 173-174°.

The infrared spectrum of ethylenesulfonyl chloride, with a terminal methylene group, showed a sharp peak at 10.20 μ, which is absent in the spectrum of propene-1-sulfonyl chloride (Figure 3, page 59).

E. N,N-Diethylpropene-1-sulfonamide

A solution of 8.0 g. (0.057 mole) of 1-propene-1-sulfonyl chloride in 50 ml. of ether was cooled to -70° and

a mixture of 4.2 g. (0.057 mole) of diethylamine and 6.5 g. (0.057 mole) of triethylamine in 25 ml. of ether was added at such a rate that the temperature did not exceed -50°. The mixture was then stirred while it warmed up to room temperature and then poured onto ice-water. The ether layer was washed with water and dilute sodium carbonate solution and dried over sodium sulfate. The residue after evaporation of the solvent was distilled. The yield of the sulfonamide was 4.7 g. (46%), b.p. 72-74°/0.2 mm., n_D^{25} 1.4661.

Anal. Calcd. for $C_7H_{15}NO_2S$: C, 47.43; H, 8.53; N, 7.70.
Found: C, 47.19; H, 7.84; N, 7.63.

F. n-Butyl Propene-1-sulfonate

The procedure for preparing n-butyl ethylene sulfonate was followed in this preparation. A solution of 8.5 g. (0.11 mole) of n-butyl alcohol and 17.6 g. (0.10 mole) of 2-chloropropane-1-sulfonyl chloride in 100 ml. of ether was cooled to 0°. Pyridine (17.4 g., 0.022 mole) was added at such a rate so that the temperature did not exceed 10° (two hours). The mixture was then stirred while it warmed up to room temperature, then treated with 100 ml. of 1% hydrochloric acid. The ether layer, after two washings with water, was dried with sodium sulfate. The ester was distilled in vacuum; b.p. 95-99°/1 mm. The yield was 4.98 g. (58%). The analytical sample boiled at 85-87°/0.5 mm., n_D^{25} 1.4461.

Anal. Calcd. for $C_7H_{14}O_3S$: C, 47.17; H, 7.91.
Found: C, 47.54; H, 7.90.

G. Propene-2-sulfonyl Chloride

Propylene sulfide[93].--To a vigorously stirred solution of 194 g. (2 moles) of potassium thiocyanate in 200 ml. of water was added dropwise 116 g. of propylene oxide (2 moles), keeping the temperature below 30°. Stirring was continued for five hours, then the aqueous layer was removed and a fresh solution of 100 g. of potassium thiocyanate in 100 ml. of water was added to the organic layer with stirring. There was some heat evolved and the mixture was stirred until its temperature fell back to room temperature. The organic layer was dried over calcium chloride and distilled, b.p. 73-75°. The yield was 98.8 g. (66.7%) (reported[94], b.p. 75-77°).

1-Chloropropane-2-sulfonyl chloride[74].--To 650 ml. of saturated chlorine water was added dropwise 98.8 g. of propylene sulfide with stirring, the dropping funnel having its end below the water solution. Concurrently chlorine was bubbled through the mixture at such a rate that an excess was always present. The reaction temperature was maintained at 0-12° by means of an ice-water bath and control of the propylene sulfide addition. After the propylene sulfide had been added, the rate of chlorine was reduced and stirring was continued for an hour. Air was then bubbled through the mixture to remove excess chlorine. The heavy oily product was separated, washed three times with ice-water and dried over calcium chloride. The sulfonyl chloride was distilled at 73°/4 mm. and weighed 165.6 g. (70%) (reported[74], 70%, b.p. 77-78°/8 mm.).

Propene-2-sulfonyl chloride[92].--A solution of 30.8 g. (0.175 mole) of 1-chloropropane-2-sulfonyl chloride in 100 ml. of anhydrous ether was cooled to -30° and a solution of 17.5 g. (0.175 mole) of triethylamine in 25 ml. of anhydrous ether was added between -25° to -20°. The mixture was stirred for one hour at -25° and for another hour at -10°. It was then poured into 100 ml. of ice-cold 1% sulfuric acid. The ether layer was washed with cold water and ice-cold saturated sodium chloride solution and dried over sodium sulfate. The residue after solvent removal was distilled, b.p. 40-45°/1.5 mm., n_D^{22} 1.4729. The yield of the sulfonyl chloride was 14.6 g. (50%) (reported[74], 31.5%, b.p. 70-75°/10 mm., n_D^{20} 1.4740). In earlier runs when 2,6-lutidine was employed in the dehydrobromination, poorer results were obtained.

II. Addition of Diazomethane

A. Diazomethane

Synthesis of N-nitroso-β-methylaminoisobutyl methyl ketone[95,96].--In a 2-liter three-necked flask, fitted with a mechanical stirrer, a thermometer, and a dropping funnel, was placed a solution of 142 g. (2.1 moles) of methylamine hydrochloride in 250 ml. of water. The flask was put in an ice bath and the stirrer started; 210 ml. of 10 N sodium hydroxide, 84 g. (2.1 moles), was added slowly to the ice-cold solution. Then 196 g. (2.0 moles) of mesityl oxide was added, keeping the temperature at 20°. The mixture was left

standing for half an hour without cooling. The solution was then cooled to 10° and 125 ml. of glacial acetic acid was added slowly below 15°. Then an additional 75 ml. was added rapidly. The ice bath was removed and 300 ml. of 8 N sodium nitrite, 171 g. (2.5 moles), was added in 20-30 minutes to the stirred solution, which was kept at 25-35° by intermittent cooling and the mixture was allowed to stand overnight. The oily layer was separated and the aqueous layer extracted with two 200 ml. and one 100 ml. portions of ether. The combined extracts and the oil were dried over calcium chloride. The ether was distilled at 60°, and other volatile substances were distilled at 100°/30-20 mm. The residue of the impure ketone weighed 239 g. (75%) (reported[95], 70-80%).

Preparation of diazomethane from N-nitroso-β-methylaminoisobutyl methyl ketone.--In a 250 ml. distilling flask was placed a solution of 7.3 g. (0.12 mole) of potassium hydroxide in 40 ml. of n-propyl alcohol and 100 ml. of anhydrous ether. To the mixture was added a solution of 15.8 g. (0.1 mole) of crude N-nitroso-β-methylaminoisobutyl methyl ketone in 20 ml. anhydrous ether through a dropping funnel, keeping the flask in a water bath at 55°. The diazomethane co-distilled with the ether. The receiver containing 120 ml. of anhydrous ether was kept in a Dry Ice bath. The yield of diazomethane was 4.2 g. (70%).

For analysis an aliquot portion (about one-twentieth) of the solution was allowed to react at 0° with a solution of an accurately weighed sample of about 1.3 g. of pure

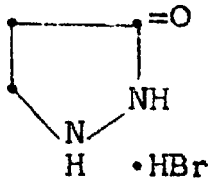
benzoic acid in 50 ml. of absolute ether. The benzoic acid must be in excess as evidenced by the complete decolorization of the diazomethane solution. The unreacted benzoic acid was titrated with standard 0.2 N alkali[97].

B. Diazomethane and N,N-Diethylethylenesulfonamide

Formation of the adduct.--To a solution of 6 g. (0.036 mole) of N,N-diethylethylenesulfonamide in 15 ml. of anhydrous ether was added an equimolar amount of diazomethane in ether at room temperature. The color of diazomethane disappeared after 24 hours. When the ether was evaporated, there remained 6.8 g. (92%) of an oily product, which could not be distilled under vacuum nor crystallized from various solvents. Thus, it was characterized by bromine dehydrogenation.

Bromine dehydrogenation of the adduct.--To a vigorously stirred solution of 3 g. (0.0147 mole) of the crude addition product of diazomethane and N,N-diethylethylenesulfonamide in 35 ml. of chloroform was added a solution of 2.7 g. (0.0168 mole) of bromine in 10 ml. of chloroform through a dropping funnel at room temperature at such a rate that there was no appreciable rise in temperature. The mixture became orange in color. The stirring was continued for six hours and the mixture was allowed to stand overnight. There formed 1.2 g. of fine precipitate which melted at 188-190°. After it was recrystallized from 95% ethanol, its melting point became 206-207°. A sodium fusion on the purified sample indicated the presence of bromine and nitrogen

but no sulfur. The yield of the purified pyrazolidone hydrobromide was 0.8 g. (32%); its mixed melting point with an authentic sample was 205-207°.



