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THE SYNTHESIS AND SOLVOLYSIS OF
(1α, 2β, 5β, 6α, 7β)-TRICYCLO-[4.3.2.$0^{2,5}$]-
UNDECA-3,8,10-TRIENE-7-ol: AN UNUSUAL $(CH)_{11}$
REARRANGEMENT.

The University of Michigan, Ph.D., 1975
Chemistry, organic

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THE SYNTHESIS AND SOLVOLYSIS OF (1α, 2β, 5β, 6α, 7β)-TRICYCLO-[4.3.2.$0^{2,5}$]-UNDECA-3,8,10-TRIENE-7-ol: AN UNUSUAL $(CH)_{11}$ REARRANGEMENT

by

Christian Albert Bernhardt

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Chemistry)
in The University of Michigan
1975

Doctoral Committee:

Assistant Professor John T. Groves, III, Chairman
Professor Rowland H. Davis
Professor Richard G. Lawton
Professor Michael M. Martin
Associate Professor Paul G. Rasmussen

DEDICATION

To Sharon,

my love, friend and wife

ACKNOWLEDGEMENTS

It is with a great deal of pleasure that I acknowledge those people who helped me immeasurably in the attainment of the Ph.D. degree.

To Jay Groves, whose friendship and patience afforded me the opportunity to learn, thank you.

I want to thank my committee members, who helped with their constructive criticism of this work. The personal contributions of Professors Dauben, Martin and Wiseman will always be remembered.

I want to acknowledge the friendship and many helpful discussions which I had with my good friend Matt Ebner and the other members of my research group.

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To those friends and associates, whom I have sub-consciously forgotten to mention, thank you.

Sharon, my best friend and wife, deserves this thesis as much as I, as she saw the light at the end of the tunnel and remained my friend when things looked their worst, thank you, my love.

C.A.B.

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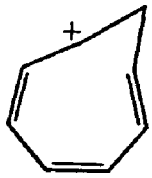
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INTRODUCTION:

The concept of aromaticity[1] has maintained the current interest in non-benzenoid $(CH)_n$ systems. Winstein[2] first recognized that the reactivity of ions derived from molecules, which contained a Hückel set of electrons (4n + 2) that were no longer contiguous due to intervening carbon atoms (defined as homo-interactions), could best be explained by invoking aromatic character to those ions. The homotropylium ion 1[3] and the bishomocyclopentadienide anion 2[4] are just two examples of this behavior.

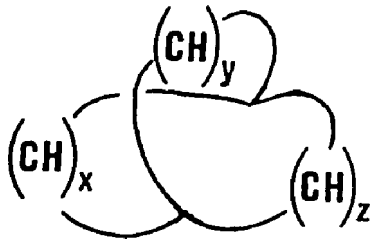


1



2

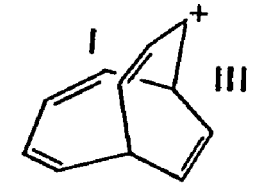
These concepts were elaborately extended by Goldstein and Hoffmann[5] to include the topology of $(CH)_n$ bicyclic (x, y, z) systems (longicycles in their terminology).



The predicted[5] electronic behavior of these bicyclic $(CH)_n$ systems can be quite simply and effectively viewed as the sum of the Hückel electronic behavior on each of the three faces: $(CH)_x$-$(CH)_y$, $(CH_x$-$(CH)_z$, and $(CH)_y$-$(CH)_z$.

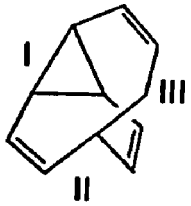
The bicyclic $(CH)_7^{+6}$, $(CH)_8^{7}$, $(CH)_9^{+8}$, $(CH)_9^{-8}$ and $(CH)_{10}^{9}$ manifolds have been extensively investigated, whereas similar efforts to determine the relative importance of electronic and conformational effects in the $(CH)_{11}^{+}$ system, have, until recently,[11] been wanting.

The 4,3,$^{+}$2 cation (3)[5] and the homobullvalenyl cation (4) represent two theoretically predicted bicycloaromatic species, when they are compared to their isoelectronic cyclic counterpart 5.



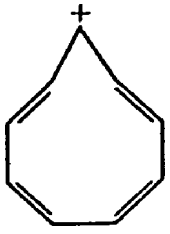
3

$\sum_{I}^{III}$ = +



4

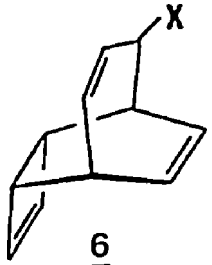
$\sum_{I}^{III}$ = +3



5

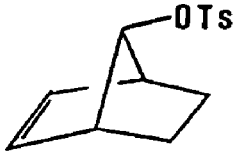
4n ⟶ −

The tricyclic triene 6 is of interest as it represents a potentially novel synthetic entry to either the bicyclic cation 3 or the tricyclic cation 4, and it affords the opportunity to examine the relative reactivities of a π bond and a cyclobutene sigma bond to a spatially proximate allylic cation.



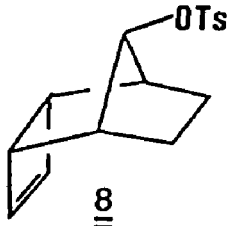
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The relative reactivities of a π and cyclobutene sigma bond to a proximate secondary cation are known from the work in the 7-norbornyl system by Winstein.[12]



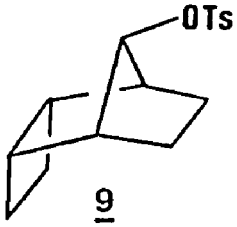
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10^{11}



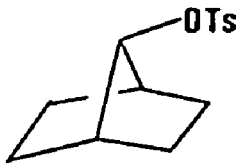
8

$10^{5.8}$



9

$10^{4.3}$



10

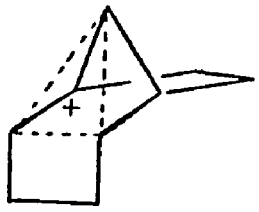
10^{0}

The enhanced reactivity and products isolated from the acetolysis of the anti-norbornene 7 were viewed as the contribution of the bishomocyclopropenyl cation 11 (aromatic) early in the transition state for the solvolysis of 7.



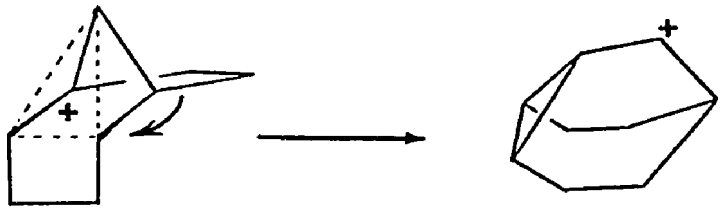
11

The lower relative reactivity of the cyclobutene and cyclobutane σ bond in the tosylates 8 and 9 relative to the 7-norbornene 7, but enhanced reactivity relative to 10 and the products isolated from the acetolysis of the cyclobutane 7-norbornyl tosylate 9, can be interpreted as the result of the differing polarizability of a π bond versus a σ bond and the formation of a bishomocyclopropenyl cation 12 in the solvolysis of 8 and 9.



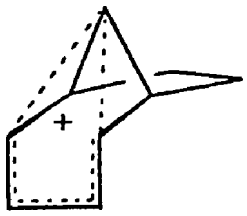
12

The major product isolated from the solvolysis of the cyclobutane-7-norboryl tosylate 9, 9-tetrahydrobarbaralylacetate (13) supported the intermediacy 12, as it would result from a Wagner-Meerwein shift in 12.



12 13

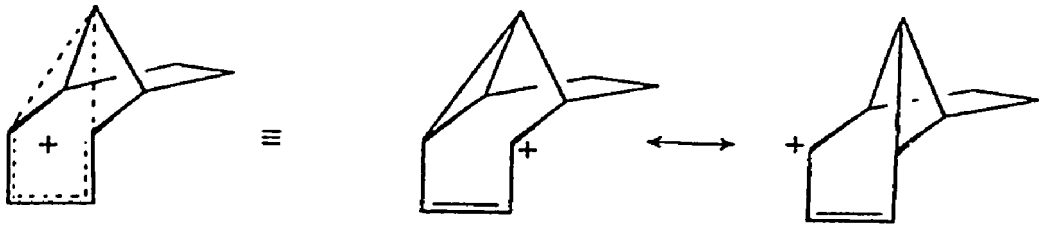
The enhanced reactivity of the cyclobutene 7-norboryl tosylate 8 ($10^{5.8}$) relative to the cyclobutane analog 9 ($10^{4.3}$) is very interesting as it can be interpreted in one of two ways. If the π bond is participating in the delocalization of the positive charge at C-7 in 8, it would be expected a priori to suppress its reactivity, as it is a destabilizing 4n interaction.



8

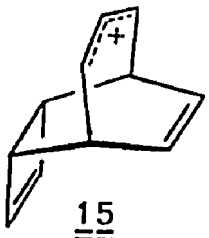
In this context, it would be concluded that the π bond in 8 is not participating in the delocalization of charge at C-7.

The greater reactivity of the cyclobutene 7-norbornyl tosylate 8 can be viewed in an alternative manner. The π bond in the cyclobutene is indeed participating in the delocalization of charge at C-7, but that the expected destabilization in 8 is compensated for by the greater relief of strain found in the cyclobutene and the stabilization of the resonance form, the allylic cation 14.



14 14

The cation derived from the tricyclic triene 6, 15, is of particular interest with respect to the known chemistry of the norbornyl system,as it is the vinylog of that norbornyl system.



15

As the vinylog, 15 would be expected to exhibit inverse reactivity to that found in the norbornyl system. Interaction of the polarizable π bond in the 2 bridge of 15 with the proximate allylic bridge should be greatly suppressed as it represents a destabilizing 4n bishomo interaction. If the π bond of the cyclobutene group in the tricyclic cation 15 is involved in the delocalization of charge by the σ bond, the reactivity of the σ bond should be greatly enhanced as it represents a stabilized 4n + 2 bishomotropylium species.

On the other hand, if the π bond of the cyclobutene is not involved in the participation of the cyclobutene σ bond, previously found in the norbornyl system, its interaction with the proximate allylic cationic system will mirror that of the π bond in the two bridge. In this case, predicting the outcome of two potentially destabilizing, competing interactions is less than obvious, with the

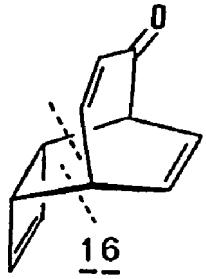
distinct possibility of delineating previously unobserved reactivities of destabilizing interactions.

RESULTS AND DISCUSSION

I. Synthesis of tricyclo-[4.3.2.$0^{2,5}$]-undeca-3,8,10-triene-7-one (16).

A. Four carbon annelation of tropone with cyclobutadiene.

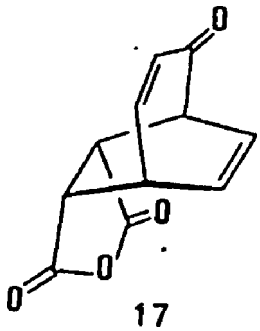
A direct approach to the synthesis of the enone 16, the logical precursor of the interesting tricyclic triene 6, is the Diels-Alder 4-carbon annelation of a 7 carbon unit.



16

(4 + 7)

The Diels-Alder reaction between maleic anhydride and tropone was known to give 17 in good yield,[13] which indicated

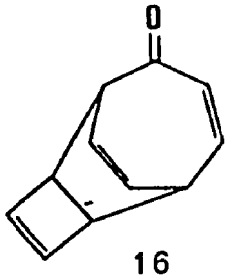


17

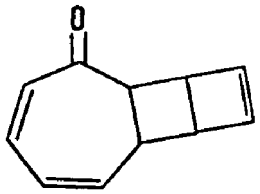
that tropone would function as a diene with a reactive dieneophile.

With this in mind, cyclobutadiene was an obvious candidate for reaction with tropone. When cyclobutadiene was generated *in situ*[14] from the ceric ion oxidation of excess cyclobutadieniron tricarbonyl in the presence of freshly distilled tropone, only one volatile product was detected by analytical glpc. After a careful chromatography, a 14% yield (tropone as the limiting reagent) of a 1:1 adduct (m/e: 158) was isolated.

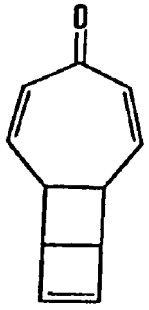
Four 1:1 adducts, consistent with the six vinyl and four bridgehead protons found in the pmr spectrum, containing a cyclobutene group (pmr: 6 δ, s 2H; ir: 1560 cm^{-1}) [15] are possible.



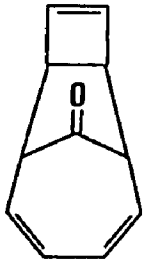
16



18



19



20

From the spectral data, it was possible to prove the structure of the 1:1 adduct. The presence of an α-β unsaturated carbonyl (ir: 1680 cm^{-1}) eliminates 20 as a possibility. The lack of symmetry exhibited in the pmr spectrum with only one α-β unsaturated carbonyl unit present (7.0 δ; d,d; 1H): 5.7 δ; d,d; 1H) excludes 19 from consideration. The spin decoupled spectrum revealed that the β-carbon of the α-β unsaturated carbonyl unit was adjacent to a bridgehead proton, leaving 16 as the only remaining viable structure.

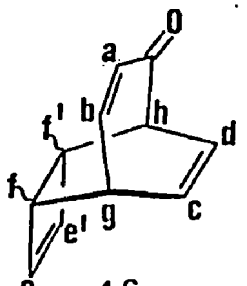
Both the coupling constants and chemical shifts found in the pmr spectrum of the enone 16 give excellent agreement with those found in the model compounds listed in Table II.

The allylic alcohol 21 (ir: 3540, 3400, 1025 cm^{-1}) was obtained in excellent yield from the low temperature reduction of enone 16 with lithium aluminum hydride in anhydrous ethylether. The spectral data of 16 left the stereochemical relationship of the 4 and 3 bridge in doubt. By analysis of the europium shifted pmr[18] spectrum, in conjunction with the spin decoupled spectrum of the allylic alcohol 21, it was possible to definitely assign the stereochemistry of both the 4 bridge and the alcohol.

The spin decoupled spectrum and the europium shifted data when analyzed separately, each assign the protons in the allylic alcohol 21, as indicated. Only in the instance of the cyclobutene hydrogens, e and f, was the data used

Table I

pmr Spectrum of Enone 16

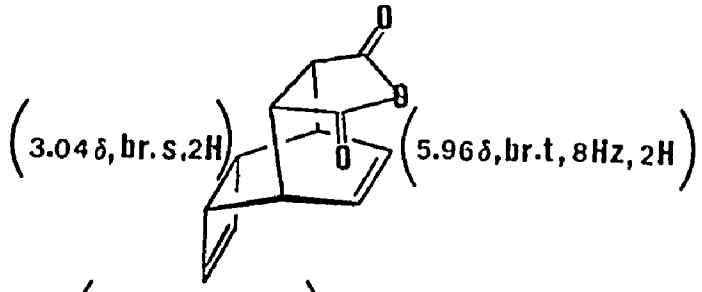


16

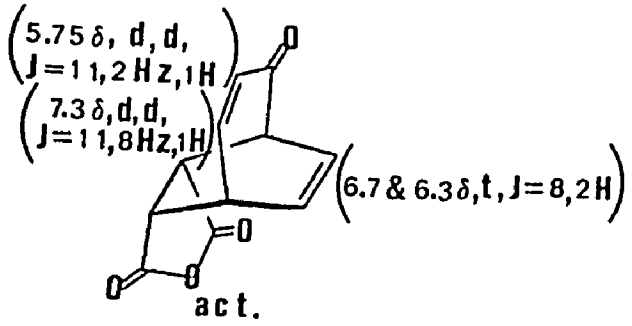
δ	a	b	c	d	e,e'	f,f'	g	h	apparent multiplicity
a	5.7	11 Hz					2 Hz		d,d
b	11 Hz	7.0					8 Hz		d,d
c			6.2	8 Hz			8 Hz		t
d			8 Hz	5.9				8 Hz	t
e,e'					6.0				s
f,f'						3.18			br s
g	2 Hz	8 Hz	8 Hz				3.25		t
h				8 Hz				3.44	d

Table II

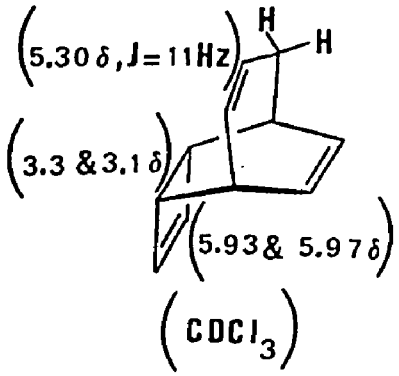
Tricyclic Model Compounds



$CDCl_3$



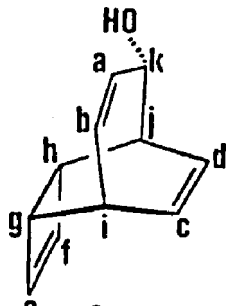
17



26

Table III

pmr Data of Allylic Alcohol 21



21

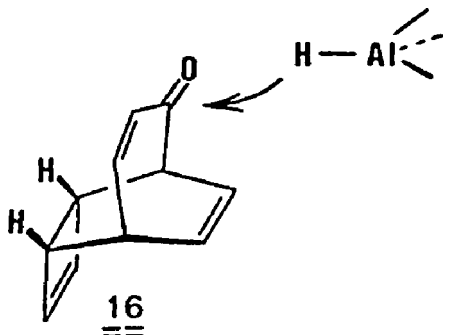
(CCl_4)

δ	a	b	c	d	e	f	g	h	i	j	k	apparent multiplicity	Δδ ppm
a	5.24	11 Hz							3 Hz		2.5 Hz	d,t	1.35
b	11 Hz	5.8							8 Hz				0.8
c			6.10	8 Hz					8 Hz			t	0.3
d			8 Hz	5.72						8 Hz		t	0.6
e					5.96	2.7 Hz						d	0.28
f					2.7 Hz	5.80						d	0.35
g							3.16	3 Hz	3 Hz			t	0.6
h							3 Hz	3.45		1-2 Hz		br s	1.4
i	3 Hz	8 Hz	8 Hz						2.62			br t	0.5
j				8 Hz						2.39	3 Hz	br d	1.27
k	2.5 Hz									3 Hz	4.25	br s	5.4

in conjunction to assign the adsorptions. Aside from being internally consistent, the data can be used to assign the stereochemical configuration of 21. The magnitude of the change in chemical shift for the protons k (5.4 ppm), a (1.35 ppm) and j (1.27 ppm) are expected for an allylic alcohol of this structure. However, the magnitude of the contact shift for h (1.4 ppm, cyclobutene bridgehead) when compared to the shift for d (0.6 ppm, 2-bridge vinyl) fixes the stereochemistry of the alcohol on the same side of the three bridge as the four bridge. This fact, in conjunction with the comparison of the contact shift of h (1.4 ppm) and f (0.35 ppm, cyclobutene vinyl with largest shift), fixes the cyclobutene four bridge with the bridgehead cyclobutene proton spatially close to, and the cyclobutene vinyl proton spatially removed from the alcohol function or exo to the three bridge. Thus, it is possible to identify 21 as (1α, 2β, 5β, 6α, 7β)-tricyclo-[4.3.2.$0^{2,5}$]-undeca-3,8,10-triene-7-ol. See Section IV for a discussion of the nomenclature system used.