Anal. Calcd. for $C_3H_7BrN_2O$: C, 21.57; H, 4.22; N, 16.39; Br, 47.85; N.E. 167.

Found: C, 21.49; H, 4.32; N, 16.98; Br, 47.8 (Volhard); N.E. 160.

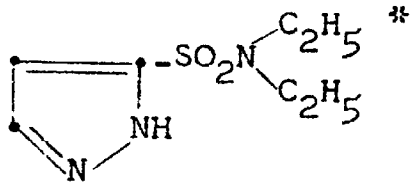
When the crude pyrazolidone hydrobromide was dissolved in 95% ethanol to be recrystallized, there was 0.08 g. of an ethanol-insoluble substance. After two recrystallizations from aqueous methanol, it melted at 254°, which was not depressed on admixture with an authentic sample of hydrazine sulfate.

Anal. Calcd. for $H_6N_2O_4S$: H, 4.60; N, 21.34; S, 24.43.

Found: H, 4.55; N, 21.35; S, 24.40.

The chloroform filtrate from the pyrazolidone hydrobromide was extracted with three 20 ml. portions of water and the organic layer was evaporated on a water bath. There was 2.2 g. of residue obtained which crystallized on cooling (m.p. 95-105°). When it was recrystallized from benzene and low-boiling petroleum ether pair (insoluble in the latter), it melted at 112-113°. The yield of the purified product was 1.7 g. A sodium fusion on the purified compound indicated

the presence of sulfur and nitrogen but no bromine.



Anal. Calcd. for $C_7H_{12}N_3O_2S$: C, 41.36; H, 6.45; N, 20.67.
Found: C, 41.57; H, 6.41; N, 20.38.

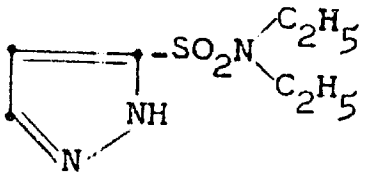
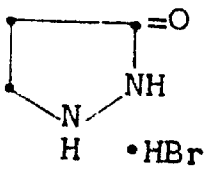
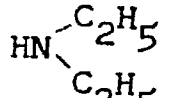
The aqueous extracts of the organic layer were combined and concentrated on a steam bath. The resultant solution was acidified with one drop of dilute hydrochloric acid and a solution of barium chloride was added dropwise until all the sulfate present was precipitated (0.72 g.). The filtrate was then extracted thoroughly with chloroform and the combined extracts evaporated to dryness, there formed 0.5 g. of impure diethylamine hydrobromide. After it was recrystallized from 95% ethanol, it melted at 213-214° and did not depress the melting point of an authentic sample of diethylamine hydrobromide.

Anal. Calcd. for $C_4H_{12}BrN$: C, 31.18; H, 7.85; N, 9.09.
Found: C, 31.03; H, 8.11; N, 9.01.

The following is a summary of the products from this reaction:

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*Its ultraviolet spectrum showed no maximum above 2200 Å.

Crude addition product		
3 g. (0.0147 mole)	2.2 g. (0.0108 mole, 73%) purified, 1.7 g. (0.0083 mole, 56%)	1.2 g. (0.007 mole, 47%) purified, 0.8 g. (0.047 mole, 32%)
	$N_2H_4 \cdot H_2SO_4$	$BaSO_4$
0.5 g. (0.003 mole)	0.08 g. (0.006 mole, 4.1%) (crude, 20%) purified wt. not taken	0.72 g. (0.003 mole, 20%)

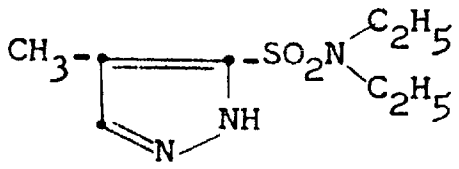
C. Diazomethane and N,N-Diethylpropene-1-sulfonamide

Formation of the adduct.--To a solution of 6.25 g. (0.035 mole) of N,N-diethylpropene-1-sulfonamide in 20 ml. of anhydrous ether was added 100 ml. of 0.36 N ethereal diazomethane at room temperature. The color of diazomethane disappeared after four days. When all the ether was evaporated off, there remained 7.65 g. (99%) of an oily product, which failed to crystallize when treated with various solvents, such as methanol, nitromethane, acetonitrile, dioxane, chloroform and low-boiling petroleum ether. Thus, it was characterized by bromine dehydrogenation.

Bromine dehydrogenation of the adduct.--To a vigorously stirred solution of 4.43 g. (0.0202 mole) of the impure addition product of diazomethane and N,N-diethylpropene-1-sulfonamide in 35 ml. of chloroform was added a solution of 3.2 g. (0.0202 mole) of bromine in 10 ml. of chloroform

dropwise at room temperature. The stirring was continued for six hours and the mixture was then allowed to stand overnight. There formed a trace of precipitate, which was proved to be hydrazine sulfate ($N_2H_4 \cdot H_2SO_4$) by its mixed melting point with an authentic sample.

The filtrate from the hydrazine sulfate was extracted with three 20 ml. portions of water and the organic layer was evaporated on a steam bath. About 3 g. of residue was obtained which, when subjected to sublimation at 110°/0.1 mm., produced 2.6 g. (59%, 0.012 mole) of N,N-diethyl-4-methyl-3-pyrazolesulfonamide. It melted at 127° after recrystallization from acetonitrile and water, λ_{max} (C_2H_5OH) 2250 Å, $\varepsilon = 4.92 \times 10^3$.

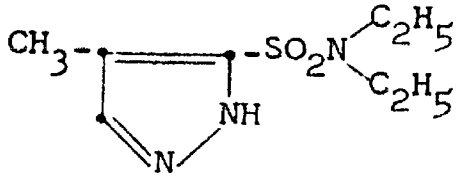
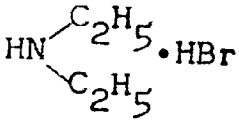
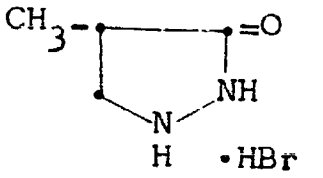


Anal. Calcd. for $C_8H_{14}N_3O_2S$: C, 44.10; H, 6.93; N, 19.06.
Found: C, 44.20; H, 6.96; N, 19.34.

The water extracts of the organic layer were combined and concentrated on a steam bath. The resultant solution was acidified with one drop of hydrochloric acid followed by dropwise addition of a solution of barium chloride until no more barium sulfate was formed (0.4 g.). The filtrate from the barium sulfate was then evaporated to dryness and the residue extracted with chloroform and ethanol successively. From the chloroform extract was isolated 0.58 g. (0.0037 mole) of diethylamine hydrobromide, which melted at 213-214° after one recrystallization from 95% ethanol and showed no depression

when a mixed melting point was taken with an authentic sample of diethylamine hydrobromide. The ethanol extract was evaporated to dryness and the residue sublimed; a trace of 4-methylpyrazolidone hydrobromide was obtained, m.p. 166-169°; mixed m.p. with authentic sample was 166-168°.

The following is a summary of the products obtained from this reaction.

Crude addition product		
4.43 g. (0.0202 mole)	2.6 g. (0.012 mole, 59%)	0.58 g. (0.0037 mole, 18%)
$N_2H_4 \cdot H_2SO_4$	$BaSO_4$	
trace	0.4 g. (0.0016 mole, 12%)	trace

D. Diazomethane and Methyl Ethylenesulfonate

Formation of the adduct.--To a solution of 3.0 g. (0.025 mole) of methyl ethylenesulfonate in 15 ml. of dry ether was added an equimolar amount of diazomethane in ether at room temperature. The color of diazomethane disappeared instantaneously and there formed 4.1 g. of yellow deposits, which could not be purified. A sodium fusion on the crude product indicated the presence of sulfur and nitrogen.

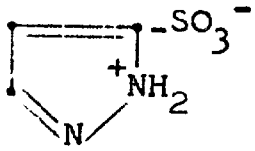
Attempted isolation of pyrazole from the adduct.--A mixture of 3.5 g. of the crude adduct in 20 ml. of 2% sodium hydroxide was refluxed for two hours, followed by ether extraction. When a saturated ethereal solution of picric acid was added to the ether extract, no pyrazole picrate separated.

E. Diazomethane and n-Butyl Ethylenesulfonate

Formation of the adduct.--To a solution of 10 g. (0.061 mole) of n-butyl ethylenesulfonate in 30 ml. of dry ether was added an equimolar amount of diazomethane in ether at room temperature. The color of diazomethane disappeared quite rapidly and the reaction was completed in three hours. When all the ether was evaporated, there remained 13.3 g. of oil, which failed to crystallize when treated with various organic solvents. It could not be distilled under vacuum. The gain in weight indicated a quantitative yield of the addition product. The addition product was characterized by bromine dehydrogenation.

Bromine dehydrogenation of the adduct.--To a solution of 3.1 g. (0.015 mole) of the crude addition product of diazomethane and n-butyl ethylenesulfonate in 35 ml. of chloroform was added a solution of 2.4 g. (0.015 mole) of bromine in 10 ml. of chloroform through a dropping funnel at room temperature. The mixture became orange in color. After five hours stirring, it was allowed to stand overnight. There formed 2.04 g. of an oily precipitate which was dissolved in absolute methanol leaving 0.13 g. of insoluble

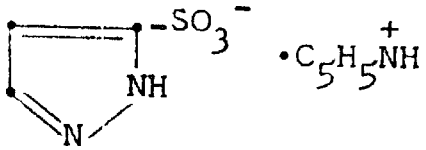
substance (V). The methanol filtrate from (V) was evaporated with a stream of air, and the crude crystalline product thus obtained was recrystallized from methanol and acetonitrile pair (insoluble in the latter), 1.6 g., it melted at 257° (dec.). A sodium fusion on the purified compound indicated the presence of sulfur and nitrogen but no bromine.



Anal. Calcd. for $C_3H_4N_2O_3S$: C, 24.32; H, 2.72; N, 18.91; N. E., 148.

Found: C, 24.42; H, 2.74; N, 17.91*; N. E., 151.6.

Pyrazoline-3-sulfonic acid was found to give a pyridine salt instantly when pyridine was dropped on the crude compound at room temperature. The salt, recrystallized from methanol and acetonitrile pair (insoluble in the latter), melted at 169-170°.



Anal. Calcd. for $C_8H_9N_3O_3S$: C, 42.28; H, 3.99; N, 18.49; N. E., 227.

Found: C, 41.85; H, 4.06; N, 18.28; N. E., 225.2.

The methanol-insoluble substance (V) was recrystallized from aqueous methanol, m.p. 238° (dec.). A sodium

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*The analyst reported that ±0.5% should be allowed for the nitrogen value.

fusion of the compound indicated the presence of sulfur and nitrogen but no bromine.

Anal. Calcd. for $C_6H_{10}N_4O_3S$: C, 32.98; H, 4.61; N, 25.77; N. E.,

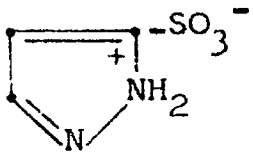
Found: C, 33.80; H, 4.67; N, 24.85; N. E., 219.

The chloroform filtrate from the impure pyrazole-3-sulfonic acid was extracted with three 20 ml. portions of water. The organic layer was concentrated under reduced pressure and the residue thus obtained was extracted with ether. The ether extract was again evaporated at room temperature and the oil thus obtained (1.5 g.) was dissolved in 10 ml. of absolute ethanol and refluxed for 45 minutes with 1 g. of powdered thiourea, followed by addition of 1 g. of picric acid. The mixture was heated until clear. Upon cooling, there formed some precipitate (0.23 g.), which after several recrystallizations from ethanol, melted at 170-172°; a mixed melting point with an authentic sample of n-butylisothiouronium picrate (m.p. 174-175°) was 171-173°.

The aqueous extracts from the above were combined and concentrated on a steam bath. The resultant solution was acidified with a few drops of hydrochloric acid followed by dropwise addition of a solution of barium chloride until no more barium sulfate was formed. There formed 1.00 g. of barium sulfate. The filtrate from the barium sulfate was made basic with sodium hydroxide followed by ether extraction. To the ether extract, which had been concentrated somewhat,

was added 2 ml. of saturated ethereal picric acid. There formed some pyrazole picrate (0.17 g.), which melted at 160° after one recrystallization from ethanol. Its melting point was not depressed on admixture with authentic pyrazole picrate.

The following is a table of products from this reaction:

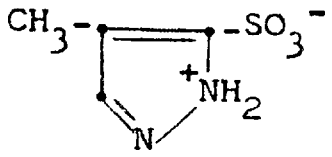
Crude addition product	 V
3.1 g. (0.015 mole)	2.04 g. (0.0138 mole, 92%) purified, 1.6 g. (0.0108 mole, 72%)

$BaSO_4$	Pyrazole picrate	n-Butyl bromide
1 g. (0.004 mole)	(qualitatively)	(qualitatively)

F. Diazomethane and n-Butyl Propene-1-sulfonate

Formation of the adduct.--To a solution of 5.3 g. (0.03 mole) of n-butyl propene-1-sulfonate in 15 ml. of anhydrous ether was added an equimolar amount of diazomethane in ether at room temperature. The reaction was completed in five hours. When the ether was evaporated, there remained 6.18 g. (0.028 mole, 95% yield) of oil, which failed to crystallize when treated with various solvents, such as ethanol, petroleum ether, acetonitrile, ethyl acetate and dioxane. Thus, the addition product was characterized by bromine dehydrogenation.

Bromine dehydrogenation of the adduct.--To a vigorously stirred solution of 3.1 g. (0.014 mole) of the impure addition product of diazomethane and n-butyl propene-1-sulfonate in 35 ml. of chloroform was added dropwise a solution of 2.2 g. (0.014 mole) of bromine in 10 ml. of chloroform at room temperature. After four hours of stirring, the mixture was allowed to stand overnight. There formed 1.5 g. of fine precipitate. After it was recrystallized from methanol-chloroform pair, 1.2 g. (0.0074 mole) of purified 4-methyl-3-pyrazolesulfonic acid was obtained which melted at 275° (with decomposition). A sodium fusion on the purified compound indicated the presence of nitrogen and sulfur and the absence of bromine.



Anal. Calcd. for $C_4H_6N_2O_3S$: C, 29.62; H, 3.73; N, 17.28; N. E., 162.

Found: C, 29.55; H, 3.66; N, 17.52; N. E., 163.

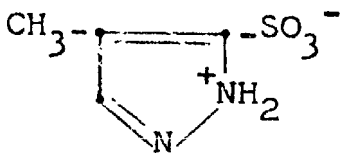
When the crude 4-methylpyrazole-3-sulfonic acid was dissolved in methanol to be recrystallized, there was 0.08 g. of methanol-insoluble substance. After two recrystallizations from water-methanol pair, it melted at 252°, mixed melting point with an authentic sample of hydrazine sulfate, 252°.

The filtrate from the impure 4-methylpyrazole-3-sulfonate was extracted with three 20 ml. portions of water.

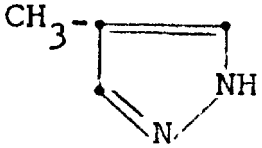
The organic layer was evaporated and the residue extracted with ether. The ether extract was then evaporated and the oil thus obtained (1.5 g.) was dissolved in 10 ml. of absolute ethanol and refluxed with 1 g. of powdered thiourea for 45 minutes, followed by addition of 1 g. of picric acid. The mixture was heated until clear. Upon cooling, there formed some precipitate (0.25 g.), which, after several recrystallizations from ethanol, melted at 170-172°; its mixed melting point with a sample of authentic n-butylisothiouronium picrate (m.p. 174-175°) was 171-173°.

The aqueous extracts were combined and concentrated on a steam bath. The resultant solution was acidified with a few drops of hydrochloric acid, followed by dropwise addition of a solution of barium chloride. There formed 1.2 g. of barium sulfate. The filtrate from the barium sulfate was made basic with sodium hydroxide and then extracted with ether. To the ether extract, which had been concentrated somewhat, was added 2 ml. of a saturated solution of picric acid in ether. There formed 0.2 g. of 4-methylpyrazole picrate, which melted at 142° after one recrystallization from ethanol (reported , m.p. 142°).