From the stereochemistry of the allylic alcohol 21, it is evident that the reduction of the enone 16 has occurred with preferential approach of the nucleophile, hydride, from the least hindered side.

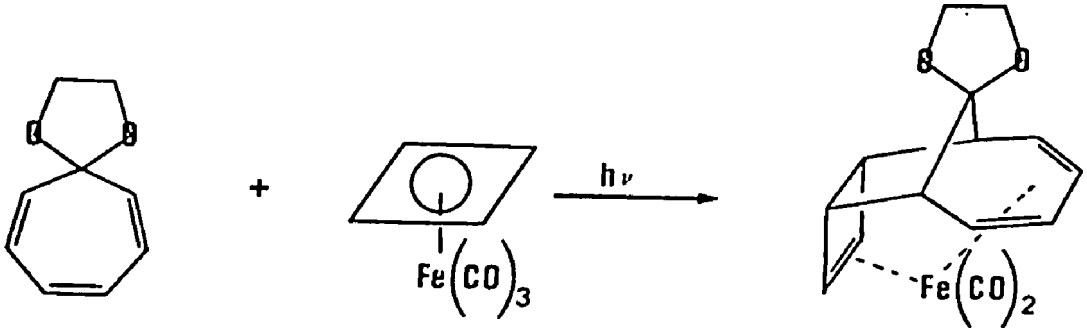
When the allylic alcohol 21 was oxidized under modified Sarrett conditions,[19] the enone 16 was isolated in 85% yield, as shown by analytical glpc and comparison of the pmr spectra with authentic material. Thus the cyclobutene



16

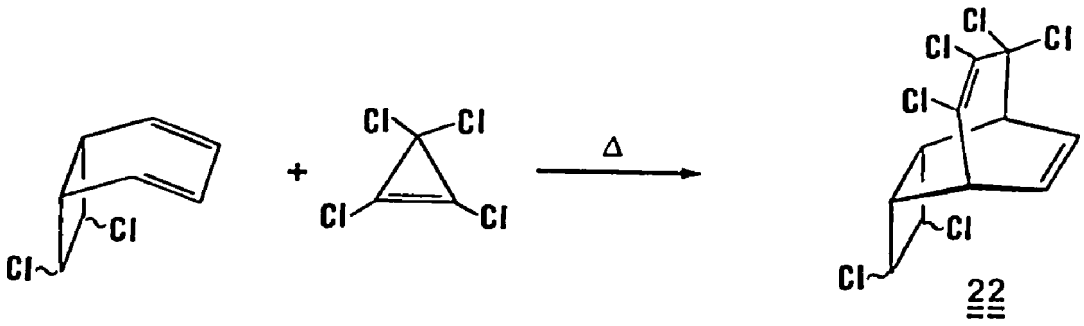
ring is exo to the three bridge or the zero bridge is on the β side of the main ring in the eneone 16 as well.

From the stereochemistry of the enone 16, cyclobutadiene has evidently reacted as a reactive dienophile in accord with the endo rule without apparent involvement of the iron, as had been observed by Grubbs[20] and Paquette.[21] The thermal reactivity of cyclobutadiene in this instance is contrasted with its photochemical decomposition in the presence of tropone ketal as observed by Pettit.[22]



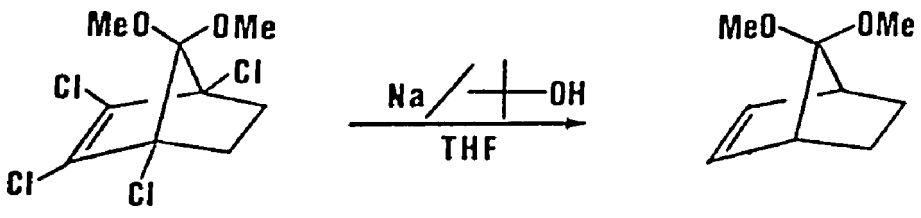
B: Three carbon annelation of eight carbon unit:

While the direct one-step approach of a 4 carbon cycloaddition annelation with a 7 carbon unit was successful, the yields of the enone 16 remained disappointingly low. At the time that this work was in progress, J. T. Groves and M. A. Ebner[23] had demonstrated that the 3-carbon cycloaddition annelation of tetrachlorocyclopropene with the eight carbon unit, 7,8-dichlorobicyclo[4.2.0]-2,4-octadiene (COT-Cl_2), produced the hexachloride isoskeletal analog, 22, of the enone 16.

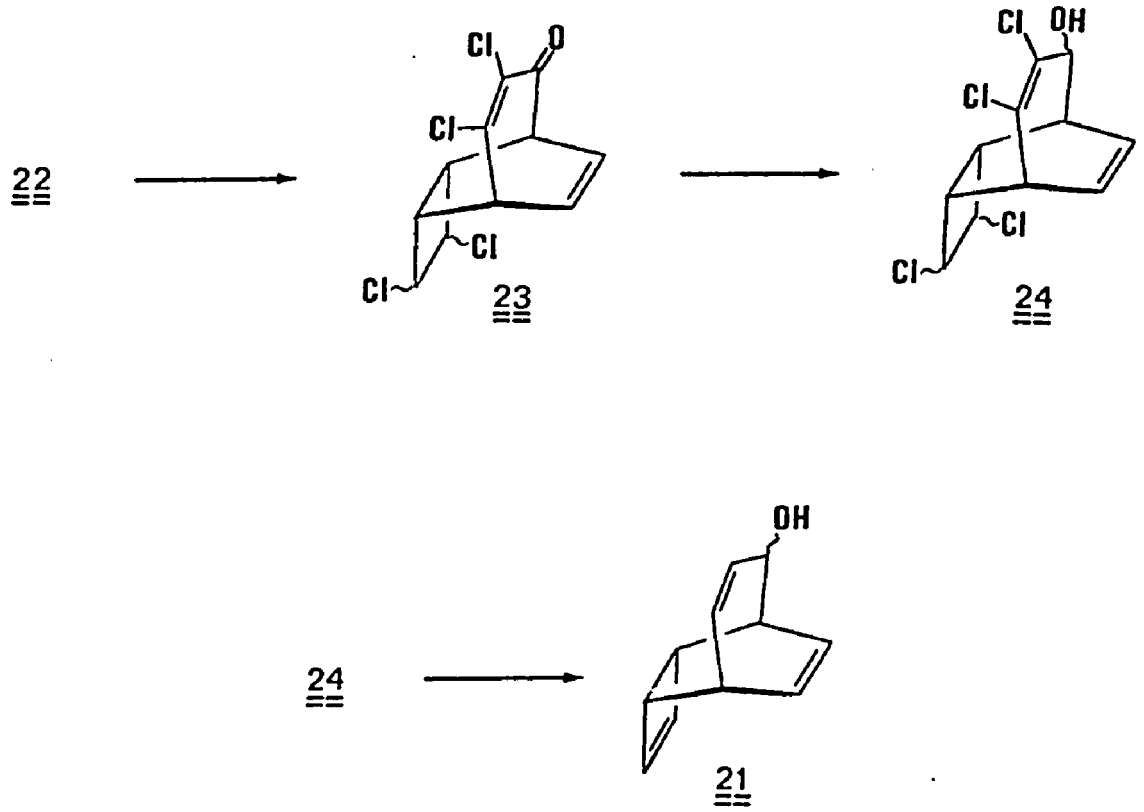


22

The modification of 22 to 16 appeared straightforward based on the work done in a similar system by Gassman.[24]



With this in mind, the following scheme for the chemical modification of the hexahalide 22 was envisioned.



When the hexachloride 22 was hydrolyzed with silver nitrate in aqueous dioxane, a 78% yield (based on isolated AgCl) of the tetrachloroketone 23 was isolated. 23 Could then be reduced with aqueous sodium borohydride, without isolation of the tetrachloroketone 23, to the tetrachloro-alcohol 24 in good yield.

The sodium/t-butanol/tetrahydrofuran (THF) reduction of the tetrachloroalcohol 24 to the desired allylic alcohol 21 proved to be quite complex. Analysis by analytical glpc indicated the formation of 3 major products and 3 minor

components from the reduction of 24. One of the major components was shown, by coinjection with authentic material and comparison of its pmr spectrum, to be the desired allylic alcohol 21.

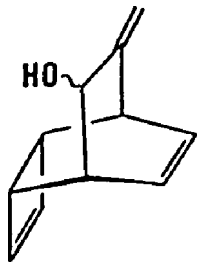
The formation of this complex mixture lead to the investigation of the relationship between the purity of the tetrachloroalcohol 24 and the side products formed during the reduction. Two sources of pure 24 were reduced. 24 Could be chromatographed on silica gel to yield material which was 85% pure by analytical glpc. Pure tetrachloroalcohol 24 could also be obtained from the sodium borohydride reduction of pure tetrachloroketone 23, which had been subjected to a dry bag chromatography on silica gel (100% pure by analytical glpc). When either source of pure tetrachloroalcohol 24 was reduced with sodium/t-butanol, a product mixture identical by analytical glpc with that mixture resulting from reduction of crude 24 was obtained, except for the disappearance of one of the minor components, with no increase in the yield of the desired allylic alcohol 21.

Since the complex reaction mixture did not substantially result from the reduction of impurities present in samples of impure tetrachloroalcohol 24, the nature of the side products formed was investigated.

The components of the reaction mixture were separated by a column chromatography, followed by preparative glpc of those fractions which were an inseparable mixture. The

Table IV

Spectral Data of Exocyclicallylic Alcohol 25

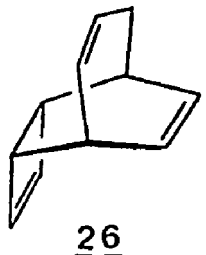


25

pmr, CCl_4, δ: 5.93 (t, 1H, 8 Hz); 5.90 (t, 1H, 8 Hz); 5.80 (s, 2H); 5.03 (t, 1H, 3 Hz); 4.95 (d,d, 1H, 2,3 Hz); 3.90 (br m, 1H); 2.90 (m, 2H); 2.65 (s, 2H); 1.05 (s, 1H).

ir, CCl_4: 3590, 3100, 3030, 2905, 1650, 1300, 1060, 1040 cm^{-1}.

minor component, which was a function of the purity of the tetrachloroalcohol 24, was identified as the exocyclic-allylic alcohol 25 on the basis of its pmr spectrum, found in Table IV. The most volatile major component was identified as a mixture of isomers related to, and including 26, on the basis of the mixture's retention time, pmr spectrum, odor and coinjection with authentic material.[23]



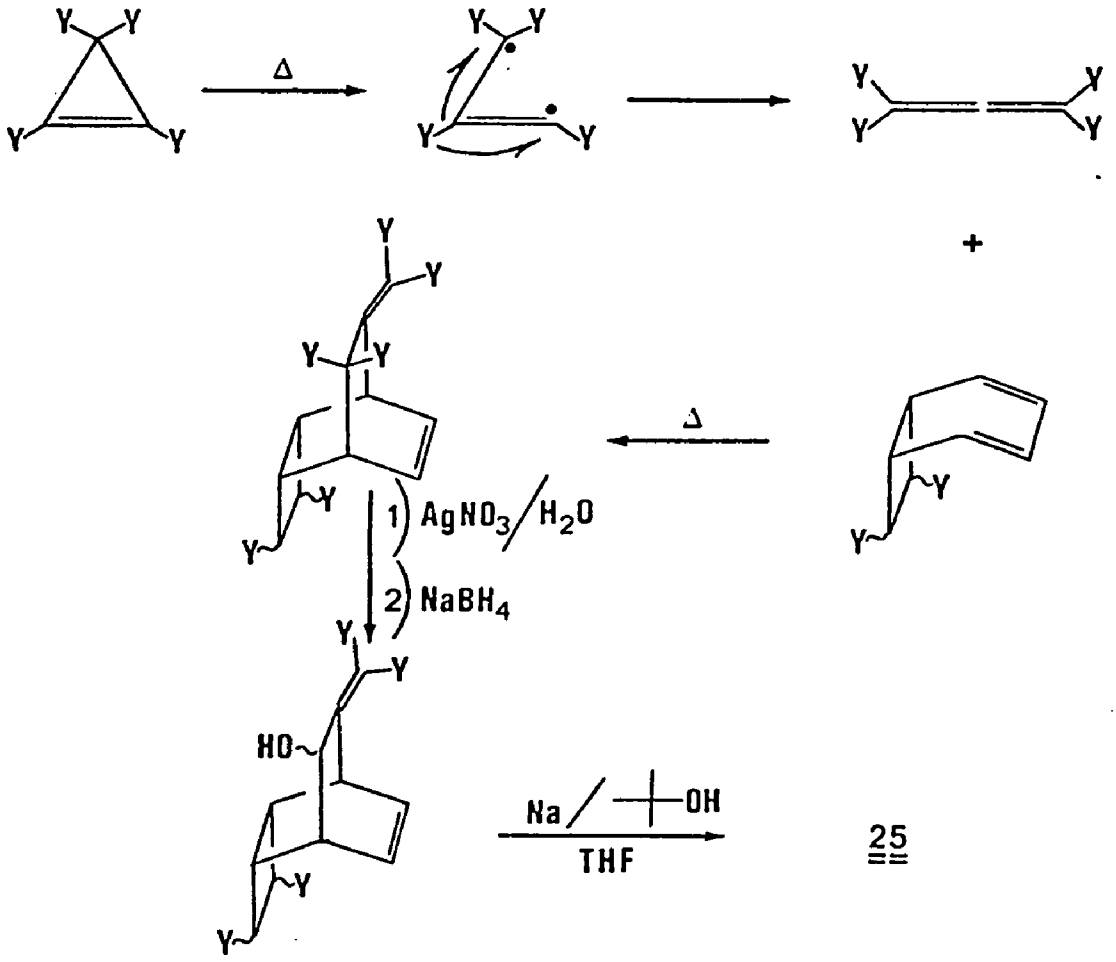
26

The remaining major component was identified as material structurally analogous to the allylic alcohol 21, as evidenced by the similarity of the vinyl adsorptions in the pmr spectrum, but where extensive reduction of the olefinic carbons had occurred, as indicated by the complex adsorptions between 2.0 and 0.8 δ.