The following is a table of products obtained from this reaction:



Crude addition product		$BaSO_4$
3.1 g. (0.014 mole)	1.2 g. (0.0074 mole, 52.7% yield)	1.2 g. (0.005 mole, 36%)



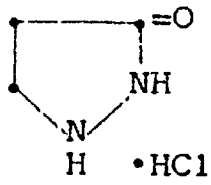
•Picric acid

	$N_2H_4 \cdot H_2SO_4$	n-Butyl bromide
0.2 g. (0.00064 mole, 4.6%)	0.08 g. (0.0006 mole, 4%)	qualitatively

G. Diazomethane and Ethylenesulfonyl Chloride

Reaction of diazomethane and ethylenesulfonyl chloride.--(1) To a solution of 4.7 g. (0.037 mole) of ethylenesulfonyl chloride in 10 ml. of anhydrous ether was added an ethereal solution of diazomethane at room temperature in small portions until the solution was tinged yellow due to a slight excess of diazomethane (0.074 mole). The color of diazomethane disappeared instantaneously after each addition and there formed 4.0 g. of white deposit on the reaction flask. There was no evolution of gas. The deposit became oily on standing and could not be purified by recrystallization. It appeared to be polymeric and gave a neutralization equivalent of 690 against standard base. A sodium fusion on the crude product indicated the presence of nitrogen, sulfur and chlorine. However, after several months standing, a part of the oil

crystallized into needles (1.00 g., 22% based on the weight of the chloride), m.p. 185-195°. After it was purified by sublimation the compound melted at 199-200°. A sodium fusion on the purified compound indicated the presence of nitrogen and chlorine but no sulfur. Its melting point was not depressed on admixture with authentic pyrazolidone hydrochloride.



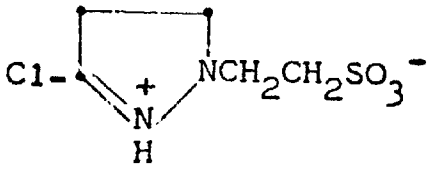
Anal. Calcd. for $C_3H_7ClN_2O$: C, 29.40; H, 5.75; N, 22.85; N. E., 122.5.

Found: C, 29.28; H, 5.89; N, 22.55; N. E., 125.0.

(2) To a solution of 2.26 g. (0.0179 mole) of ethylenesulfonyl chloride in 20 ml. of anhydrous ether was added 46 ml. of 0.194 N ethereal solution of diazomethane (0.009 mole) dropwise at room temperature (1 hour). The color of diazomethane disappeared instantaneously after each addition and there formed 0.55 g. of ether-insoluble oil on the bottom of the reaction flask. Attempts to crystallize the oil were not successful.

When 0.30 g. of the oil was dissolved in a minimum amount of water and the solution evaporated to dryness on a steam bath, there remained 0.33 g. of taffy-like residue, which appeared to be polymeric and could not be purified either by recrystallization or sublimation.

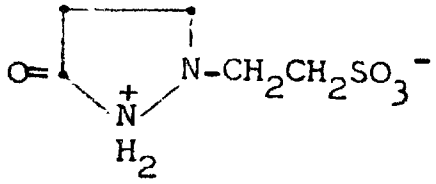
When the ether supernatant solution was evaporated under reduced pressure at room temperature, there remained 1.98 g. of viscous oil which became insoluble in ether and gave 0.94 g. of an oily solid on standing overnight. After it was recrystallized from methanol and ethyl acetate pair (insoluble in the latter), it melted at 168-169° (dec.). A sodium fusion on the purified compound indicated the presence of sulfur, nitrogen and chlorine.



Anal. Calcd. for $C_5H_9ClN_2O_3S$: C, 28.25; H, 4.27; N, 13.18; S, 15.07; Cl, 16.67; N. E., 212.

Found: C, 29.09; H, 4.39; N, 13.21; S, 14.72; Cl, 16.28; N. E., 222.

The analysis indicates presence of a small amount of 2-(1-proto-5-keto-2-pyrazolidinyl)ethanesulfonate

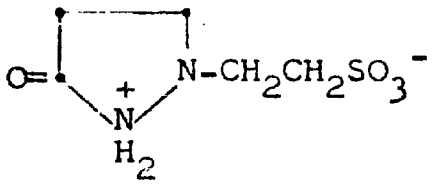


,

with a higher carbon content (30.93).

A solution of 0.74 g. of the oily solid in 5 ml. of water was evaporated to dryness; the residue, when treated with ethanol, became crystalline (0.38 g., 51% based on the weight of the oily solid) and was recrystallized from water and methanol pair (insoluble in the latter), m.p. 258-259° (dec.). A sodium fusion on the purified compound indicated

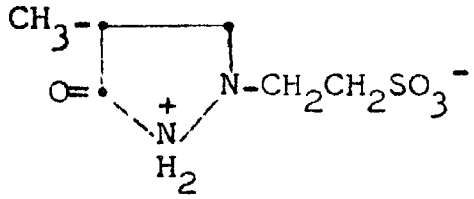
the presence of sulfur and nitrogen but no chlorine.



Anal. Calcd. for $C_5H_{10}N_2O_4S$: C, 30.93; H, 5.17; N, 14.44; S, 16.51; N. E., 194.

Found: C, 31.04; H, 5.16; N, 14.27; S, 16.41; N. E., 196.

Reaction of 4-methyl-3-pyrazolidone and n-butyl ethylenesulfonate.--A mixture of 1.0 g. (0.01 mole) of 4-methyl-3-pyrazolidone[104] and 1.65 g. (0.01 mole) of n-butyl ethylenesulfonate in 20 ml. of absolute ethanol was refluxed on a steam bath for two hours. There formed 0.60 g. (29%) of ethanol-insoluble precipitate, m.p. 271-272° (dec.). After it was recrystallized from aqueous acetonitrile, it melted at 275° (dec.).



Anal. Calcd. for $C_6H_{12}O_3S$: C, 34.61; H, 5.80; N, 13.45; N. E., 208.

Found: C, 34.39; H, 5.72; N, 13.23; N. E., 211.

H. Diazomethane and Propene-1-sulfonyl Chloride

To a solution of 4.8 g. (0.034 mole) of propene-1-sulfonyl chloride in 10 ml. of anhydrous ether was added an

ethereal solution of diazomethane at room temperature in small portions until the solution was tinged yellow due to a slight excess of diazomethane (0.68 mole). The color of the diazomethane disappeared instantaneously after each addition and there formed 2.7 g. of yellow deposit (XV), which turned into an oil on contact with moisture.

The following solvents and solvent pairs were tried in recrystallizing XV but without success:

Water, methanol, ethanol, nitromethane, acetonitrile and acetic acid (XV soluble).

Dioxane, chloroform, ethyl acetate, acetone, nitrobenzene, propanol (XV partially soluble).

Benzene, ether, petroleum ether (XV insoluble).

Ethanol and ether, aqueous methanol, aqueous ethanol, ethanol and ethyl acetate, acetic acid and sodium acetate, aqueous dioxane, benzene and acetonitrile, benzene and methanol, methanol and dioxane, carbon disulfide and chloroform, methanol and methylpropylcarbinol, chloroform and ethyl acetate.

A solid was obtained by first dissolving XV in chloroform and then scratching the oil thus formed with petroleum ether (30-60°), m.p. 65° (dec.).

Anal. Calcd. for $C_{11}H_{20}ClN_5O_2S$: C, 41.05; H, 6.26; N, 21.76; S, 9.96; Cl, 11.01; N. E., 322.

Found: C, 41.97; H, 6.28; N, 20.94;
C, 42.64; H, 6.87; N, 19.00;
C, 43.97; H, 6.57; N, 18.22;
S, 10.24; Cl, 11.63; N. E., 590.
N. E., 550.

The following attempts were made to prepare derivatives of II:

1. With phenyl isocyanate: XV was dissolved in phenyl isocyanate, but no precipitate was formed after heating on the steam bath.

2. With acetyl chloride: acetyl chloride was used in the above manner, but no results were obtained.

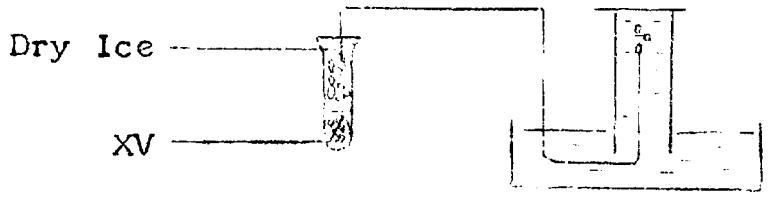
3. With picric acid: XV was dissolved in 96% ethanol (in water on another try) and the solution was treated with a saturated solution of picric acid in 95% ethanol, a momentary cloudiness (probably emulsion) appeared, but it soon settled out as dark oil drops.