The isolation of the exocyclic allylic alcohol 25 from the reduction of crude tetrachloroalcohol 24 can be best rationalized as the result of reduction of the exocyclic tetrachloro alcohol 27, which was formed from the Diels-Alder reaction of tetrachloroallene and (COT-Cl_2). This hypothesis is also in accord with the observation that the amount of exocyclicallylic alcohol 25 isolated from the

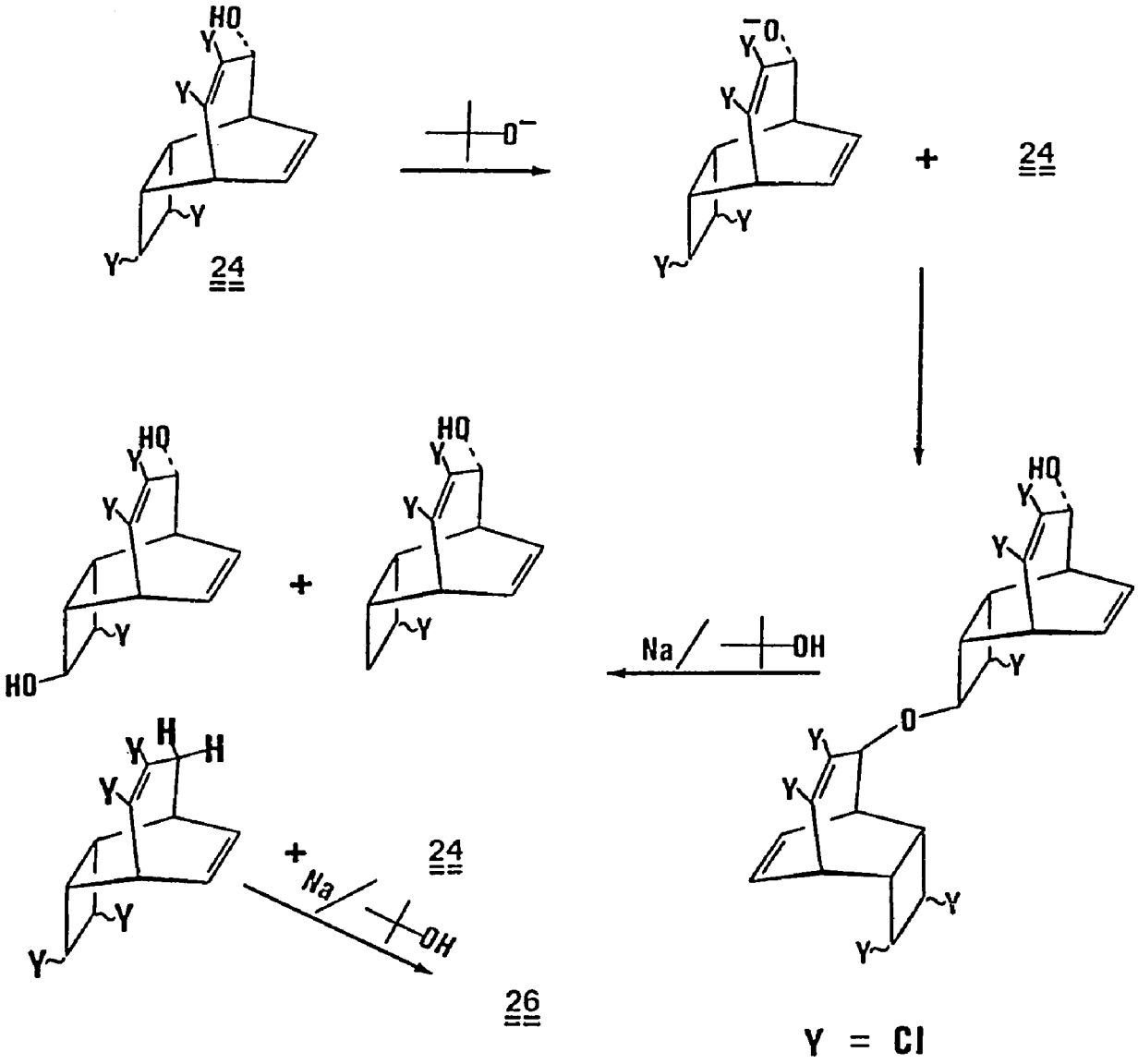
reduction of tetrachloroalcohol 24 decreased as the temperature for the Diels-Alder reaction between tetrachlorocyclopropene and COT-Cl_2 was lowered below 90°C.[25]

A tetrahaloallene has been postulated by West[26] to explain the products isolated from the thermal chemistry of tetrabromocyclopropene.



Y = Cl

The formation of hydrocarbons analogous to the tricyclic triene 26 from the reduction of pure tetrachloroalcohol 24 is of interest, as the reduction of unreacted hexachloride 22 is eliminated as a reasonable explanation. A plausible explanation for the isolation of the tricyclic triene 26 involves the reductive cleavage of a dimeric ether formed from the reaction of the anion of the tetrachloroalcohol 24 with another molecule of 24.



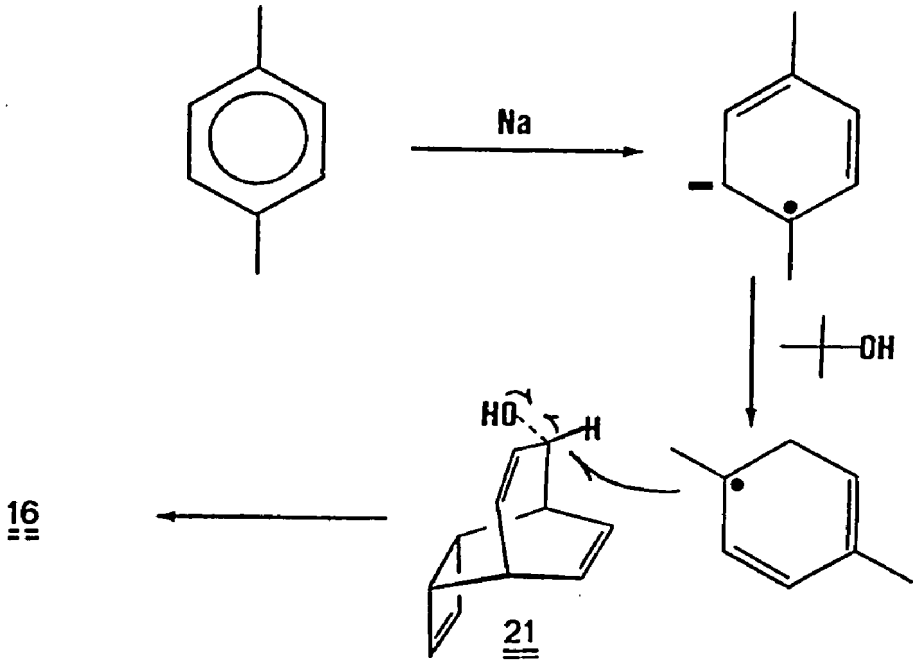
This reductive scheme for the formation of the triene 26 is only one of the several which can be postulated using intermediates which would be formed during the sequential reduction of tetrachloroalcohol 24 to the desired allylic alcohol 21, but it is illustrative of a possible mechanism for the formation of 26.

Several different reducing systems were explored in an attempt to alter the course of the observed side product formation. Among the systems investigated were: sodium dispersion-t-butanol-THF; sodium sand from mineral oil or p-xylene-t-butanol-THF; sodium-ammonia-THF; and sodium amide-sodium-ammonia-THF. All of these reducing systems gave a similar product mixture to that obtained from sodium-t-butanol-THF (by analytical glpc). However, there was one interesting exception to the product composition observed with these different metal reducing systems.

When crude tetrachloroalcohol 24 was reduced with a sodium sand, which had been prepared from hot p-xylene, the tricyclic enone 16 was isolated in approximately 1% yield by a dry bag chromatography. The structure of the enone 16 was confirmed by the identity of its pmr spectrum with that of authentic material. The isolation of the enone 16 from a metal reducing system is unusual and leads to interesting speculation.

The only difference between the reducing system which lead to the isolation of enone 16 and all of the other metal reducing systems explored, where 16 was never observed,

was the presence of small amounts (approximately 1%) of p-xylene which had been used to prepare the sodium sand. A possible mechanism which allows for the formation of the enone 16 involves p-xylene in a Connizzaro-like process, with the abstraction of a hydrogen by a p-xylene radical.

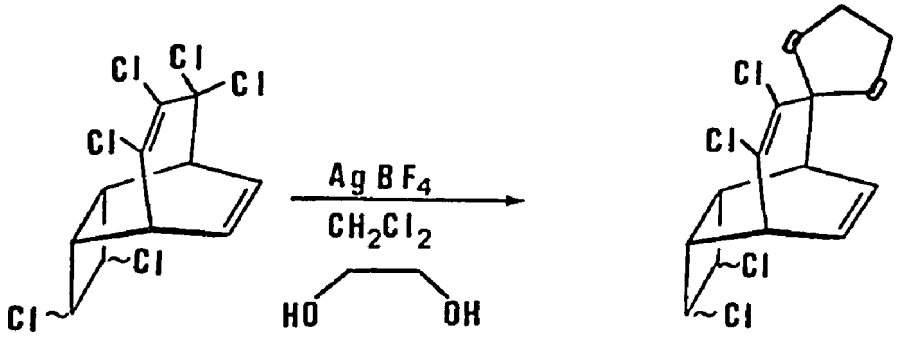


For this mechanism to be a viable process, three factors are assumed. First, the rate of further reduction of the enone 16 must be slow enough to allow for its isolation. The p-xylene radical, must have a lifetime long enough under the reaction conditions to allow it to abstract the allylic hydrogen of the radical of 21, and the allylic hydrogen of 21 must be active enough to allow for its abstraction in the first place. Nonetheless, regardless of the exact mechanistic details, the isolation of the

enone 16 from the reduction of the tetrachloroalcohol 24 is an interesting and unusual observation.

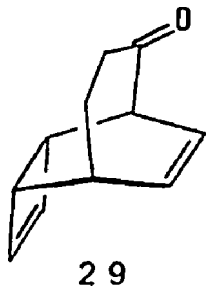
The persistence of the hydrocarbon side products, despite the variety of specific reducing systems employed, lead to the consideration of protecting the 7 position of the tricyclic system. The mechanistic speculation employed to account for the isolation of the hydrocarbons analogous to triene 26, indicated that for each mole of hydrocarbon formed, two moles of the tetrachloroalcohol precursor 24 to the allylic alcohol 21 had been consumed. Thus, the elimination of this one side reaction, should lead to a 200% increase in the yield of the allylic alcohol 21.

The tetrachloro ketal 28 appeared to be the best candidate for the elimination of the process leading to the hydrocarbon 26. The tetrachloroketal 28 was prepared in excellent yield by the hydrolysis of the hexachloride 22 with silver fluoroborate in an anhydrous methylene chloride-ethylene glycol solution.



22 28

Pure ketal 28, isolated from a column chromatography, when reduced by sodium-t-butanol in THF gave a mixture of seven products, with only one major component. When the crude reaction mixture was hydrolyzed with dilute acid, the major product, ketone 29, was isolated by a column chromatography in 25% yield. Ketone 29 was identified by the analysis of its spectral data.

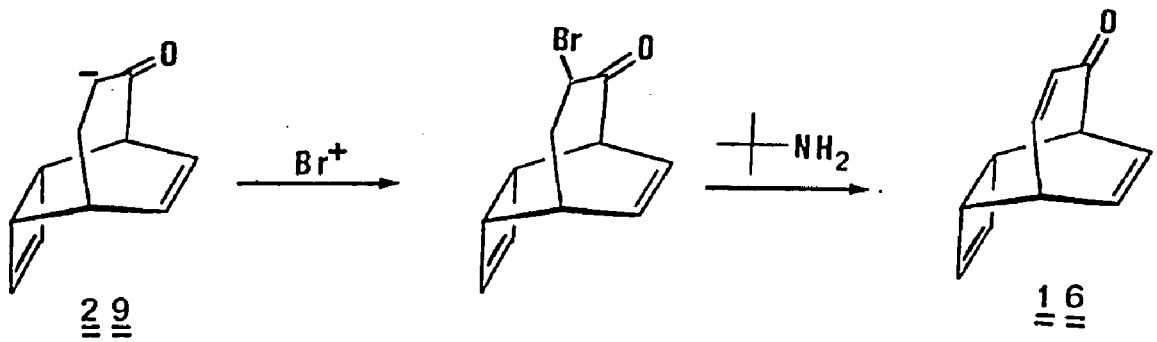


29

The desired enone 16 was not a product of the reduction of the ketal 24, as it could not be detected when the crude acidic hydrolyzate of the sodium/t-butanol reduction of 28 was analyzed by analytical glpc. All other reducing systems surveyed for the reduction of ketal 28 proved to be less efficient and selective than the sodium-t-butanol-THF system originally employed, and in no case was the enone 16 observed as a product from the reduction of the tetrachloroketal 28.

The ketal protecting group had obviously activated the allylic double bond to further reduction. A chemical transformation of the ketone 29 to the desired enone 16, was considered, employing an α-bromination of the enolate of

ketone 29, followed by the formation of the enone 16 with a sterically hindered base.



29 16

Consideration of the expected overall yield of this two-step process in conjunction with the 25% yield of ketone 29, led to the conclusion that no material gain of the enone 16 would be realized over that which was already available from the reduction of the tetrachloroalcohol 24. As a result of these considerations, the chemistry of the ketone 29 was not investigated.

C. Isolation of allylic alcohol 21.

The isolation of pure allylic alcohol 21 from the reduction of tetrachloroalcohol 24 proved to be quite difficult. All attempts to purify 21 by chromatography of the crude reaction mixture from the sodium-t-butanol-THF reduction of tetrachloroalcohol 24 led to the isolation of allylic alcohol 21 as a mixture of 21 and two other components. When once chromatographed 21 was rechromatographed, the formation of two additional components with 30%

recovery of material containing 21 with no increase in purity, was noticed. On the basis of this observation it was concluded that the allylic alcohol 21 was unstable to chromatographic conditions.

However, pure allylic alcohol 21 could be isolated in 14% overall yield from tetrachloroalcohol 24, by oxidation of the crude reaction mixture from the reduction of 24 under modified Sarrett conditions,[19] followed by purification of the enone 16 by column chromatography and then low temperature LAH reduction of pure enone 16 to yield pure allylic alcohol 21.

II. Solvolysis of esters of the allylic alcohol 21:

A. 118°/glacial acetic acid.

The 3,5-dinitrobenzoate (30) and the allylic acetate 31 (spectral data, page 143) could be synthesized in excellent yield from the allylic alcohol 21 by the reaction of 21 with either recrystallized 3,5-dinitrobenzoylchloride or distilled acetic anhydride, in refluxing dry pyridine. Both the benzoate 30 and the allylic acetate 31 were shown to be unrearranged by their reduction with LAH and the coinjection of the one alcohol produced with authentic allylic alcohol 21.

Three volatile acetates were isolated when either the benzoate 30 or the acetate 31 was solvolyzed in refluxing glacial acetic acid. The most volatile peak of the two

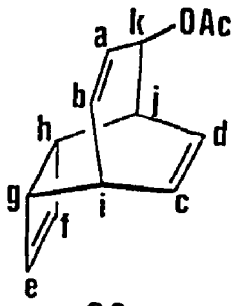
detectable by analytical glpc, which coinjected with authentic pure allylic acetate 31, was shown to be a mixture of two acetates as evidenced by the two acetate adsorptions near 2.0 δ in the pmr spectrum.

When this mixture of acetates was reduced with LAH at -78°C, two alcohols were isolated by preparative glpc. One of the alcohols was shown to be the allylic alcohol 21 by the identity of its pmr spectrum and coinjection with authentic material. The other alcohol 33 was identified as the epimer of the allylic alcohol 21 by the oxidation of the epimeric alcohol 33 to the enone 16 coinjection with and identity of pmr spectrum with authentic 16, and the acetylation of 33 to give the epimeric acetate 32, which coinjected with the allylic acetate 21. The conversion of the benzoate 30 to the solvolysis products 31, 32 and 34 was 100% after 4 hr. The relative yields of 31, 32 and 34 were 1.5:1.5:1.

The structure of the remaining acetate 34 was determined by the analysis of its spectra data in conjunction with the consideration of all the possible structures that can be derived from all the $C_{10}H_{10}$ structures, tabulated by Balaban,[27] consistent with the basic structural units present in 34, if a $(CH)_{11}$ structure is assumed, vide infra.

Table V

pmr Spectrum of Epimeric Acetate 32



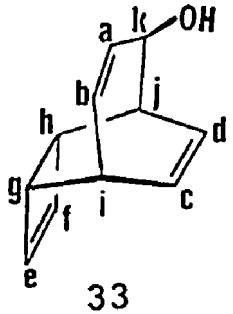
32

(CCl_4)

δ	a	b	c	d	e	f	g,h	i	j	k	Ac	apparent multiplicity
a	5.24	11 Hz						2 Hz		4 Hz		d,d,d
b	11 Hz	6.02						8 Hz				d,d
c			6.12	8 Hz				8 Hz				t
d			8 Hz	5.60					8 Hz			t
e					5.94	3 Hz						d
f					3 Hz	5.84						d
g,h							3.00					s
i	2 Hz	8 Hz	8 Hz					2.56				t
j				8 Hz					2.75	4 Hz		m
k	4 Hz								4 Hz	5.04		t
Ac											1.92	s

Table VI

pmr Spectrum of Epimeric Allylic Alcohol 33

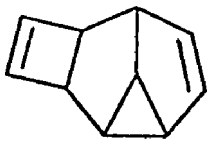


33

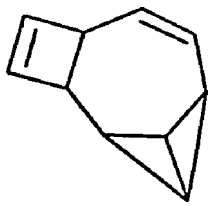
(CCl_4)

δ	a	b	c	d	e	f	g,h	i	j	k	apparent multiplicity
a	5.40	11 Hz						2 Hz		4 Hz	d,d,d
b	11 Hz	6.10						8 Hz			d,d
c			6.24	8 Hz				8 Hz			t
d			8 Hz	5.72					8 Hz		t
e					6.04	3 Hz					d
f					3 Hz	5.92					d
g,h							2.96				m
i	2 Hz	8 Hz	8 Hz					2.56			m
j				8 Hz					2.84	4 Hz	m
k	4 Hz								4 Hz	3.86	t

A cyclobutene ring is present in the molecule as evidenced by the two doublets at 6.32 δ and 6.02 δ with J = 3 Hz[28] (see pmr spectra of allylic alcohol 21 and the epimeric allylic alcohol 33). The adsorption of three hydrogens at 1.56 δ indicates a cyclopropyl ring, and an additional vinyl unit is present as evidenced by the two protons at 5.98 δ (1H) and 5.56 δ (1H). There are only two structures, 35 and 36, from the tabulated list of Balaban, which contain the units of a cyclobutene ring, a cyclopropyl ring and one additional vinylic unit.



35

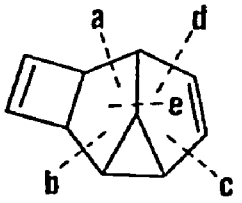


36

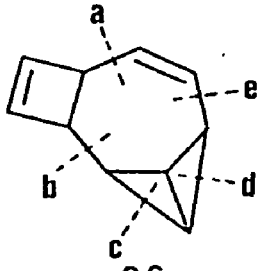
From each structure, there is a set of homologations, ignoring stereochemistry, which would maintain these basic structural units. This set of possible homologations, found in Table VII, generates the family of ten structures possible for the acetate 34.