4. Hydrolysis with 10% NaOH: an aqueous solution of XV was treated with 10% NaOH and boiled for a few minutes. The resultant solution was extracted with ether and the extract treated with ethereal picric acid. No precipitate was obtained except some oil.

5. Hydrolysis with 6 N HCl: XV was dissolved in 6 N hydrochloric acid and heated on a steam bath for a few minutes. The mixture was then treated with Norite and neutralized slowly with $NaHCO_3$, followed by an ether extraction. The ether extract did not give any derivative with ethereal picric acid.

6. Attempt to sublime XV: a trace of compound was obtained from 0.1 g. of XV but the results were not repeated with subsequent tries. XV decomposes slowly at 100°/0.1 mm.

7. XV heated under CO_2: about 0.22 g. of XV was placed under Dry Ice in a test tube in the following set up:



When CO_2 had completely replaced the air in the test tube, the test tube was connected with the system. At 125°, the compound rose up and liberated 7 ml. of gas.

8. With benzenesulfonyl chloride: a little of XV was dissolved in $C_6H_5SO_2Cl$, but only a tar resulted.

When the clear ether solution from XV was evaporated under reduced pressure, there remained 3 g. of yellow oil. Attempts to purify this oil were not successful.

I. Diazomethane and Propene-2-sulfonyl Chloride

To a solution of 1.3 g. (0.0074 mole) of propene-2-sulfonyl chloride in 10 ml. of anhydrous ether was added an ethereal solution of diazomethane in small portions until the solution was tinged with yellow due to a slight excess of diazomethane. There formed a small amount of deposit, which could not be purified. The reaction solution, after solvent removal, gave 1.1 g. of dark orange oil. It was soluble in acetone, acetonitrile and pyridine but failed to crystallize. Sublimation of the oil proved to be unsuccessful.

III. Addition of Phenyl Azide

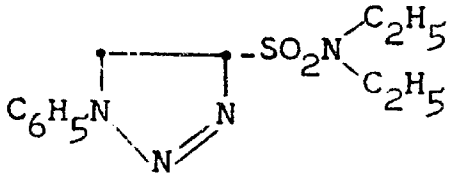
A. Preparation of Phenyl Azide[98]

A solution of 14.5 g. (0.21 mole) of reagent grade sodium nitrite in 50 ml. of water was added dropwise to a vigorously stirred mixture of 18.6 g. (0.2 mole) of freshly distilled aniline, 80 ml. of water, and 45 ml. of concentrated hydrochloric acid at 0-5°. The stirring was continued for another hour. The yellow-green solution was filtered into a 2-liter beaker surrounded by an ice bath. With stirring, a solution of 13 g. (0.2 mole) of sodium azide in 50 ml. of water was added. After all the nitrogen had been evolved (15-20 minutes), the brown oil was separated and the aqueous layer was extracted twice with 50 ml. portions of ether. All the organic layers were combined and dried over calcium chloride. After removal of ether, the residue was distilled in vacuum, b.p. 24-26°/1.5 mm. The yield of the

azide was 10.76 g. (50%) (reported, 63-60%[98], 49-50°/5 mm.[99]).

B. Phenyl Azide and N,N-Diethylethylenesulfonamide

Formation of the adduct.--A mixture of 4.32 g. (0.0266 mole) of N,N-diethylethylenesulfonamide and 3.59 g. (0.0292 mole) of phenyl azide in 25 ml. of benzene was refluxed gently for 16 hours. No solid product separated. When the residue obtained after solvent removal was vacuum distilled, 1.1 g. (30%) of phenyl azide was recovered. The residue in the distilling flask yielded 1.77 g. (31.0% based on unrecovered azide) of crystalline substance when it was cooled, m.p. 87-91°. It was recrystallized from dioxane and water pair (insoluble in the latter), m.p. 92.5-93.5°.



Anal. Calcd. for $C_{12}H_{18}N_4O_2S$: C, 51.05; H, 6.43; N, 19.85.
Found: C, 51.29; H, 6.40; N, 19.35.

Attempted dehydrogenation of N,N-diethyl-1-phenyl-1,2,3-triazoline-4-sulfonamide.--(1) p-Quinone as the dehydrogenation agent: A mixture of 0.282 g. (0.001 mole) of N,N-diethyl-1-phenyl-1,2,3-triazoline-4-sulfonamide and 0.108 g. (0.001 mole) of p-quinone in 6 ml. of benzene was kept at 80° for seven hours. It was then extracted with dilute aqueous sodium hydroxide, followed by 1% hydrochloric acid, and dried over sodium sulfate. The residue after solvent removal solidified, 0.22 g. After two recrystallizations from aqueous dioxane, it melted at 92.5-93.5°, mixed

m.p. with authentic N,N-diethyl-1-phenyl-1,2,3-triazoline-4-sulfonamide, 92-93.5°.

(2) N-Bromosuccinimide as the dehydrogenation agent: A mixture of 0.79 g. (0.0028 mole) of N,N-diethyl-1-phenyl-1,2,3-triazoline-4-sulfonamide, 0.5 g. (0.0028 mole) of N-bromosuccinimide and 10 mg. of benzoyl peroxide in 25 ml. of carbon tetrachloride was refluxed gently for 20 minutes. The mixture was then filtered from the insoluble succinimide, washed with three 10 ml. portions of water and dried over sodium sulfate. After the removal of solvent, there remained 0.70 g. of black residue from which no identifiable product could be isolated.

(3) Bromine dehydrogenation: To a vigorously stirred solution of 0.82 g. (0.00284 mole) of N,N-diethyl-1-phenyl-1,2,3-triazoline-4-sulfonamide in 15 ml. of chloroform was added a solution of 0.5 g. (0.003 mole) of bromine in 6 ml. of chloroform dropwise at room temperature. The mixture became dark red in color and some crystalline product began to separate. After an additional 2-1/2 hours stirring, the mixture was allowed to stand overnight.

The crystalline product was filtered, 0.08 g. (0.00035 mole), m.p. 270° (dec.). After two recrystallizations from methanol and ethyl acetate (insoluble in the latter), it melted at 278° (dec.). A sodium fusion on the purified compound indicated the presence of nitrogen and bromine but no sulfur.



Anal. Calcd. for $C_8H_{10}BrN_3$: C, 42.12; H, 4.42; Br, 35.04; N. E., 228.

Found: C, 41.63; H, 4.89; Br, 35.60; N. E., 220.

The chloroform filtrate from 1-phenyl-1,2,3-triazoline hydrobromide was extracted with three 10 ml. portions of water and the organic layer was evaporated under reduced pressure. There remained 0.70 g. of black tarry residue from which no identifiable product could be isolated. A sodium fusion on the residue indicated presence of nitrogen, bromine and sulfur.

The aqueous extract of the organic layer were combined and concentrated on a steam bath. To the resultant solution was added aqueous barium chloride dropwise until all the sulfate present was precipitated (0.014 g., 2.1%). The filtrate was then evaporated to dryness and the residue extracted with chloroform. After the removal of chloroform, there remained 0.26 g. (0.0017 mole, 60%) of impure diethylamine hydrobromide. It was recrystallized from 95% ethanol, m.p. 213-214°. Its mixed m.p. with an authentic sample was not depressed.

C. Phenyl Azide and N,N-Diethylpropene-1-sulfonamide

A mixture of 3 g. (0.017 mole) of N,N-diethylpropene-1-sulfonamide and 2.02 g. (0.017 mole) of phenyl azide in

20 ml. of tetrahydrofuran (peroxide-free) was refluxed for 48 hours. After solvent removal, 1 g. of phenyl azide was recovered by vacuum distillation. The residue (2.9 g.) did not crystallize nor sublime and appeared to be polymeric.

D. Phenyl Azide and n-Butyl Ethylenesulfonate

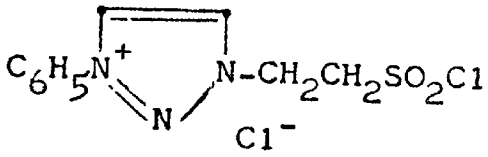
A mixture of 4.62 g. (0.03 mole) of n-butyl ethylenesulfonate and 4.5 g. (0.03 mole) of phenyl azide in 30 ml. of benzene was refluxed gently on a water bath for three and one half hours. The color turned dark. There formed about 20 mg. of precipitate, which did not show any melting point but charred around 300°. The filtrate, after removal of benzene, yielded 2 g. of unreacted phenyl azide upon vacuum distillation. Attempts to crystallize the residue by various solvents or to sublime it were not successful.