Table VII

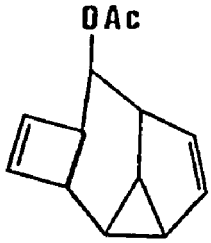
Structural Possibilities for Acetate 34



35



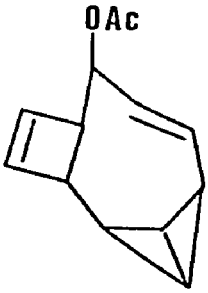
36



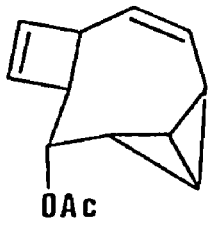
a



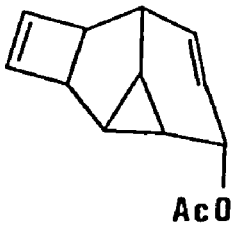
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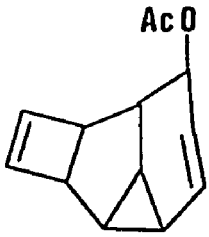
a



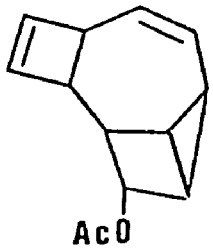
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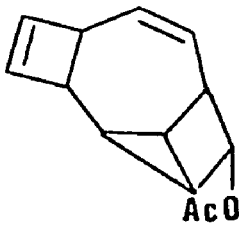
c



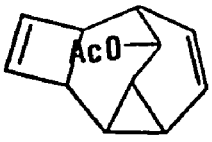
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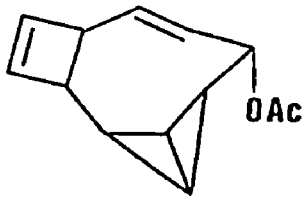
c



d



e



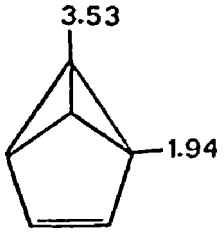
e

The structures 36a, 36b, and 36c all have a bicyclobutane unit present. From the consideration of the model bicyclobutane compounds in Table VIIA, it is seen that the minimum chemical shift difference for the O-bridge protons and the outer protons of the bicyclobutane is .3 ppm. When the outer protons of the bicyclobutane in benzavalene and the saturated 5-membered ring analog are compared, there is only a 0.1 ppm difference. When the chemical shift for the α vinyl proton in the allylic acetate 31 (s δ, 5.4) is compared to that proton in the olefin 26 (s δ, 5.3), a small change of only 0.1 ppm is observed. With these small observed chemical shift differences caused by an acetate methine and a vinyl unit, the bicyclobutane unit can be eliminated, as three nearly chemically equivalent cyclopropyl hydrogens are seen in the cyclopropyl acetate 34.

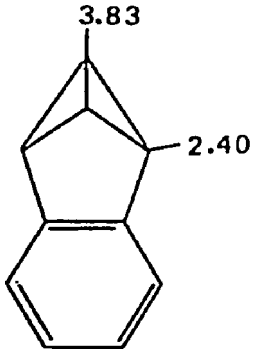
The chemical shift for the acetate methine at 5.56 δ seems too low for any acetate other than an allylic acetate.[30] This was confirmed when the cyclopropylacetate 34 was reduced to the alcohol 37 and a chemical shift of 4.48 δ was observed for the alcoholic methine. The structures 36c, 36d and 35a can be eliminated from consideration on the basis of their lack of an allylic methine, which is confirmed by the C-O stretch[30] in the ir at 1022 cm^{-1} for the cyclopropyl acetate 34 and 1015 cm^{-1} for the corresponding cyclopropyl alcohol 37.

Table VIIA

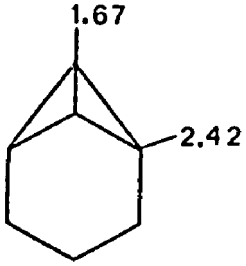
Model Bicyclobutane Compounds



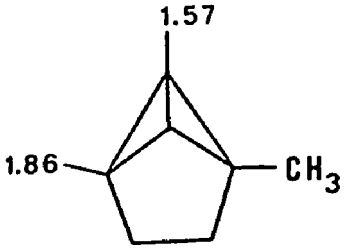
a



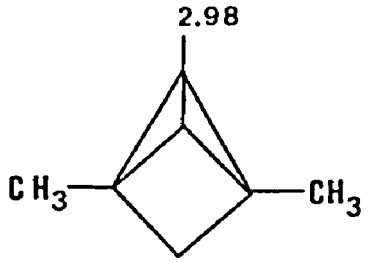
b



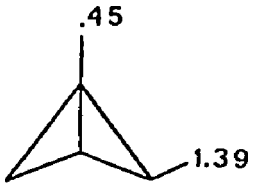
c



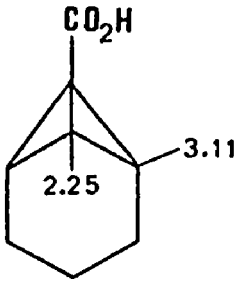
d



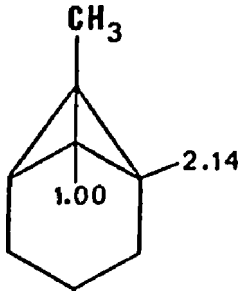
d



f

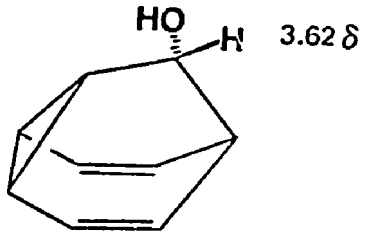


e



e

The question remains, however, whether a cyclopropyl carbinyl methine such as that in 35b or 35e would be found in the pmr spectrum as low 5.56 δ for the acetate, or 4.48 δ for the alcohol. A good model that can be used to answer this question is found in barbarol 38, where the alcohol methine is found at 3.62 δ.

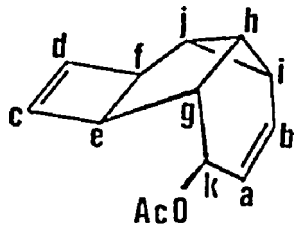


38

Since the adsorptions at 5.56 δ for the acetate methine and 4.48 δ for the alcohol methine can only be reasonably accounted for if that methine is allylic, the structures 35c and 35d are the only ones left by the process of elimination.

Table VIII

pmr Spectrum of Cyclopropylallylic Acetate 34



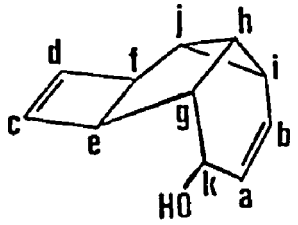
34

(CCl_4)

δ	a	b	c	d	e,f	g	h,i,j	k	Ac	apparent multiplicity
a	5.56									m
b	8 Hz	5.98								d
c			6.32	3 Hz						d
d			3 Hz	6.04						d
e,f					3.00					m
g						2.80	<5 Hz	<5 Hz		br s
h,i,j							1.56			br s
k								5.56		
Ac									1.6	s

Table IX

pmr Spectrum of Cyclopropyl Allylic Alcohol 37



37

(CCl_4)

δ	a	b	c	d	e	f	g	h,i,j	k	apparent multiplicity
a	5.64	10 Hz							7 Hz	d,d
b	10 Hz	6.06								d
c			6.28	2.8 Hz						d
d			2.8 Hz	6.00						d
e					3.10	3.5 Hz				d
f					3.5 Hz	3.00				d
g							2.90			br m
h,i,j								1.64		s
k	7 Hz								4.48	br s

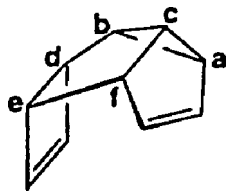
The molecules 35c and 35d are allylic isomers of the same carbon skeleton, where 35c is a cross conjugated system and 35d is an extended conjugated system. The structure 35d would be the preferred one on the basis of stability and election density of an intermediate carbonium ion leading to its formation.

An indication that the structure 35d is indeed correct is obtained by the analysis of the expected coupling constants for the β proton of the allylic acetate vinyl in 35d and 35c. It is assumed here that the coupling of 10 Hz that the β proton experiences is due to a vincinal vinyl proton in a six-membered ring,[28] and that the α and β protons of the allylic vinyl unit will have approximately the same relative chemical shifts as found in 31 and 32, which is consistent with the assigned structure of the cyclopropyl allylic acetate 34. The observed coupling of <4 Hz is in agreement with the expected value of 2 Hz[31] for the β proton-cyclopropyl proton coupling, as their dihedral angle in 35d is 55%. In 35c the dihedral angle between the β proton and the bridgehead proton is 0° with an expected coupling constant of 8 Hz.[32]

The stereochemistry of the acetate in the cyclopropyl allylic acetate 34 is assigned as syn to the cyclopropyl ring on the basis of consideration of the least hindered approach by acetate to a carbonium ion precursor, and the magnitude of the vicinal methine-vinylic coupling constant. Examination of models shows that the dihedral angle for the

vinyl and methine protons would be approximately 15° for the syn acetate and 90° for the anti acetate. The observed coupling of J = 7 Hz is only consistent with the syn acetate, based on the Karplus equation.[32]

The stereochemical relationship of the cyclobutene and the validity of the previous coupling constant arguments is indicated by the comparison of the pmr spectrum of 34 with the analogous 38a.[32]



38a

The vinyl region of 38a is remarkably similar to that of 34. There are two dissimilar cyclobutene vinyl absorptions at 6.2 and 5.5 δ as compared to 6.3 and 6.04 δ in the cyclopropylallylic acetate 34. The cyclopentene vinyls in 38ashow 5.65 and 5.0 δ absorptions compared to 5.56 and 5.98 δ in 34.

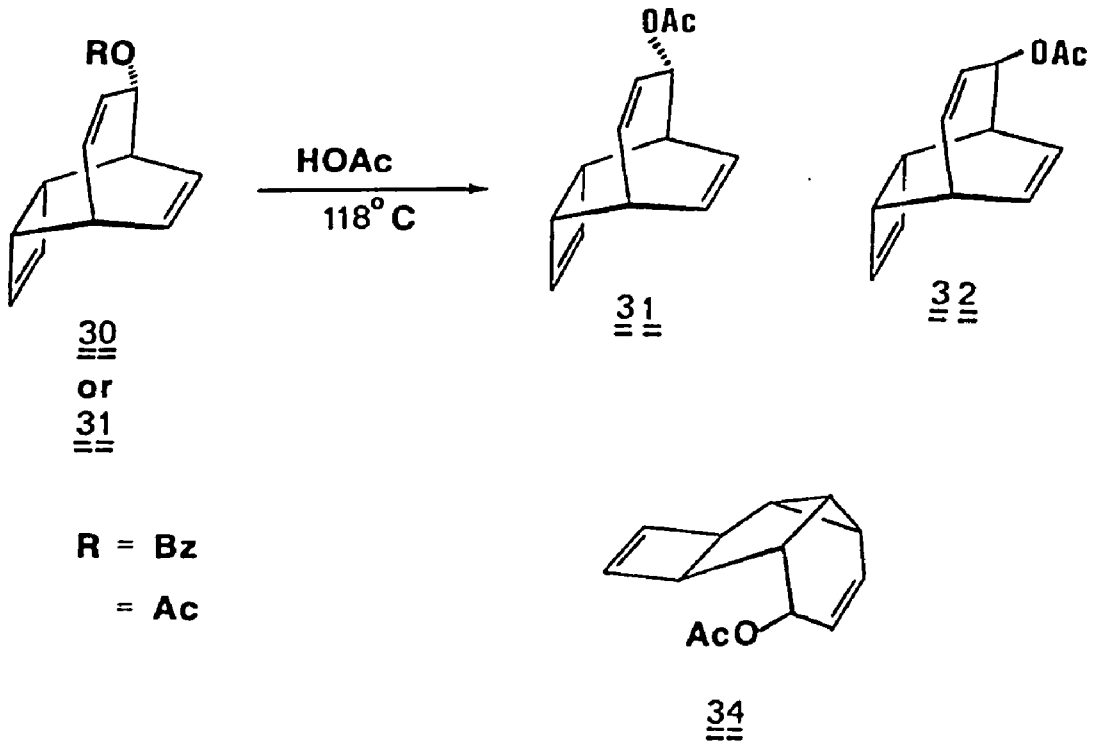
The cyclobutene bridgehead protons $H_{e,d}$ in 38a are found between 3.9 and 3.6 δ with the analogous protons in 34 at 3.00 δ. The cyclopropyl proton H_a and the bridgehead H_f in 38 at 1.68 δ and 3.16 δ correspond well with the values of 1.5 and 2.8 δ found in 34.

One of the cyclopropyl protons, either H_c or H_f, does not correlate with the cyclopropyl protons in 34, as one of the remaining protons (H_c or H_b) adsorbs at 2.95 δ, with the other cyclopropyl found at 0.98 δ. This is not too disconcerting, however, as 38a possesses more strain than 34, (when the strain of a cyclopentene ring and a cyclohexene ring are compared) and the pmr spectrum of 38a used for this comparison was taken in D_6 benzene.

In addition to the chemical shift similarity between 38a and 34, which lends support to the proposed structure for 34, analysis of the coupling constants found for H_d in 38a supports the assigned stereochemical relationship of the cyclobutene ring in 34, which is consistent with the mechanistic arguments formulated for the isolation of 34 (see Section III).

In 38a, the $J_{d,b}$ is approximately 5-7 Hz, which reflects the dihedral angle of H_d-H_b being 10°.[31] If the stereochemical assignment of the cyclobutene in 34 were reversed, a similar coupling should be observed, as the corresponding dihedral angle in 34 is approximately 15°. With the assigned stereochemistry, the dihedral angle between the cyclobutene bridgehead and cyclopropyl protons is 88°, which is consistent with the small observed coupling.

With the structure of the cyclopropylallylic acetate 34 known, the products of the acetolysis of the benzoate 36 or the allylic acetate 31 were shown to be the following:



30 or 31

R = Bz
= Ac

31

32

34

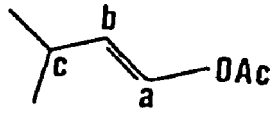
B. Acetolysis of the allylic benzoate 30 or the allylic acetate 31 at elevated temperatures:

The acetolysis of the benzoate 30 at elevated temperatures was explored in an attempt to observe a rearrangement where the cyclobutene group had participated. When a solution of the benzoate 30 was heated at 190°C in degassed glacial acetic acid for 2 hr, in an evacuated, sealed combustion tube, four acetates were isolated. The conversion of the benzoate 30 to the acetates was complete after no more than 1 hour. The relative ratio of the three most volatile acetates (glpc) remained constant, with the

absolute ratio of the least volatile acetate to the remaining acetates a function of time. This acetate was shown to be unstable to heat by kinetic measurements.

The three most volatile acetates were shown to be the allylic acetate 31, the epimeric allylic acetate 32 and the cyclopropyl allylic acetate 34 by coinjection with and the identity of their pmr spectra with authentic material. The remaining acetate (39) was a $C_{11}H_{11}$-acetate (m/e: 202) with the cyclobutene apparently no longer present, as evidenced by the eight vinyl proton adsorptions. The structure of this new acetate 39 was determined by the analysis of its spectral data.

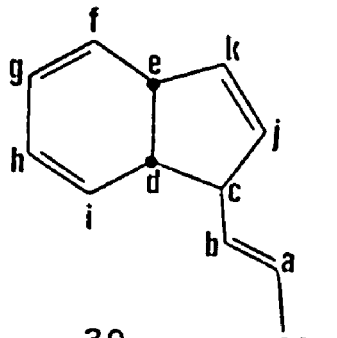
The ir adsorption at 1765 cm^{-1} and the adsorptions at 7.05 δ and 5.18 δ are unique for an enol acetate unit.[33] The J_{ab} coupling of 12.8 Hz defines the enol acetate with trans geometry.[34] Spin decoupling located the β carbon of the enol acetate adjacent to a bridgehead proton with J_{bc} = 9.8 Hz, thus defining the following structural unit.



The bridgehead proton, H_c, was shown to be adjacent to only one bridgehead proton, H_D, with J_{CD} = 8.2 Hz and H_D, in turn, was adjacent to the remaining bridgehead proton

Table X

Spectral Data of Enol Acetate 39



39

(CCl_4)

δ	a	b	c	d	e	f-k	Ac	apparent multiplicity
a	7.05	12.8 Hz	1.0 Hz					d,d
b	12.8 Hz	5.18	9.8 Hz					d,d
c	1.0 Hz	9.8 Hz	3.48	8.2 Hz		$J_{c,j}$= 1 Hz		t
d			8.2 Hz	3.12	12.3 Hz	$J_{d,i}$=3.9 Hz		heptet
e				12.3 Hz	3.62			d
f-k						5.70		m
Ac							2.08	s

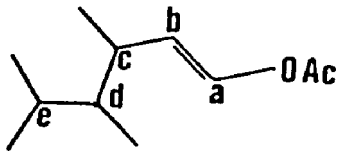
ir, $CDCl_3$: 3030, 2950, 2890, 1765, 1740, 1430, 1375, 1290, 1250, 1225, 400 cm^{-1}.

uv, 95% EtOH: λ_{max} 213, 255, 262, 272 nm, ε_{262} = 3,100.

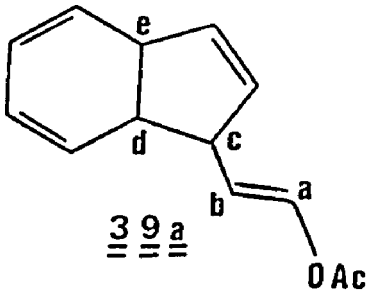
MS m/e (rel. intensity): 202 (6.1), 160 (72), 142 (100, base), 104 (81), 95 (62), 91 (71).

cmr; $CDCl_3$, ppm from TMS: 167.8, 135.0, 133.2, 132.8, 126.1, 125.8, 123.0, 120.7, 116.2, 49.7, 43.6, 38.2, 14.7.

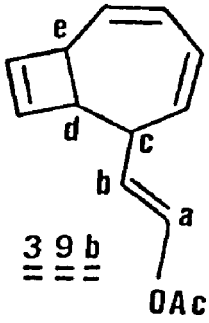
H_e with $J_{d,e}$ = 12.3 Hz, completing the following structural unit.