E. Phenyl Azide and n-Butyl Propene-1-sulfonate

A mixture of 2 g. (0.011 mole) of n-butyl propene-1-sulfonate and 1.5 g. (0.01 mole) of phenyl azide was allowed to stand at room temperature for six months. The mixture turned dark, and gradually there formed some black precipitate. After one recrystallization from methanol and acetonitrile pair (insoluble in the latter), the dark brown compound melted at 245°. The compound weighed 0.5 g. and became insoluble in water or methanol on standing. Further purification proved to be unsuccessful.

F. Phenyl Azide and Ethylenesulfonyl Chloride

Formation of the adduct.--To a solution of 3 g. (0.025 mole) of phenyl azide in 10 ml. of benzene was added 6 g. (0.05 mole) of ethylenesulfonyl chloride in small portions. After half an hour, there appeared some precipitate. The reaction was mildly exothermic and completed itself in five hours. The yield of the crude addition product was 6.7 g. (98%), based on two moles of chloride to one mole of azide*, which melted at 120-127°. When it was recrystallized from methanol and ethyl acetate pair (insoluble in the latter) three times, the melting point became 129-130°. A sodium fusion on the purified compound indicated the presence of sulfur, nitrogen and chlorine.



Anal. Calcd. for $C_{10}H_{11}Cl_2N_3O_2S$: C, 38.87: H, 3.7[illegible] N, 13.60; S, 10.38; Cl, 22.95; N. E., 154.

Found: C, 38.67; H, 5.01; N, 14.05; S, 10.66; Cl, 15.90; N. E., 170, 180, 140.**

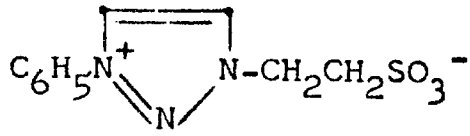
The addition product was easily converted into a new compound, containing no chlorine, during recrystallization. When a solution of 0.36 g. of the crude adduct (m.p. 120-127°)

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*In previous runs, one mole of azide per mole of double bond as well as two moles of azide per mole of double bond were reacted. However, the products were the same in all cases.

**The chlorine analysis was done on a different analytical sample which had probably partially decomposed to the sulfonate. The N. E. varies according to the age of the sample.

in 10 ml. of water was evaporated to dryness, there formed 0.27 g. (91%) of crystalline residue. It was also recrystallized from methanol and ethyl acetate. The purified product melted at 215-216° and was not titratable.



Anal. Calcd. for $C_{10}H_{11}N_3O_3S$: C, 47.43; H, 4.38; N, 16.59; S, 12.66.

Found: C, 47.49; H, 4.61; N, 16.62; S, 13.04.

Addition of 1-phenyl-1,2,3-triazole to ethylenesulfonyl chloride.--A mixture of 1.45 g. (0.01 mole) of 1-phenyl-1,2,3-triazole and 1.26 g. (0.01 mole) of ethylenesulfonyl chloride in 15 ml. of benzene was refluxed gently on a steam bath for six hours. There formed 2.7 g. (99.8%) of crystalline substance from the reaction mixture, m.p. 195-202°. After it was treated with Norite and then recrystallized from methanol and ethyl acetate pair (insoluble in the latter), the compound melted at 215-216°; its melting point was not depressed on admixture with previously obtained 2-(1-phenyl-1-proto-1,2,3-triazol-3-yl)ethanesulfonate.

Reaction of 1-phenyl-1,2,3-triazole with acrylonitrile.--A mixture of 1.45 g. (0.01 mole) of 1-phenyl-1,2,3-triazole and 0.53 g. (0.01 mole) of acrylonitrile in 25 ml. of benzene was refluxed on a steam bath for seven hours. No solid product separated. After solvent removal, there remained

1.36 g. of residue, which solidified at room temperature, m.p., 51-54°. After it was recrystallized from ether, it melted at 53-55°; mixed m.p. with authentic 1-phenyl-1,2,3-triazole, 52-55° (94% recovery).

Reaction of 1-phenyl-1,2,3-triazole with glacial acrylic acid.--A mixture of 1.45 g. (0.01 mole) of 1-phenyl-1,2,3-triazole and 0.72 g. (0.01 mole) of glacial acrylic acid in 25 ml. of benzene was refluxed on a steam bath for 11 hours. No solid product separated. After solvent removal, there remained 1.34 g. of residue, which solidified upon cooling. After it was recrystallized from ether, it melted at 53-55°; mixed m.p. with authentic 1-phenyl-1,2,3-triazole, 53-54° (92.5% recovery).

Reaction of 1-phenyl-1,2,3-triazole with methanesulfonyl chloride.--A mixture of 1.45 g. (0.01 mole) of 1-phenyl-1,2,3-triazole and 1.14 g. (0.01 mole) of methanesulfonyl chloride in 25 ml. of benzene was refluxed for 12 hours on a steam bath. No solid product separated. After solvent removal, there remained 1.63 g. of residue, which partially solidified at 0° C. The mixture was filtered cold and 1.30 g. of 1-phenyl-1,2,3-triazole was recovered (90% recovery), m.p. 55-56°; mixed m.p. with an authentic sample was 55-56°.

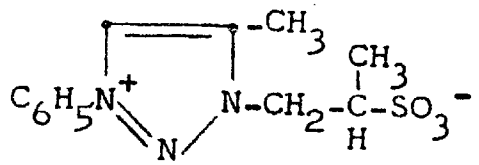
G. Phenyl Azide and Propene-1-sulfonyl Chloride

A mixture of 3.5 g. (0.025 mole) of propene-1-sulfonyl chloride and 3 g. (0.02 mole) of phenyl azide in 25 ml. of benzene was refluxed gently for three hours. The solution

turned dark. After removal of the solvent, 1.5 g. of phenyl azide was recovered by vacuum distillation. The dark viscous residue, soluble in methanol, ethanol, partially in acetone and water, could not be recrystallized or sublimed.

H. Phenyl Azide and Propene-2-sulfonyl Chloride

To a solution of 0.5 g. (0.0042 mole) of phenyl azide in 15 ml. of chloroform was added 1.2 g. (0.0085 mole) of propene-2-sulfonyl chloride in small portions. The mixture was then refluxed on a steam bath for six hours. When the solvent was removed, there remained 1.4 g. of dark oil, which, upon cooling in an ice bath, yielded 0.5 g. (0.00187 mole, 45% based on one mole of phenyl azide and two moles of the chloride) of solid product melted at 240-260° (dec.). After three recrystallizations from hot ethanol, the compound melted at 268° (dec.). A sodium fusion on the purified compound indicated the presence of sulfur and nitrogen but no chlorine. It was not titratable against standard sodium hydroxide solution.

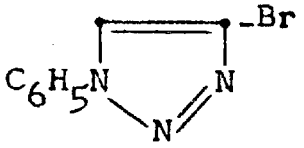


Anal. Calcd. for $C_{12}H_{15}N_3O_3S$: C, 51.23; H, 5.37; N, 14.93.
Found: C, 51.08; H, 5.62; N, 14.61.

I. Phenyl Azide with 1-Bromoethene-1-sulfonyl Chloride[72,100]

To a solution of 0.6 g. (0.005 mole) of phenyl azide in 15 ml. of chloroform was added 1.02 g. (0.005 mole) of

1-bromoethene-1-sulfonyl chloride in small portions. The mixture was then refluxed gently for one hour on a steam bath. After the solvent was removed by an air stream, there remained 0.50 g. (0.0022 mole, 45%) of solid product, m.p. 117-120°. After it was recrystallized several times from aqueous methanol, it melted at 121.5-122.5° (0.38 g.). A sodium fusion on the purified compound indicated the presence of nitrogen and bromine but no sulfur.