There are only two possible structures with 3 remaining double bonds which can be imagined for the enol acetate 39.



39a



39b

The structure 39b is eliminated on the basis of two pieces of information. The ε = 3100 for a homoannular diene (λ = 255, 262, 272) is too small for a homoannular diene in a seven-membered ring (ε = 8000),[35] and is consistent with that found in cis and trans 3a, 7a-dihydroindenes (ε_{cis} = 4580, ε_{trans} = 3700).[36] In addition the

magnitude of the coupling constant $J_{d,e}$ = 12.8 Hz is too large for a cyclobutene ring (vide supra) and is only consistent with a cis-fused 3a, 7a-dihydroindene.[37]

The stereochemical relationship between H_d and H_c is the only information left in doubt from the spectral data already considered. Examination of molecular models reveals that the dihedral angle for H_d-H_c in a cis configuration would be approximately 27°.

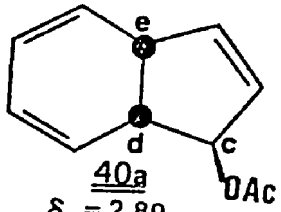
If H_d and H_c are in a trans configuration, the dihedral angle would vary between 100° and 155°, depending upon the preferred conformation of the ring system. The Karplus[32] equation predicts: $J_{d,c-27°}$ = 6.3 Hz; $J_{d,c-100°}$ = 0.3 Hz; and $J_{d,c-155°}$ = 8.0 Hz.

The observed magnitude of $J_{d,c}$ = 8.3 Hz appears to eliminate H_d and H_c being in a cis orientation. Consideration, by the examination of molecular models, of which of the two conformations would be preferred with H_d and H_c trans to one another, indicates that the two cis 1,3 interactions, H_c-H_i and H_e-C_b, are relieved to the extent of 0.6 Å and 1.3 Å, respectively, if the dihedral angle of H_c-H_d is 155° versus 100°. Based upon the conclusion that the preferred conformation of the enol acetate 39 would have a H_c-H_d dihedral angle approaching 155°, the observed coupling of $J_{c,d}$ = 8.3 Hz would be consistent with H_c and H_d in a trans relationship.

The pmr spectrum of 39 correlates very well with analogous cis-3a,7a-dihydroindenes found in Table XI.

Table XI

Model cis-3a, 7a-Dihydroindenes



40a

ref.

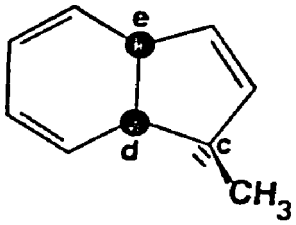
38

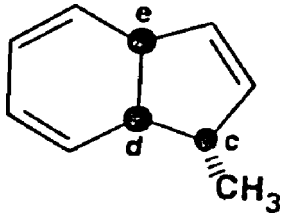
δ_d = 2.89

δ_e = 3.46

$J_{d,e}$ = 11.5 Hz

$J_{c,d}$ = 3 Hz





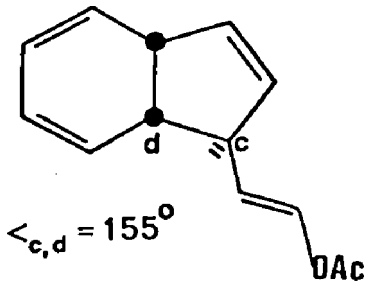
37a

δ_d = 2.6

δ_e = 3.6

$J_{d,e}$ = 12 Hz

$J_{c,d}$ = 7 Hz



$\angle_{c,d} = 155^{\circ}$

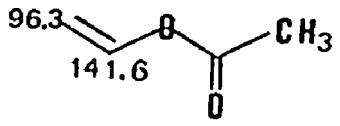
$J_{c,d} = 8.0\,Hz$

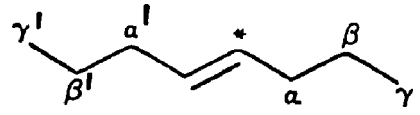
39

The corresponding coupling of $J_{c,d}$ = 3 Hz found in 40a[38] is not inconsistent with this analysis, as the severity of the H_e-OAc 1,3 interaction is much less than that found for H_e-C_b in 39 and the H_c-H_d angle in 40a would be expected to decrease from 155°.

However, more definitive evidence for the H_c-H_d stereochemistry is found from the consideration of the cmr data. It was possible to assign all of the carbon-13 resonances by a combination of heteronuclear spin decoupling, calculation of expected chemical shifts and comparison with model compounds.

The expected chemical shifts of the enol acetate carbons in 39 can be calculated using vinyl acetate as the reference point and the empirically derived parameters for the calculation of chemical shift values of the olefinic carbons.[39]





$\alpha = 10.6$ ppm $\quad \alpha' = -7.9$ ppm

$\beta = 7.2 \quad \beta' = -1.8$

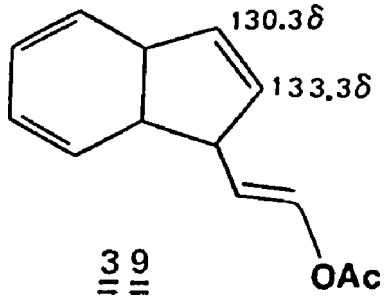
$\gamma = -1.5 \quad \gamma' = 1.5$

Using these empirically derived parameters the calculated chemical shifts for the a and b carbons of the enol acetate 39 are 134.6 ppm and 117.8 ppm, respectively. These calculated chemical shift values were confirmed by heteronuclear spin decoupling of the H_a and H_b nuclei. Irradiation of the H_a proton at 7.05 ppm gave a carbon-13 singlet at 135.0 ppm and similar irradiation of H_b at 5.18 ppm showed a carbon-13 singlet at 116.2 ppm. Thus, the C_a and C_b adsorptions are known to be 135.0 and 116.2 ppm, respectively.

The remaining carbon resonances can be determined with reasonable certainty by the comparison of calculated values with the appropriate model compounds.

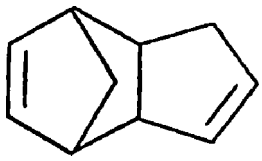
If it is assumed that the adsorptions at 128.8 and 134.8 ppm in the dihydroindene ester 40 are due to the cyclopentene olefinic carbons, based on the chemical shift

values found in cyclopentene and dicyclopentadiene, chemical shift values of 130.3 and 133.3 ppm are calculated for the C_k and C_j carbons of the enol acetate 39.



39

These calculated chemical shift values are remarkably close to the observed values of 132.8 and 133.2 ppm. The accuracy of these calculations can be checked by comparing the similarly calculated values for dicyclopentadiene with cyclopentene as the reference compound.



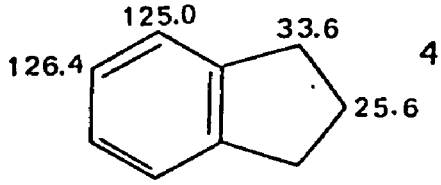
obs.	calc'd
136.0δ	[131.8δ]
131.9δ	[134.8δ]

(*Chemical shift assignments not proven by authors,[44] so that they could be reversed, as the calculations would indicate.)

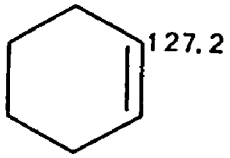
Roberts[39] estimates that the chemical shift parameters for olefinic carbons are accurate to within ± 2 ppm, which

Table XII

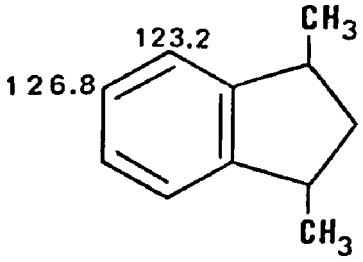
Model Compounds for C_{13} Data



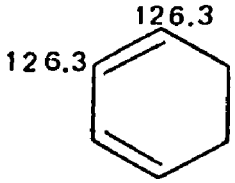
ref. 40



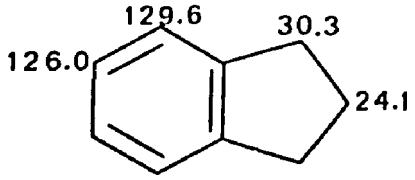
ref. 41



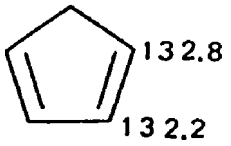
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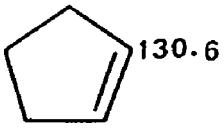
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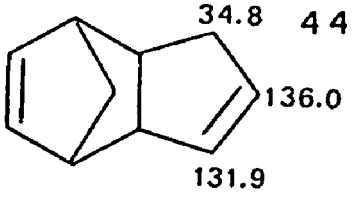
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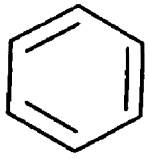
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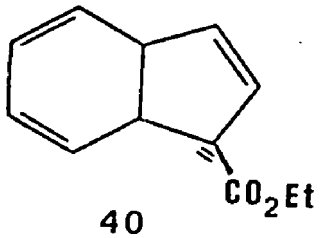


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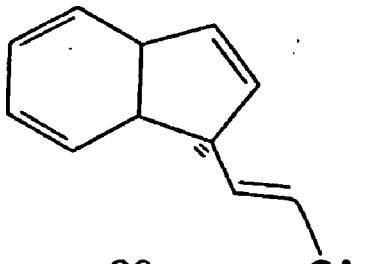
Table XIII

cmr Spectra of Enol Acetate 39 and

1-Carboethoxy-cis-3a,7a-Dihydroindene 40



40

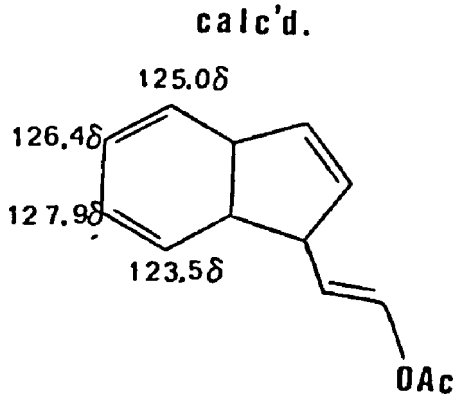


39

ppm			
121.0	60.7	116.2	49.7
121.7	59.8	120.7	43.6
125.7	44.1	123.0	38.2
127.9	39.8	125.8	14.7
128.8	14.3	126.1	
134.8		132.8	
173.8		133.2	
		135.0	
		167.8	

leaves the calculated values well within the error limits for the observed chemical shift values.

With indane as the model compound, the four diene carbons of the enol acetate are calculated to correspond to the four adsorptions between 120.7 ppm and 126.1 ppm.



obs
120.7 δ
123.0 δ
125.8 δ
126.1 δ

The chemical shifts for aliphatic hydrocarbons can be calculated to within ± 0.8 ppm using equation (1).[46] However, the calculated values for cyclic aliphatic carbons are not as accurate, as the chemical shifts are affected by steric interactions resulting from the stereochemistry of the ring.[47]

$$(1) \quad \Delta_c(k) = B_s + \sum_{m=2}^{4} D_m A_{sm} + \gamma_s N_{R3} + D_s N_{R4}$$

If equation (1) is used to calculate the expected chemical shifts of C_d and C_e, values of 44.06 ppm and 39.48 ppm, respectively, are obtained, if the contribution from

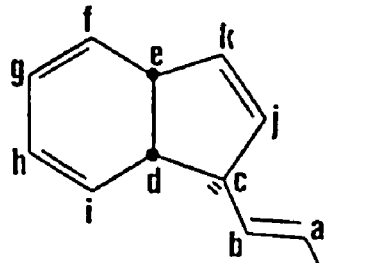
the γ carbons is ignored, as values for D_3 have not been tabulated. If the value for D_2 is used, the calculated chemical shifts are then 1 ppm higher for both carbons. The observed values of 43.6 and 38.2 ppm are in good agreement with the calculated values.

The remaining aliphatic carbon C_c can be calculated with more confidence, due to the availability of a good model comparison. Using the chemical shift of the analogous carbon in dicyclopentadiene, as the base value for calculation of the chemical shift of C_c in the enol acetate 39, and the substituent effect parameters for axial and equatorial substituents in cyclohexanes,[47] the chemical shift for C_c can be calculated for both the H_c-H_d trans and cis stereochemistry. For H_c-H_d trans, the most stable conformation of the enol acetate 39 has the enol acetate in a pseudo equatorial relationship to the five-membered ring and the calculated chemical shift for C_c is 49.3 ppm. If H_c-H_d has cis stereochemistry, the most stable conformation of 24 would have the enol acetate in a pseudo axial orientation, and the calculated value of the chemical shift of C_c is then 41.1 ppm. Based upon these calculated chemical shifts, and the previously calculated chemical shifts for C_d and C_e, the adsorption at 49.7 ppm would then be identified as that of C_c, with H_c-H_d having trans geometry, which is in accord with the analysis of the H_c-H_d coupling constant.

The assigned chemical shifts of the cmr spectrum of the enol acetate 39 with the comparison to the expected values is found in Table XIV

Table XIV

Comparison of Calculated and Observed C_{13} Chemical Shifts of the Enol Acetate 39



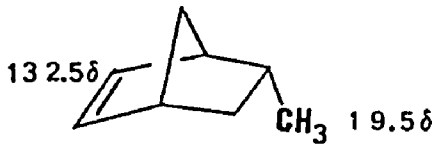
39

δ (ppm from TMS)

	a*	b*	c	d	e	f	g	h	i	j	k
obs.	135.0	116.2	49.7	43.6	38.2	120.7	126.1	125.8	123.0	133.2	132.8
calc.	134.6	117.8	49.3	44.1	39.5	125.0	126.4	127.9	123.5	133.3	130.3
Δ (obs-calc.)	+ 0.4	- 1.6	+ 0.4	- 0.5	- 1.3	- 4.3	- 0.3	- 2.1	- 0.5	- 0.1	+ 2.5

* Proved by heteronuclear spin decoupling.

Additional evidence for the stereochemistry of H_c-H_d stems from the analysis of the observed chemical shift of C_b. Steric buttressing of groups in a 1,4 relationship is known to shift the chemical shift of both groups upfield by 2 to 4 ppm.[48]



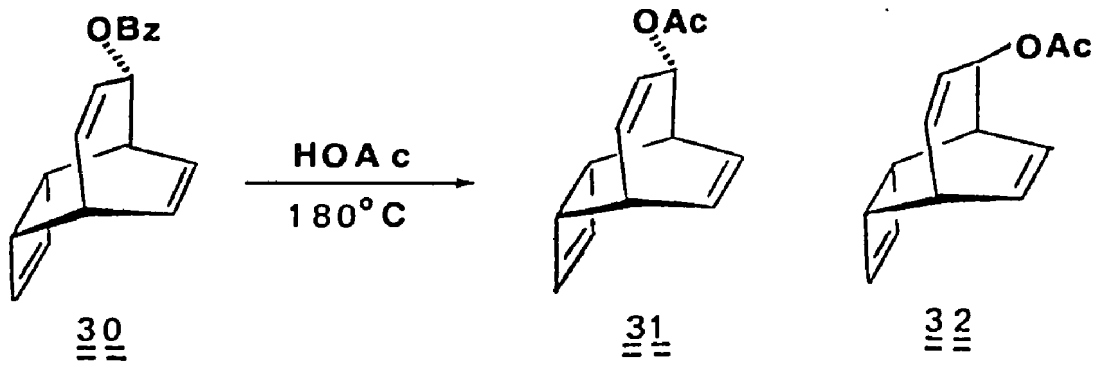




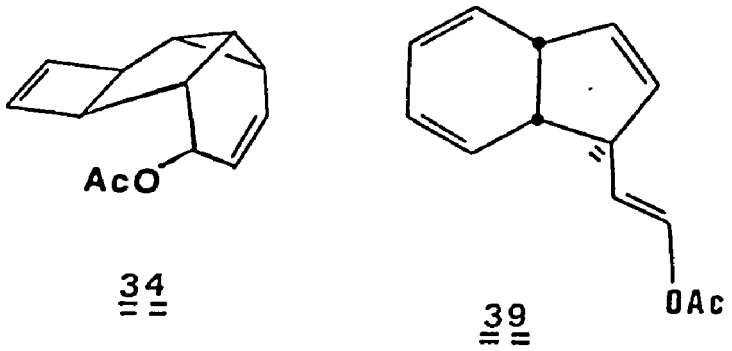
The interatomic distances for exo and endo 5-methyl norbornene are estimated to be 3.9 and 3.0 Å, respectively, with an upfield shift of 2.2 ppm for the endo methyl group and at least 3.3 ppm for C-3.

The interatomic distances, based on Drieding models, for the 1,4 relationship of C_b and C_i in the enol acetate 39 are 2.5 Å for H_c-H_d cis and 3.6 Å for H_c-H_d trans. Based upon the lack of an appreciable upfield shift for C_c with respect to its expected chemical shift, the analysis of the H_c-H_d coupling constant and the calculated chemical shift of C_c, the geometry of H_c-H_d was assigned as trans.

Based upon the preceding information, the products of the high temperature solvolysis of the benzoate 30 were then identified as the allylic acetate 31, the epimeric allylic acetate, 32, the cyclopropylallylic acetate 34 and the enol acetate 39.



30 31 32



34 39

C. Kinetics of acetolysis:

1) 118°C.

A solution of the benzoate 30 in glacial acetic acid was immersed in an oil bath at 130°C, and rapidly brought to 118°C. Aliquots of the reaction were quenched by plunging into a Dry Ice-acetone bath. The rate of disappearance of the benzoate 30 was calculated by subtracting the rate

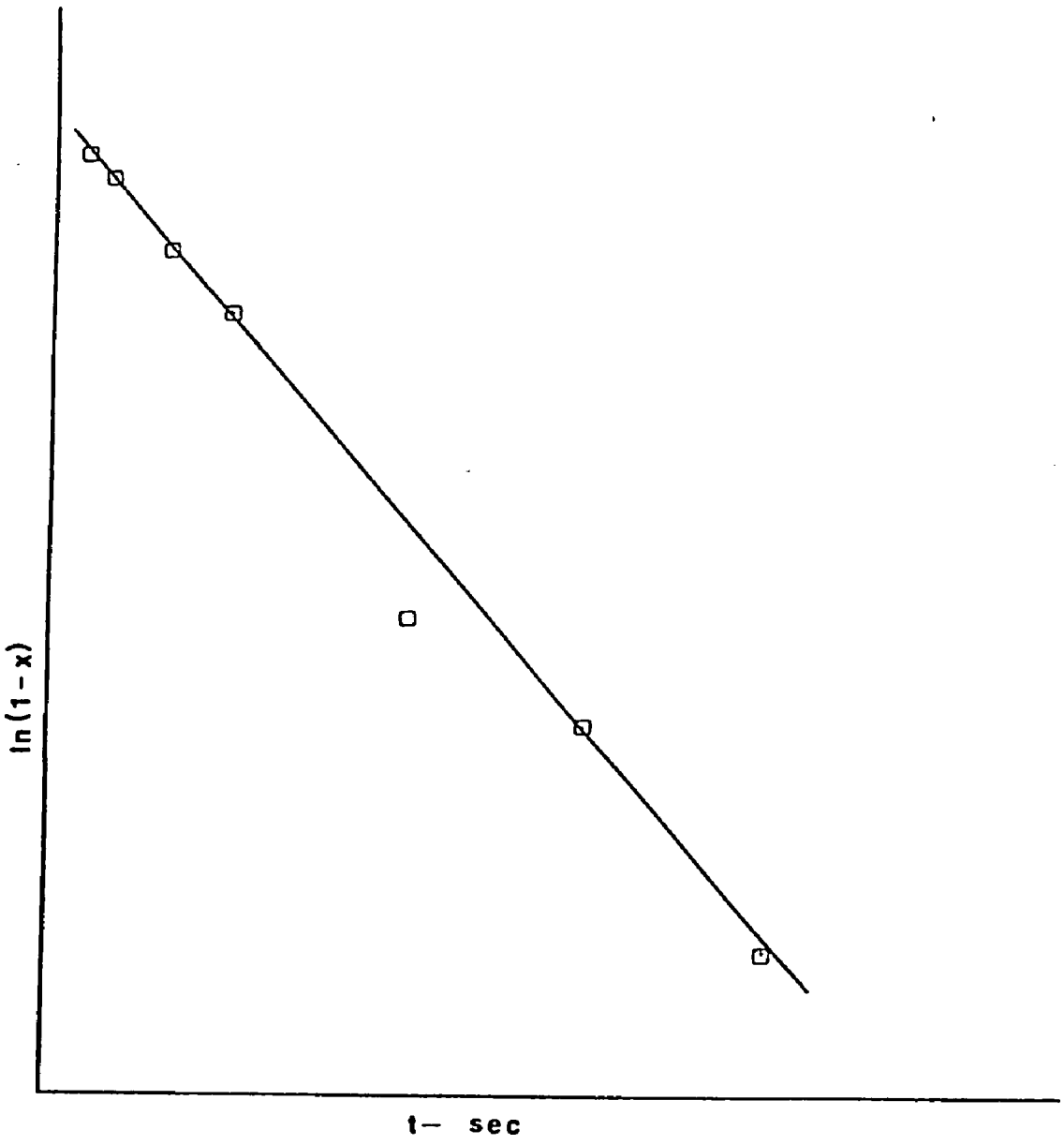


Figure 1: Kinetic Data at 118°C

of appearance of the mole fraction of the acetates 31, 32 and 34 from 1.0. The plot of the log of the mole fraction of unreacted benzoate versus time, gave good pseudo-first order kinetics, with $k = 1.12 \pm 0.01 \times 10^{-3}$ sec^{-1}, as determined by a least squares analysis.

2) Elevated temperatures--activation parameters:

A series of capillary tubes, containing a solution of the allylic acetate 31 and biphenyl in glacial acetic acid was plunged into a large oil bath, whose temperature was monitored by a copper constantor couple. Samples were then removed at various time intervals, quenched at -78°C and the rate of decrease of the equilibrated mixture of acetates monitored by analytical glpc, with biphenyl serving as an internal standard. The natural log of the normalized area of equilibrated acetates was plotted versus time and the slope of these plots determined by least squares analysis.

Assuming the Arrhenius equation, the energy of activation for the formation of enol-acetate 39 was determined by a least squares analysis of the plot of the natural log of the rate of loss of starting acetates versus the reciprocal of the absolute temperature.

The enthalpy of activation and entropy of activation were calculated from equations (2) and (3).

$$(2) \quad \Delta H^{\dagger} = E_a - RT$$

Table XV

Rates of Enol Acetate 39

Formation at Elevated Temperatures

$-\frac{d(31, 32, 34)}{dt}$	T(°K)
$3.7 \pm 0.7 \times 10^{-5}$	425.75
$5.4 \pm 0.6 \times 10^{-5}$	430.95
$1.4 \pm 0.2 \times 10^{-4}$	435.45
$1.5 \pm 0.2 \times 10^{-4}$	440.95
$2.2 \pm 0.3 \times 10^{-4}$	445.05
$4.2 \pm 0.4 \times 10^{-4}$	455.25

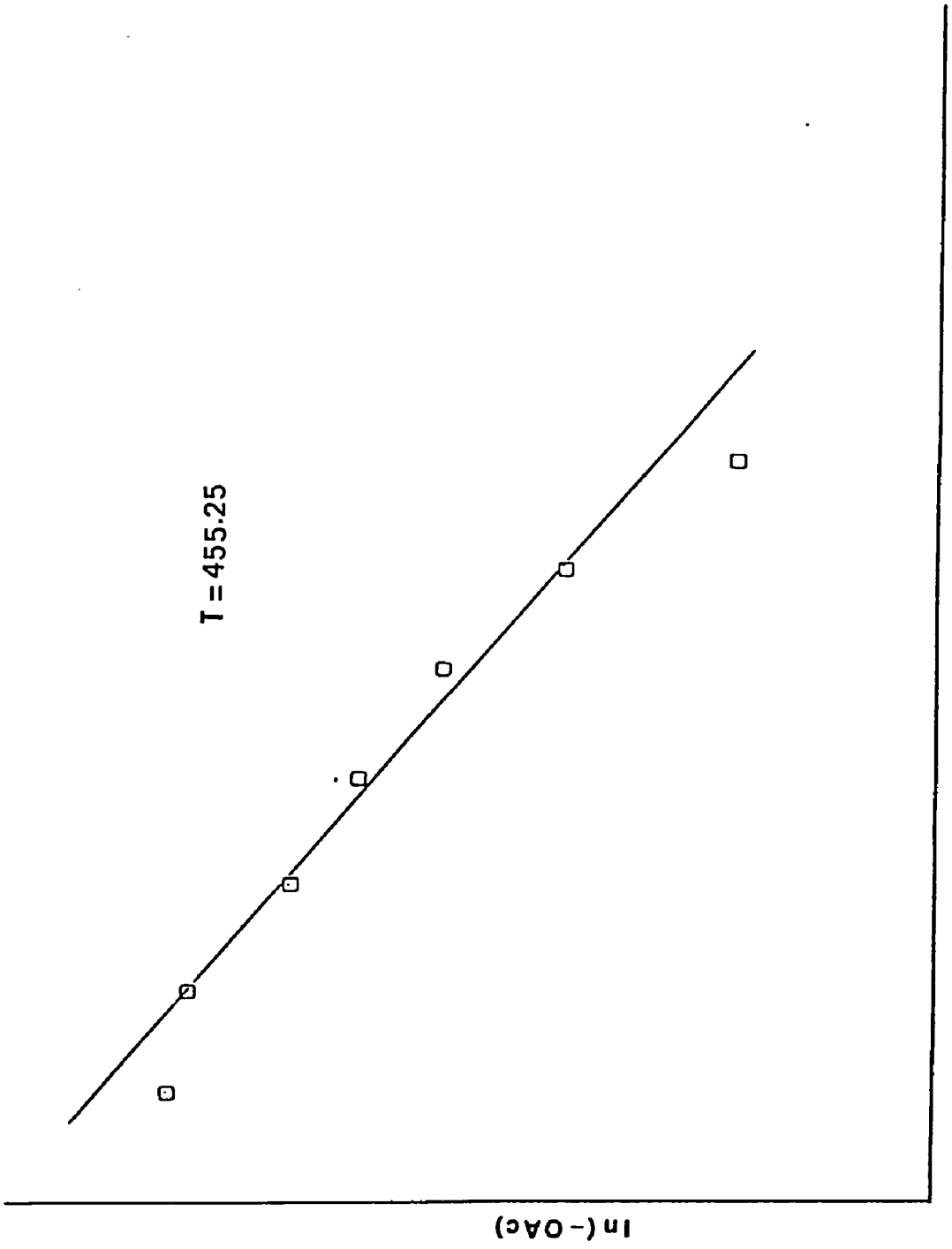


Figure 2: Representation Kinetic Data for Formation of Enol Acetate 39

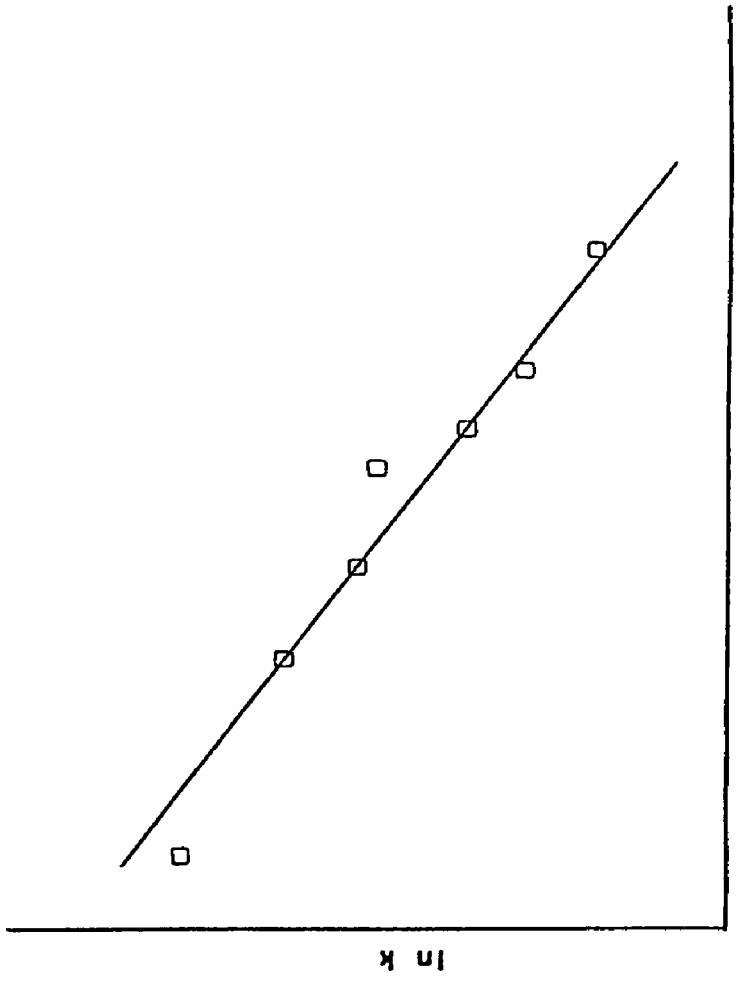


Figure 3: Arrhenius Plot for Formation of Enol Acetate 39

(3) $k_r = \frac{RT}{N_o h} e^{\Delta S^{\dagger}/R} e^{-\Delta H/RT}$

$\Delta H^{\dagger}_{425°K} = 31.2$ kcal

$\Delta S^{\dagger} = -6.2$ eu.

D. Thermal stability of the allylic acetates 17, 18 and 20.

When a solution of either the allylic acetate 31 or a mixture of the two epimeric allylic acetates 31 and 32 or a mixture of the epimeric allylic acetates, 31 and 32, and the cyclopropyl allylic acetate 34 in benzene was maintained at 180°C for two hours in a sealed capillary, no enol-acetate 39 was detected by analytical glpc. When these solutions of individual acetates, 31, 32 and 34, in glacial acetic acid were maintained at 180°C for two hours, the enol acetate 39 was observed as a product. Thus, the enol-acetate 39 could not be a thermal rearrangement product of the acetates 31, 32 and 34.

The solvolytic conversion of the cyclopropyl allylic acetate 34 to the $(CH)_{11}$ enol OAc 39 (based on the analysis of its cmr spectrum), supports the earlier assumption that the cyclopropyl allylic acetate 34 is a $(CH)_{11}$ isomer.

E. Exploration of other solvolytic media:

Other solvolytic conditions were explored in an attempt to observe new rearrangement products. At low temperatures (-78°C-0°C), trifluoroacetic acid, trifluoroacetic acid-methylene chloride, aluminum chloride-ether and sulfuric acid-water produced only the previously observed epimeric allylic alcohols 21 and 33, and the cyclopropyl allylic alcohol 37 from the benzoate 30, as shown by analytical glpc. At higher temperatures, only polymeric material, as evidenced by the lack of adsorption between 7.0 δ and 5.0 δ and the complex adsorptions between 3.5 δ and 1.0 δ in the pmr, was found from these solvolyses.

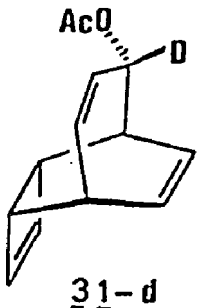
From 25°C-100°C, only the alcohols 21, 33 and 37 could be detected by analytical glpc from the solvolysis of the allylic benzoate 30 in either 80% acetone, 80% dioxane or 80% acetone-2,6-lutidine. Formic acid and trichloroacetic acid at 100°C gave rise to only three products by analytical glpc, which were not further characterized.

III. Deuterium labeling and mechanistic interpretation:

In order to probe the mechanism for the formation of the enol acetate 39, the 7-deuterobenzoate 30D and the 7-deuteroacetate 31D were synthesized from the 7-deuteroallylic alcohol 21D, which was isolated from the reduction of the enone 16 with lithium aluminum deuteride at -78°C. The deuteroallylic alcohol 21D had greater than 98% deuterium incorporation as evidenced by its pmr and mass spectra.



30-d



31-d

The deuterobenzoate 30d was solvolyzed at 118°C in glacial acetic acid and the allylic acetate 31 and epimeric allylic acetate 32 were isolated as their corresponding alcohols, 21 and 33, and the cyclopropyl allylic acetate 34 was isolated from the mixture of acetates produced from the solvolysis by preparative glpc.

Both the deuterobenzoate 30d and the deuteroacetate 31d were solvolyzed at 165°C and 175°C. The enol acetate 39 was isolated by preparative glpc from the mixture of acetates produced during the solvolysis and the epimeric acetates 31 and 32 were isolated as their corresponding alcohols 21 and 33. The cyclopropyl allylic acetate 34 could not be successfully isolated from the mixture of these acetates due to its relatively low concentration and the close proximity of its retention time to that of the enol acetate 39 under preparative glpc conditions.

The isolated products were retrapped by preparative glpc for all of the deuterium labeled solvolyses, until the pmr spectra of the components indicated that they were pure. The mass spectra of the deuterium containing solvolysis products indicated that no deuterium had been lost during the solvolyses.

The extent of deuterium scrambling in the epimeric alcohols was analyzed on the basis of the normalized areas of the pmr adsorptions with the total areas, excluding the OH adsorption, set equal to 10 protons. For the cyclopropyl allylic acetate 34 and the enol acetate 39, the areas of the pmr adsorptions were calculated with the area of the acetate-CH_3 adsorption normalized for 3 protons. In those cases where drift of the integrated areas was significant, any drift corrections were applied consistently to all of the pmr resonances. The amount of material isolated in most cases was small, due to the sequential trapping that was employed to initially separate, and finally purify the products of the solvolyses. Due to the small amounts of material available, the pmr spectra were recorded with the rf set just below saturation level, so that the gain required for a usable spectrum could be set to a minimal value, thus minimizing the drift in the integrated intensities of the observed pmr adsorptions.

The results of the deuterium labeling experiments are summarized in Tables XVI and XVIA .