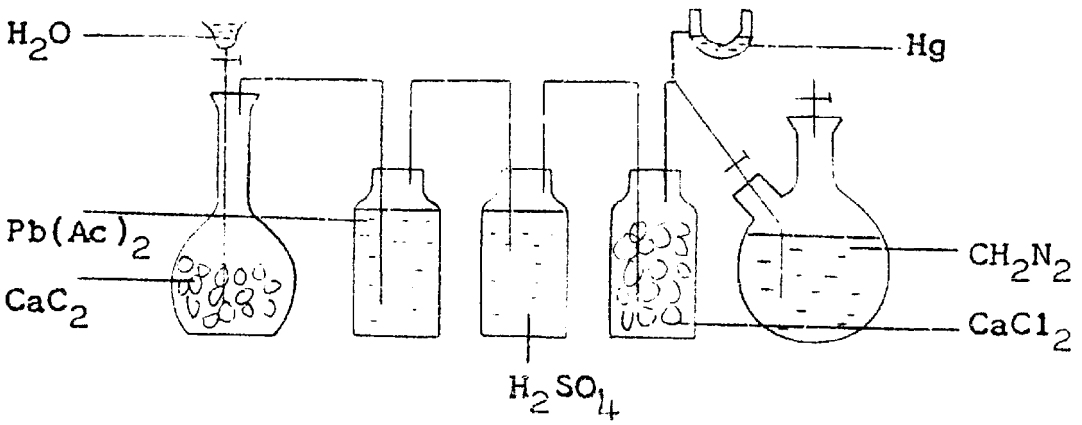
Anal. Calcd. for $C_8H_6BrN_3$: C, 42.88; H, 2.69; N, 18.75.
Found: C, 42.94; H, 2.74; N, 18.87.

The reaction of two moles of 1-bromoethene-1-sulfonyl chloride with one mole of phenyl azide was not attempted.

IV. Syntheses of Model Compounds for Spectroscopic Comparisons

A. Pyrazole and Its Derivatives[2]

Pyrazole.--In a 2-liter round-bottomed flask was placed 200 ml. of 0.3 N diazomethane in ether solution. The flask was connected to an acetylene generator and equipped with a gas outlet as shown in the following diagram:



The system was swept with acetylene and the flask was filled with a slight excess pressure of acetylene while it was kept in an ice bath. The flask was disconnected from the system and kept in the ice box at night. This process was continued for one week until the color of diazomethane disappeared. The ether was then evaporated on standing and 2 g. (50% of the theoretical) of pyrazole was obtained. It melted at 68-70°. Its U. V. spectrum showed no maximum above 2200 Å.

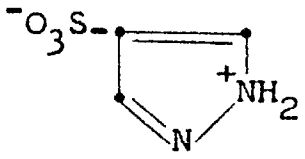
Pyrazole hydrochloride.--A little pyrazole was dissolved in 5 ml. of dry ether and dry hydrogen chloride was bubbled through the solution. The hygroscopic pyrazole hydrochloride precipitated immediately. After it was dried over potassium hydroxide in a vacuum desiccator it melted at 93-102°.

Pyrazole picrate.--Some of the pyrazole hydrochloride was dissolved in water and the solution was made basic with a few drops of sodium hydroxide solution. The basic solution was then extracted with ether. To the ether extract was added a few drops of ethereal picric acid. Pyrazole picrate precipitated as yellow crystals. It melted at 160-161° after one recrystallization from ethanol.

B. 4-Pyrazolesulfonic Acid

4-Pyrazolesulfonic acid was prepared by the procedure of Morgan and Ackerman[41] for the sulfonation of 3,5-dimethylpyrazole. A mixture of 0.7 g. (0.0104 mole) of pyrazole in 3.3 ml. of fuming sulfuric acid was heated on a steam bath

for five hours. It was then diluted with water and the resultant solution neutralized with powdered barium carbonate. The filtrate from the barium sulfate was evaporated to dryness and the residue was extracted with hot water. The water extracts were combined and acidified with dilute sulfuric acid until no more barium sulfate precipitated. The filtrate was evaporated on a steam bath and there formed 1.1 g. (73%) of crystalline product. It was recrystallized from water and melted at 345° (dec.).



Anal. Calcd. for $C_3H_4N_2O_3S$: C, 24.32; H, 2.72; N, 18.91; N. E., 148.

Found: C, 24.16; H, 2.85; N, 18.96; N. E., 154.

C. Methyl 3-Pyrazolecarboxylate

To a solution of 2.3 g. (0.033 mole) of propiolic acid in 20 ml. of ether was added an ethereal solution of diazomethane until there was a faint yellow coloration due to a slight excess of diazomethane. When the ether was evaporated, there formed 2.2 g. (53%) of white crystalline compound with a melting point of 135-144°. After two recrystallizations from hot water; it melted at 141° (reported[23] m.p. 141°). Its ultraviolet spectrum showed no maximum above 2200 Å.

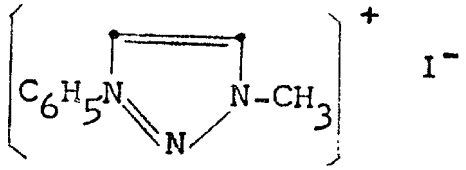
D. 1-Phenyl-1,2,3-triazole and Its Derivatives

1-Phenyl-1,2,3-triazole-4-carboxylic acid.--A mixture of 1.6 g. (0.0138 mole) of phenyl azide, 0.97 g. (0.0138 mole) of propiolic acid and 30 ml. of chloroform was refluxed for sixteen hours on a steam bath. When the solvent was removed, there remained 2.6 g. of oil which solidified into a white crystalline compound upon cooling, m.p. 160°. After two recrystallizations from ethanol, it melted at 141°, indicating that the product is perhaps a mixture of 1-phenyl-1,2,3-triazole-4-carboxylic acid and 1-phenyl-1,2,3-triazole-5-carboxylic acid. It showed a neutral equivalent of 205 against standard sodium hydroxide solution (calcd. 189). The yield of the crude product was quantitative.

1-Phenyl-1,2,3-triazole.--1-Phenyl-1,2,3-triazole-4-(or 5)-carboxylic acid, 0.1 g., was heated at 150° and the oil thus obtained was dissolved in ether. After removal of ether, there formed 0.05 g. of crystals which melted at 48-52.5°. After a recrystallization from hot water, it melted at 53-55° (reported[101], 55-56°). The yield of the crude 1-phenyl-1,2,3-triazole from the corresponding carboxylic acid was 64% of the theoretical.

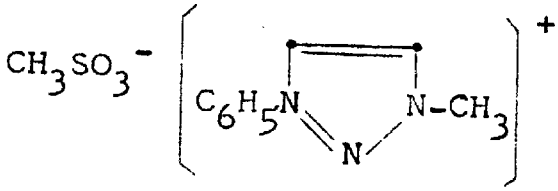
1-Phenyl-3-methyl-1,2,3-triazolium iodide.--1-Phenyl-3-methyl-1,2,3-triazolium iodide was prepared by the method of Wiley and Moffatt[63] in which they methylated 1-benzyl-1,2,3-triazole. A mixture of 1.05 g. (0.0725 mole) of 1-phenyl-1,2,3-triazole, 1 ml. of methyl iodide, 6 ml. of acetone and 5 ml. of dry ether was allowed to stand at room temperature.

After 24 hours, white needles began to separate (0.46 g.), m.p. 130-135°. After two recrystallizations from acetone and ethyl acetate pair (insoluble in the latter), it melted at 134.5-135.5°. The separation of the needles continued for two and one half weeks; total yield, 171 g. (83.5%).



Anal. Calcd. for $C_9H_{10}IN_3$: C, 37.65; H, 3.55; N, 14.63.
Found: C, 37.84; H, 3.52; N, 14.71.

1-Phenyl-3-methyl-1,2,3-triazolium methanesulfonate.--To a solution of 0.32 g. (0.011 mole) of 1-phenyl-3-methyl-1,2,3-triazolium iodide in 8 ml. of water was added a neutral solution of silver methanesulfonate dropwise until no more silver iodide precipitated. The filtrate, together with the washings of the silver iodide, were evaporated. The colorless liquid residue (0.36 g.) obtained was dissolved in methanol, followed by evaporation at room temperature; there formed 0.20 g. (72.8%) of crystals, m.p. 144-148°. After two recrystallizations from methanol and ethyl acetate pair (insoluble in the latter) it melted at 148-149.5°.



Anal. Calcd. for $C_{10}H_{13}N_3O_3S$: C, 47.05; H, 5.11.
Found: C, 47.09; H, 5.07.