Table XVI

Deuterium Scrambling Experiments

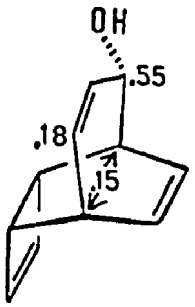
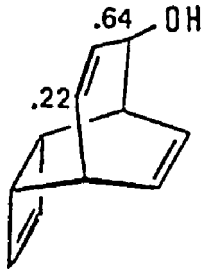
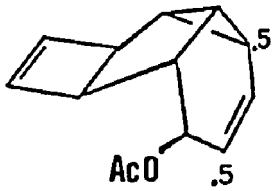
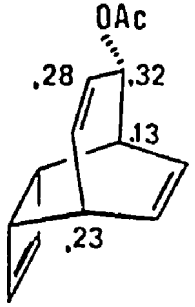
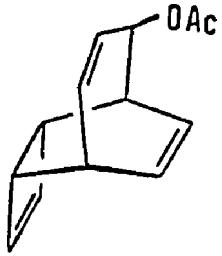
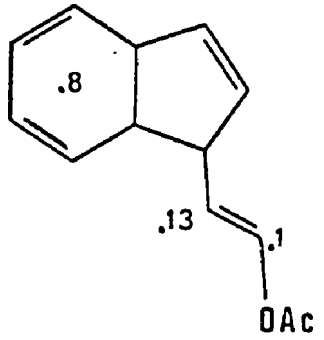
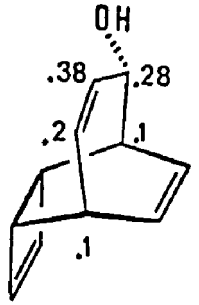
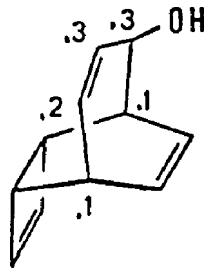
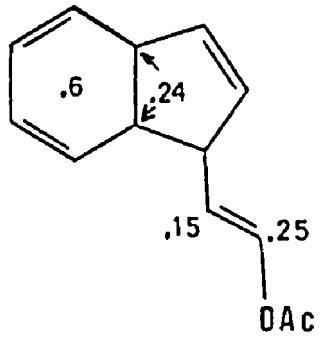
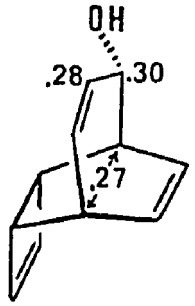
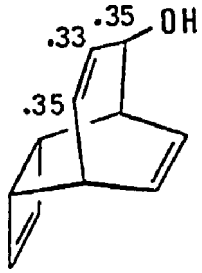
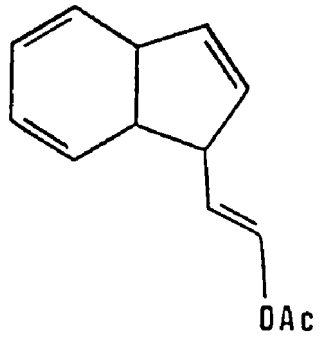
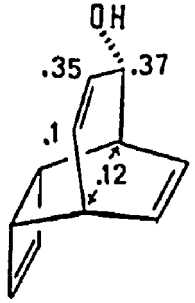
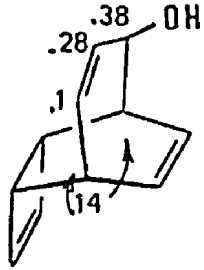
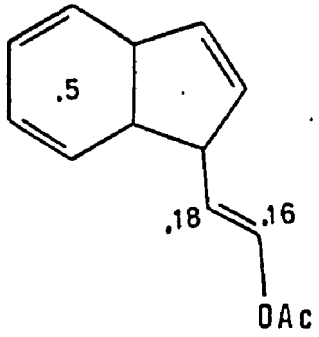
Exp't.					
1	30-d	120°			
2	30-d	165°			

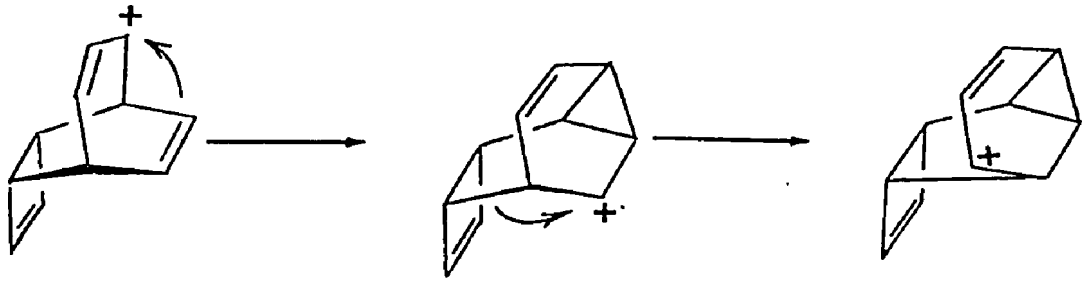
Table XVIA

Deuterium Scrambling Experiments

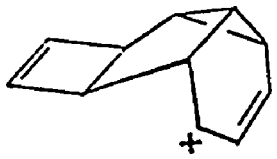
Exp't					
4	30-d	170°			
5	30-d	168°			
6	31-d	168°			

A. Low temperature results:

The isolation of the cyclopropyl allylic acetate 34 is best rationalized by the homoallylic π participation of the 2 bridge, followed by a Wagner-Meerwin shift of the C-1,2 bond.



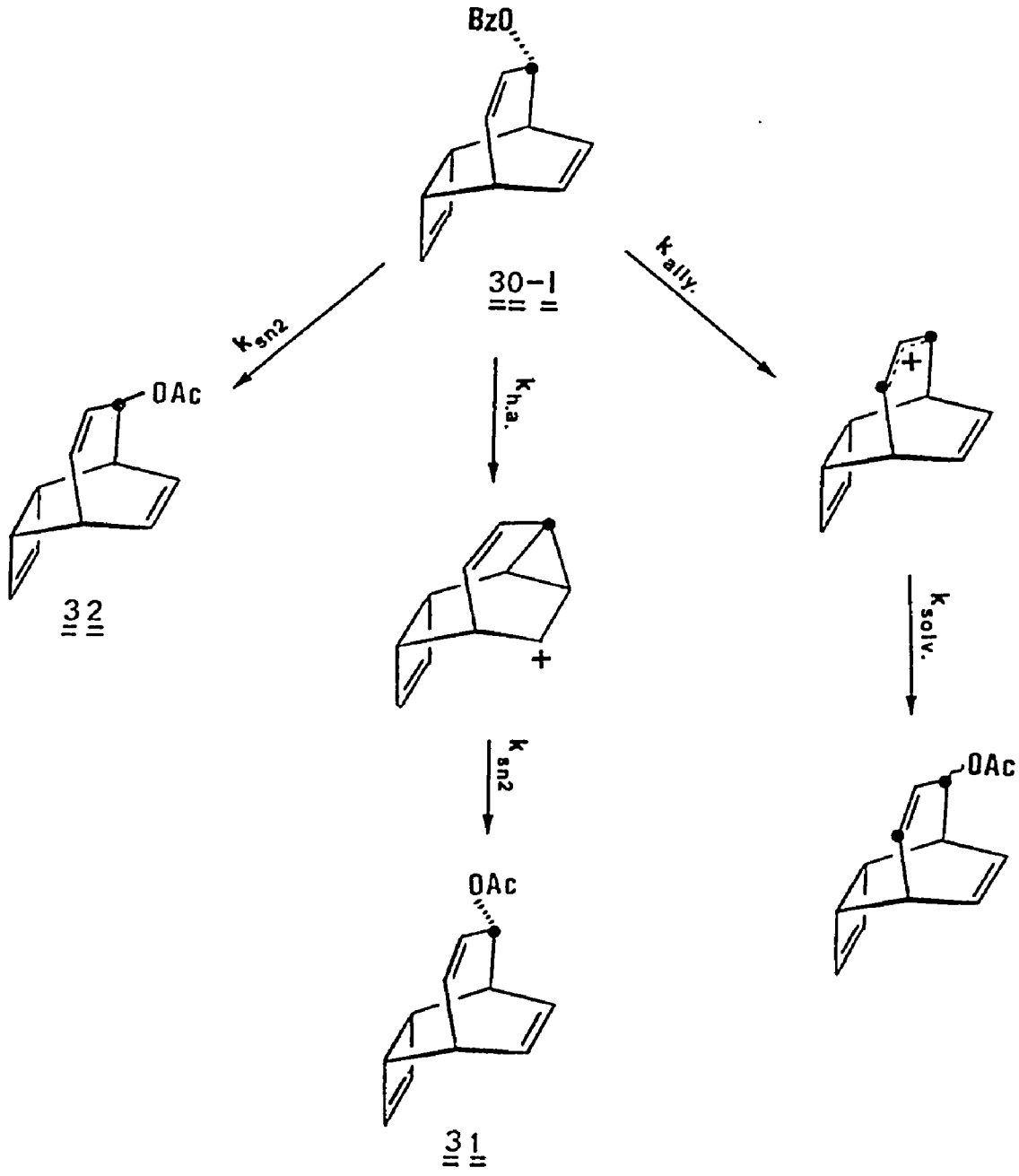
III



The most striking feature of the deuterium scrambling found in the products from the solvolysis of the benzoate 30d at 118°C is the lack of complete allylic scrambling. This lack of equilibration of the allylic system can be explained in one of several ways. There can be a kinetic competition between the formation of a symmetrical allylic species and nucleophilic displacements at the seven carbon by the solvent or the π bond of the two bridge as in scheme 1; there can be a kinetic competition between Sn2, Sn2' and homoallylic Sn2 and Sn2' attack involving external nucleo-

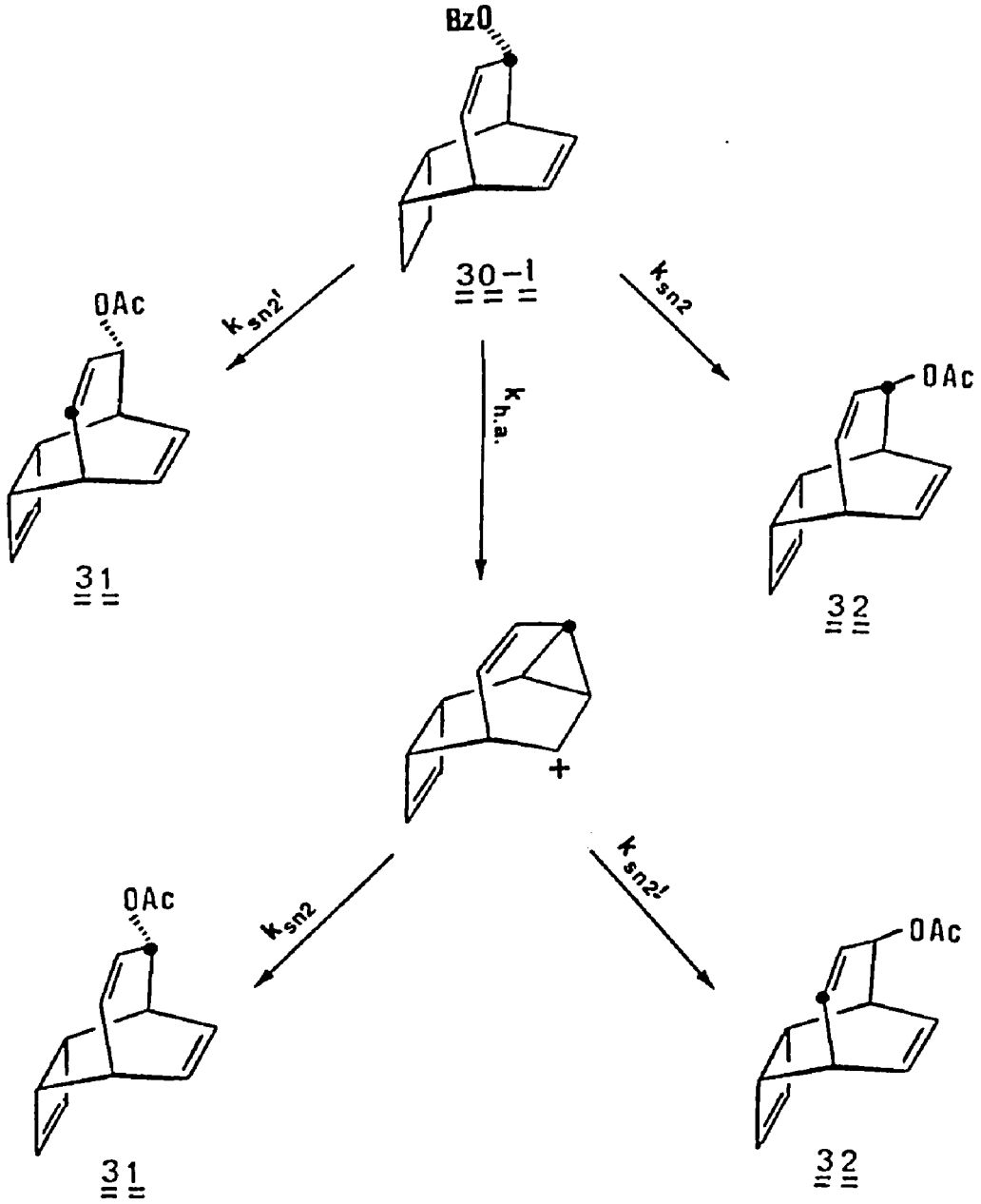
Scheme 1

Equilibration via competitive generation of an allylic cation



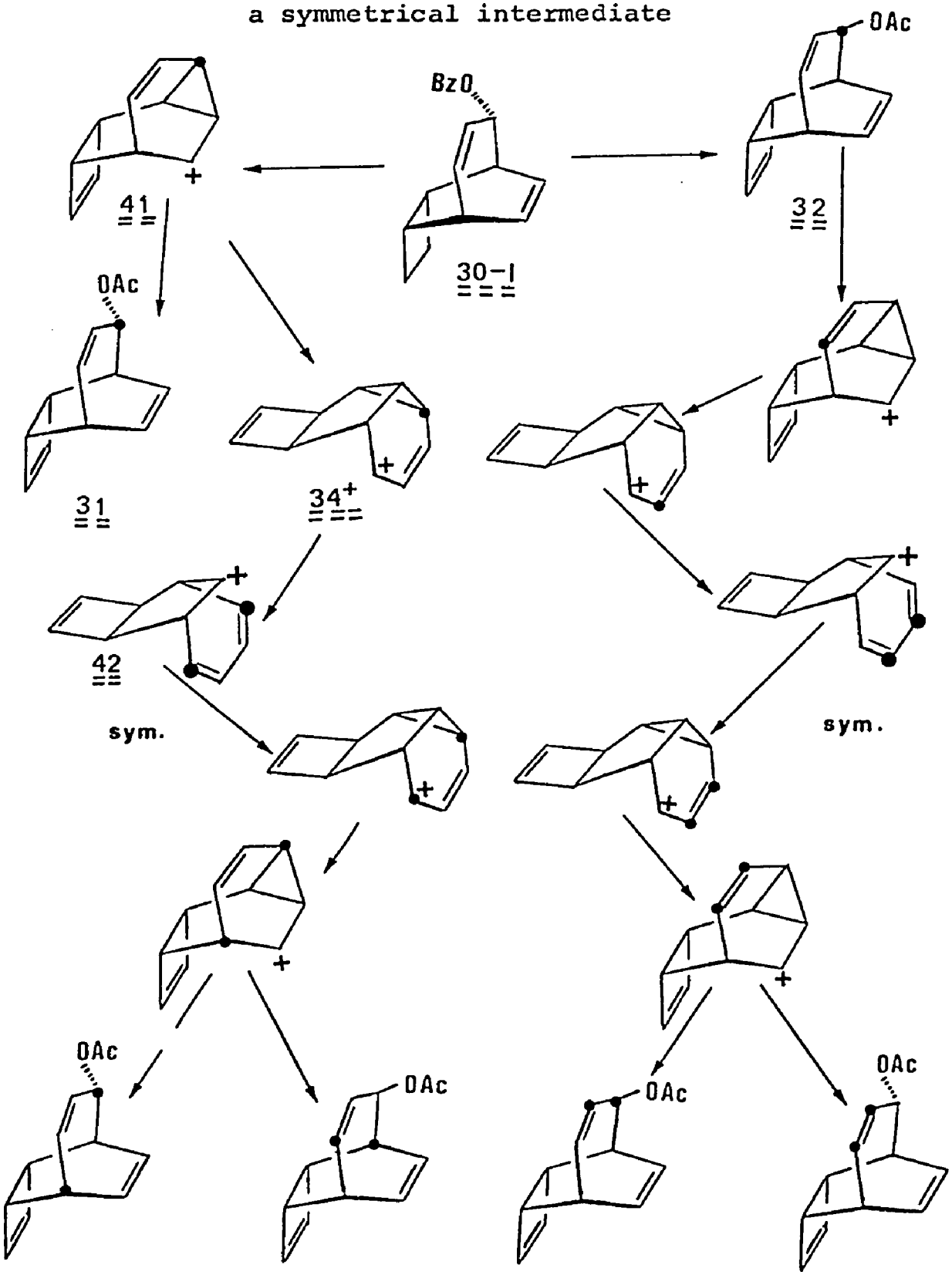
Scheme 2

Competitive Sn2 and Sn2' reactions



Scheme 3

Competitive Sn2 and Sn2' with intervention of a symmetrical intermediate



phile or the π bond as in scheme 2; or the extent of deuterium found at C-9 may be due to a kinetic competition between Sn2 attack at C-7 and homoallylic participation of the 2 bridge on both epimers as in scheme 3; or a combination of any two or all of these schemes. In all of the represented schemes, the species $\underline{\underline{30I}}$ undergoing nucleophilic attack may be the covalently bonded species $\underline{\underline{30}}$, or the intimate ion pair, associated ion pair or the solvent separated ion pair derived from $\underline{\underline{30}}$, retaining the original stereochemistry of the benzoate $\underline{\underline{30}}$. It is assumed that subsequent rearrangements of the acetates are slow relative to the starting benzoate $\underline{\underline{30}}$.

On the basis of the deuterium found at the bridgehead carbons in the allylic acetate $\underline{\underline{31}}$, part of the scrambling process found in scheme 3 is more than likely operating. While it is thought that a combination of scheme 2 and scheme 3 is determining the extent of deuterium scrambling found at low temperatures through the intermediacy of an intimate ion pair $\underline{\underline{30I}}$,[50] the symmetrical allylic carbonium ion represented in scheme 1 is suppressed energetically with respect to direct displacements by solvent at C-7. This may be due to destabilization of the allylic cation resulting from the bishomocyclopentadienyl cation interaction, or it may only reflect the high nucleophilicity of the solvent. It is not possible to distinguish between these two factors with the data available.