1-Phenyl-1,2,3-triazole hydrobromide.--Anhydrous hydrogen bromide was bubbled through a solution of 0.5 g. (0.00345 mole) of 1-phenyl-1,2,3-triazole in 15 ml. of anhydrous ether. There precipitated immediately 0.76 g. (0.00336 mole, 97.4%) of white substance. After it was recrystallized twice from methanol and ethyl acetate (insoluble in the latter), it melted at 76-77°, N. E., 225.5 (M. W. 226).

F. 3-Pyrazolidone and Its Salts

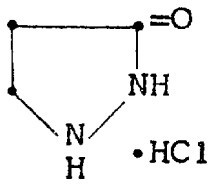
3-Pyrazolidone.--The only reference to this compound was by Rothenburg[102] who reported that 3-pyrazolidone was prepared by mixing hydrazine hydrate and acrylic acid. However, all attempts to repeat his experiments proved to be unsuccessful, including an experiment where β-bromopropionic acid was used in place of acrylic acid. Thus, the following procedure was worked out:

In a 100 ml. round-bottomed flask, fitted with a reflux condenser, were cautiously mixed 11.0 g. (0.34 mole) of anhydrous hydrazine and 29.0 g. (0.338 mole) of methyl acrylate. The mixture was kept at 80° for 24 hours until the characteristic odor of the ester disappeared. The viscous liquid remaining after removal of low boiling products was distilled; the yield of acryl hydrazide was 10.52 g. (27%), b.p. 136-140°/0.4 mm. It gave positive tests for unsaturation and condensed readily with acetone yielding a product melting at 78-81°. An attempt was made to cyclize the hydrazide by boiling it with glacial acetic acid; however, only acetyl hydrazide was obtained which gave acetone-

acetylhydrazone when treated with acetone, m.p. 133° (reported[103] 133°).

After a few days standing, the hydrazide appeared to have undergone cyclization and no longer gave a condensation product with acetone. No attempt was made to purify the pyrazolidone.

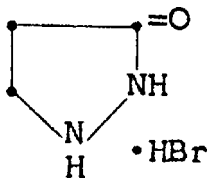
3-Pyrazolidone hydrochloride.--The crude pyrazolidone, 4.0 g., was dissolved in concentrated hydrochloric acid and the mixture was evaporated to dryness. The solid residue was extracted with absolute ethanol in a Soxhlet extractor for four hours. The ethanol extract was then evaporated to dryness under reduced pressure, and the residue (1.1 g.) thus obtained sublimed at 100°/0.05 mm. There formed 0.20 g. of white needles, m.p. 190°-200° (3.4% yield based on the hydrazide).



Anal. Calcd. for $C_3H_7ClN_2O$: C, 29.40; H, 5.75; N, 22.85; Cl, 29.01; N. E., 122.5.

Found: C, 29.60; H, 5.66; N, 23.05; Cl, 29.02; N. E., 126.0.

3-Pyrazolidone hydrobromide.--In a similar experiment, pyrazolidone hydrobromide was obtained by replacing hydrochloric acid with hydrobromic acid, m.p. 205-206° (2.5% yield based on the hydrazide). Its melting point on admixture with the pyrazolidone hydrobromide isolated in reaction IIB (page 85) was not depressed and their infrared spectra are identical.



Anal. Calcd. for $C_3H_2BrN_2O$: Br, 47.85; N. E., 167.
Found: Br, 47.68 (Volhard);
N. E., 162.5.

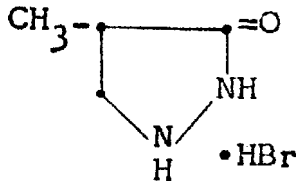
G. 4-Methyl-3-pyrazolidone and Its Salts[104]

4-Methyl-3-pyrazolidone.--In a 100 ml. round-bottomed flask, fitted with a reflux condenser, were placed 35 g. (0.30 mole) of ethyl methacrylate and 11 g. (0.34 mole) of anhydrous hydrazine (two layers). The mixture was kept at 80° by means of a water bath. With occasional shaking, the mixture suddenly came to a boil and the layers disappeared. The mixture was kept at 80° for another three hours to insure complete reaction. The viscous liquid residue remaining after removal of low boiling by-products was distilled; the yield of the pyrazolidone was 21.5 g. (71.7%), b.p. 114-117°/0.2 mm. (reported[104], 162°/12 mm.).

4-Methyl-3-pyrazolidone hydrochloride.--A little 4-methyl-3-pyrazolidone was dissolved in 5 ml. of hydrochloric acid and the mixture evaporated to dryness. After the impure 4-methyl-3-pyrazolidone hydrochloride was recrystallized twice from absolute alcohol, it melted at 177-179° (reported[104] 178°).

4-Methyl-3-pyrazolidone hydrobromide.--A little 4-methyl-3-pyrazolidone was dissolved in 5 ml. of concentrated

hydrobromic acid and the mixture was evaporated to dryness. The impure 4-methyl-3-pyrazolidone hydrobromide was recrystallized from alcohol, m.p. 168-169°.



Anal. Calcd. for $C_4H_{10}BrN_2O$: Br, 43.90; N. E., 182.05.
Found: Br, 43.56 (Volhard);
N. E., 187.5.

SUMMARY

The additions of diazomethane and phenyl azide to ethylenesulfonyl chloride, propene-1-sulfonyl chloride, their corresponding N,N-diethyl amides and n-butyl esters, and propene-2-sulfonyl chloride as well as the reaction between phenyl azide and 1-bromoethene-1-sulfonyl chloride were investigated. The reactivity of the conjugated double bond has been shown to be greatest in the chlorides, next in the esters, and the least in the amides. Diazomethane was found to be more reactive than phenyl azide in the addition to the double bond. A β-methyl group exerts an inhibiting effect on the addition reaction; the effect is greatest in the amides, next in the esters, and least in the chlorides and it is more pronounced with the phenyl azide additions than with diazomethane additions.

Diazomethane reacts with the α,β-unsaturated sulfonic acid derivatives to give the expected 3-sulfopyrazolines, the stabilities of which vary according to the sulfonyl group. The oily pyrazolines from diazomethane and the unsaturated sulfonamides and sulfonate esters (formed in almost quantitative yields), were characterized by bromine aromatization to the corresponding pyrazoles. However, a pronounced tendency for concurrent cleavage by the hydrogen bromide liberated was observed. Pyrazoline-3-N,N-diethylsulfonamide gave 56% of the normal aromatization product, pyrazole-3-N,N-diethylsulfonamide and 32% of 3-pyrazolidone hydrobromide (with

equivalent amount of diethylamine hydrobromide and sulfate) as the result of cleavage at the sulfur-carbon bond. 4-Methylpyrazoline-3-N,N-diethylsulfonamide gave 59% of 4-methylpyrazole-3-N,N-diethylsulfonamide, a trace of 4-methyl-3-pyrazolidone and 18% of diethylamine and equivalent sulfate. n-Butyl pyrazoline-3-sulfonate and n-butyl 4-methylpyrazoline-3-sulfonate undergo cleavage more readily at the ester link and gave the corresponding 3-pyrazolesulfonic acid in 72% and 52% yield respectively. n-Butyl bromide, sulfate and a trace of pyrazole or 4-methylpyrazole were the other products. In excess diazomethane, the pyrazoline from ethylenesulfonyl chloride decomposes spontaneously into 3-pyrazolidone hydrochloride, however, in the absence of excess diazomethane, the pyrazolidone adds to a second mole of ethylenesulfonyl chloride to give 2-(1-proto-5-keto-2-pyrazolidinyl)-ethanesulfonate (VIII).

The α,β-unsaturated sulfonic acid derivatives containing a β-methyl and n-butyl ethylenesulfonate did not give adducts with phenyl azide. N,N-diethylethylenesulfonamide gave the corresponding triazoline (45%) which is stable and did not aromatize to the triazole when treated with bromine. α-Bromoethylenesulfonyl chloride also gave the expected triazoline but it aromatizes spontaneously with expulsion of the chlorosulfonyl group to give 1-phenyl-4-bromo-1,2,3-triazole (45%). The triazolines from ethylenesulfonyl chloride and propene-2-sulfonyl chloride were not isolable as such owing to their extreme reactivity. They

add to a second mole of the chlorides in the Michael fashion and 2-(1-proto-1-phenyl-1,2,3-triazol-3-yl)-ethanesulfonate and 1-(1-proto-1-phenyl-4-methyl-1,2,3-triazole-3-yl)-propane-2-sulfonate were obtained in 100% and 45% yield respectively.

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