While it might appear that the assigned deuterium content found in Table XVI for the cyclopropyl allylic acetate 34 is arbitrary as the acetate methine and the α proton of the allylic vinyl, and the β-vinyl proton and a cyclobutene vinyl proton adsorptions overlap in the pmr spectrum of the acetate 34, that is not the case. The cyclobutene and β vinyl (vide supra) integrated for 1.96 H, placing no deuterium on the β carbon of the allylic acetate. The cyclopropyl protons integrate for 2.49 H. If the mechanism for the deuterium incorporation found in the bridgehead protons of the allylic acetate 31 involves the cyclopropyl allylic carbonium ion 34+, as depicted in scheme 3, the cyclopropyl protons never become scrambled in the early stages of the solvolysis. Utilizing this mechanistic argument, then the 0.5 D found in the cyclopropyl adsorptions must be at H_i, as it is represented. The presence of a full half of a deuterium in the cyclopropyl proton H_i then precludes any deuterium content at the acetate methine.

Within this mechanistic analysis, the deuterium content found in the cyclopropyl allylic acetate 34, indicates that the rate of cyclopropyl participation to scramble the deuterium into the bridgehead protons of the recovered epimeric allylic acetates 31 and 32 must be slow with respect to the competing nucleophilic processes. This may be a reflection of the relative stability of the cyclopropyl allylic cation 34+ and the symmetrical secondary methine cation 42. The lack of deeper seated scrambling found in the cyclopropyl allylic acetate 34 indicates that the reversion of 42 to 34+ is assisted by the reverse Wagner-Meerwein shift to yield the homoallylic cation 41 which is then rapidly attacked by external nucleophile.

The fact that the deuterium in 34 is found over two carbons, with equal population, implies one of two things. In order to obtain 34 with a symmetrical distribution of deuterium, the π bond of the 2 bridge must have participated with some equivalent of a symmetrical intermediate. The bidentate allylic ion pair 43 would qualify for this symmetry requirement.



43

The participation of the 2 bridge may require more positive character at the homoallylic cationic center before its interaction with that center in an allylic system becomes significant. If this is the case, scheme 1 would then best describe the lack of allylic scrambling.

More likely, in light of the deuterium found in the bridgehead carbons of 21 is the possibility that the assumption of greatly differing reactivity of the benzoate versus the acetate is invalid. That this may be the case is implied in scheme 3, which seems to generate the best internal fit of the deuterium distribution data.

B. Elevated temperature results:

Two facts are readily apparent from the deuterium scrambling observed from the high temperature solvolyses of the benzoate 30d and the allylic acetate 31d. First, a significant amount of deuterium has become incorporated into the bridgehead carbons, C-1 and C-6, and all three of the allylic 3-bridge carbons, C-7, 8, and 9 in the epimeric allylic acetates 31 and 32, without evidence of allylic scrambling. Secondly, in the enol acetate 39, a significant fraction of the deuterium present in the molecule, appears in the vinyl protons of the dihydroindene carbon skeleton.

The deuterium scrambling in the recovered epimeric acetates 31 and 32 is reminiscent of scheme 3 discussed earlier. However, in order to gain insight into the mechanism for the formation of the enol acetate 39, the

exact deuterium distribution over the vinyl carbons must be determined.

This was accomplished by the analysis of the cmr spectrum of the deuterium scrambled enol acetate 39 from deuterium experiments 3 and 5 in Tables XVI and XVIA a.

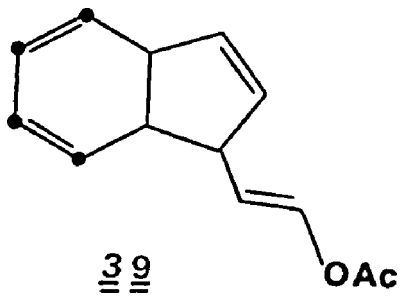
Deuterium causes an upfield geminal isotope shift of adjacent carbon atoms to the extent of 0.12 ± 0.04 ppm.[51] Occasionally, geminal and vicinal C_{13}-D couplings equal to 0.15 the geminal and vicinal C_{13}-H coupling will be observed.[52]

The cmr spectra of the enol acetate 39 from both deuterium experiments, 3 and 5, were qualitatively identical. Only the vinyl carbons at 120.7, 123.0, 125.8, and 126.1 ppm were significantly affected with the bridgehead carbons at 49.7, 43.6, and 38.2 ppm showing varying but significant deuterium isotope affects. The carbon adsorptions at 118.0 ppm and 134.5 ppm have been previously, and unambiguously identified as the carbons of the enol acetate unit. These adsorptions were totally and unambiguously unaffected by deuterium, which proves that no deuterium is found in the enol acetate group and that the integrated pmr intensity data indicating deuterium at those carbons is in fact, in error.

It is more than likely, that the cause of this error was the combination of the low amounts of the enol acetate 39 (10-20 mg) used to generate the deuterium data and the high rf employed to obtain useable spectra. The error in

the pmr deuterium data for the low temperature solvolysis (Expt. 1, Table XVI) is estimated to be less (5%) as larger amounts of the acetates 31, 32 and 34 (20-30 mg) were available.

The unambiguous lack of a deuterium effect in the previously identified vinyl carbons C_j and C_k (133.2 and 132.8 ppm), and the already noted absence of deuterium in C_a and C_b, excludes deuterium from the carbons $C_{a,b,c,d,e}$. The subtle splitting found in C_c excludes deuterium at C_d, which eliminates deuterium at the bridgehead carbons, C_d and C_e. Thus the deuterium is unambiguously located in the 4 carbons, $C_{f,g,h,i}$, of the diene unit of the enol acetate 39.

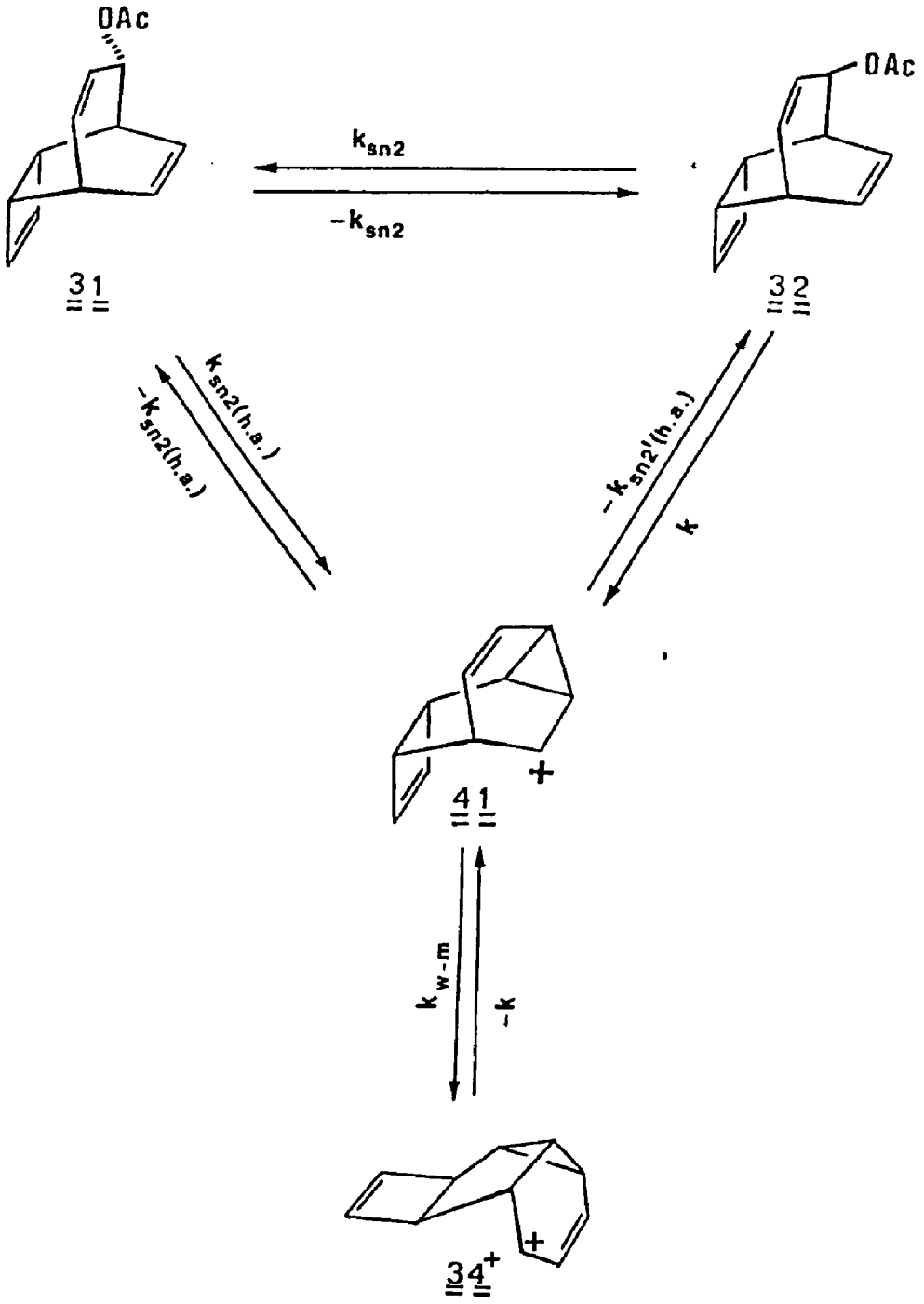


39

With the deuterium now definitively located in the enol acetate 39 carbon framework, the stereochemistry of the enol acetate 39, the isolation of the cyclopropyl allylic acetate 34 and the deuterium distribution in the recovered epimeric acetates 31 and 32, it is possible to construct a mechanism which is consistent with the observed products and their deuterium distributions. This mechanism is depicted in schemes 4 and 4a.

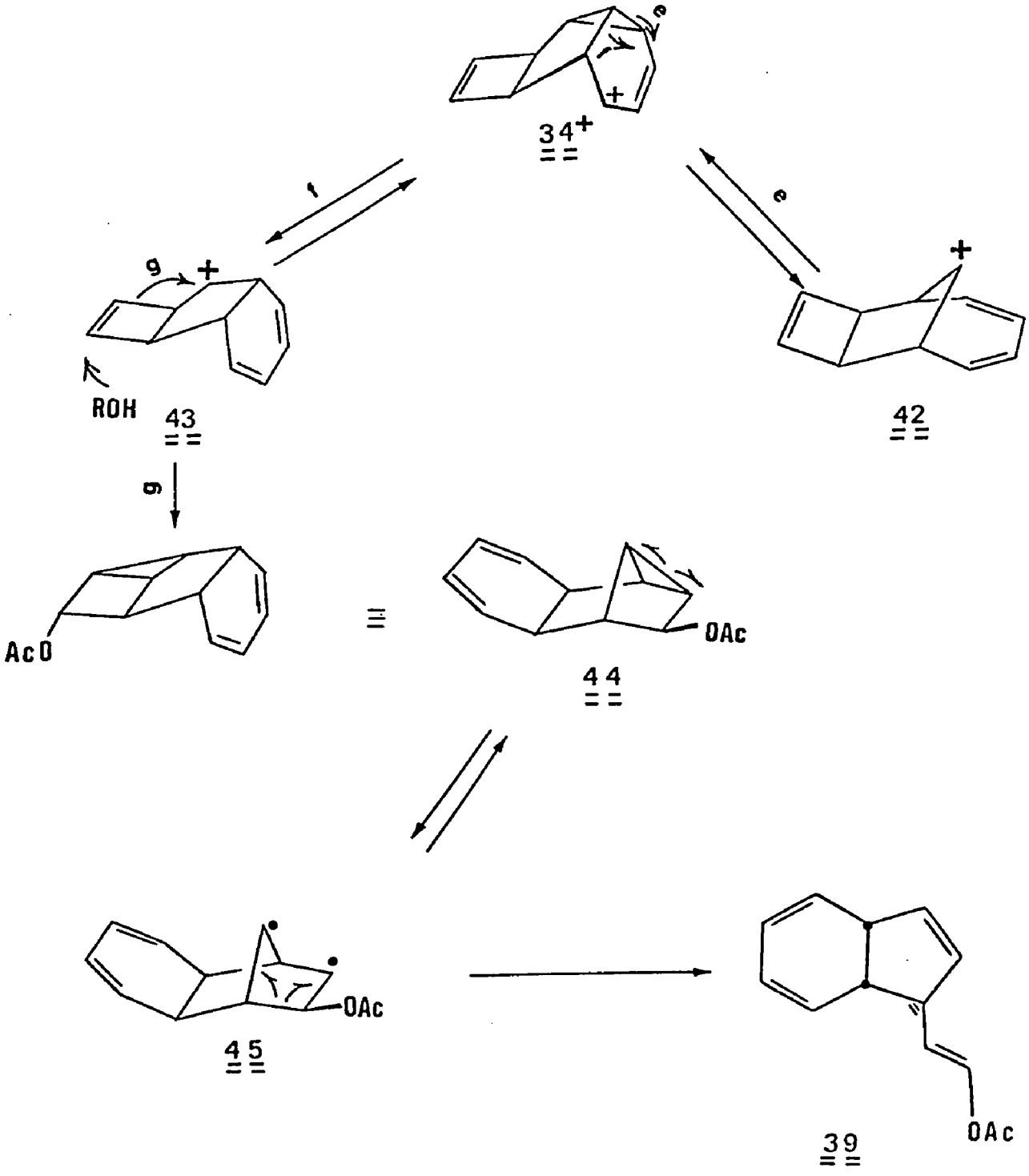
Scheme 4

Mechanism for enol acetate 39 formation



Scheme 4a

Continuation of mechanism for enol acetate 39 formation



Scheme 5

Predicted initial deuterium distribution for epimeric acetates 31 and 32

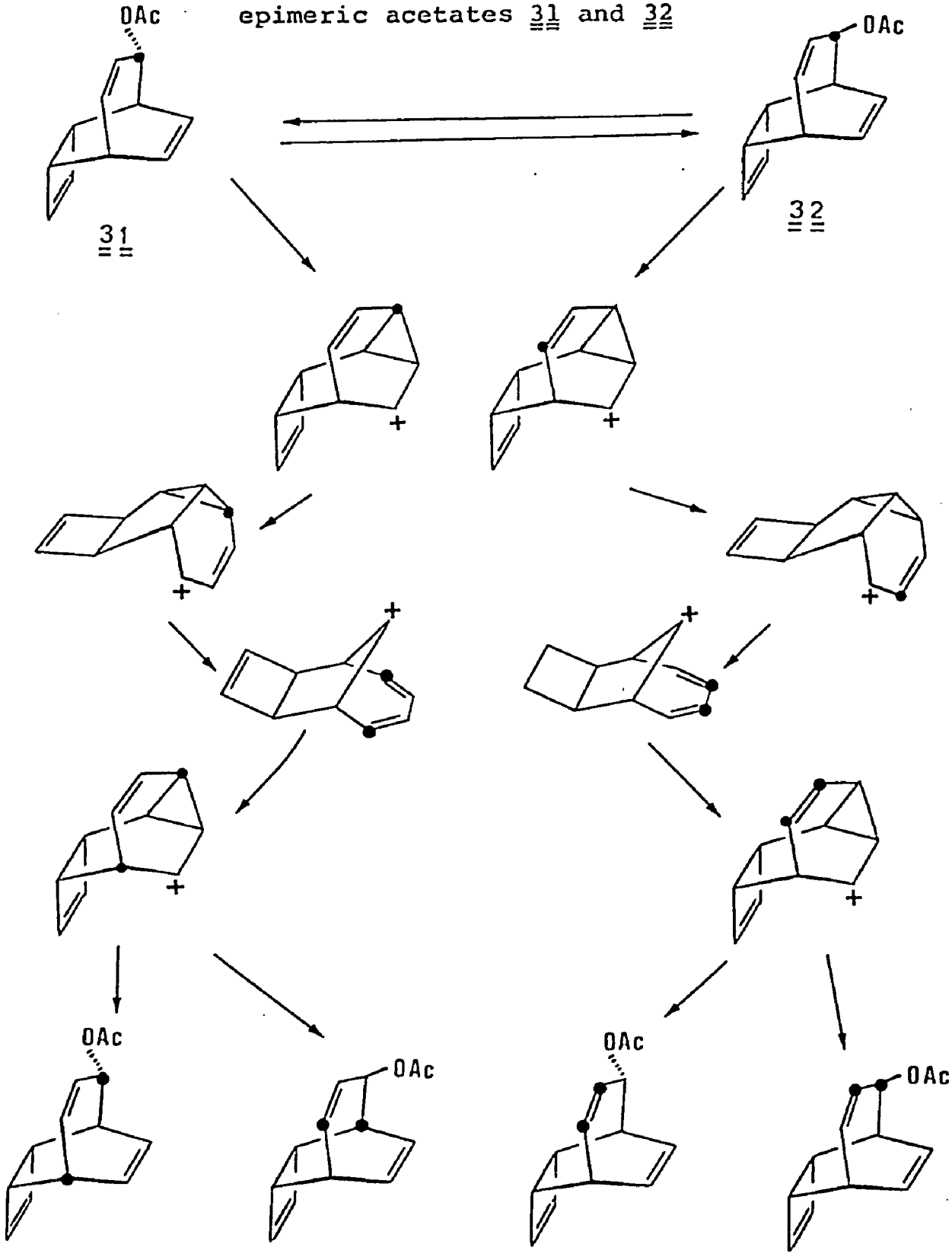
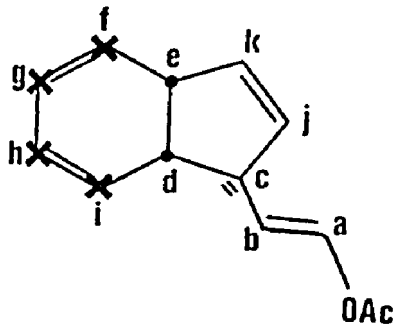


Table XVII

Analysis of Deuterium Affected Carbon Resonances

in the Enol Acetate 39



39

carbon	δ obs.	calc.	relative D intensity	1st Order multiplicity
c	49.7	49.3		slight br
d	43.6	44.1		s and d
e	38.2	39.5		slight splitting
f	120.7	125.0	0.08	t
g	126.1	126.4	0.4	t
h	125.8	127.9	0.12	1:1 d
i	123.0	123.5	0.4	t

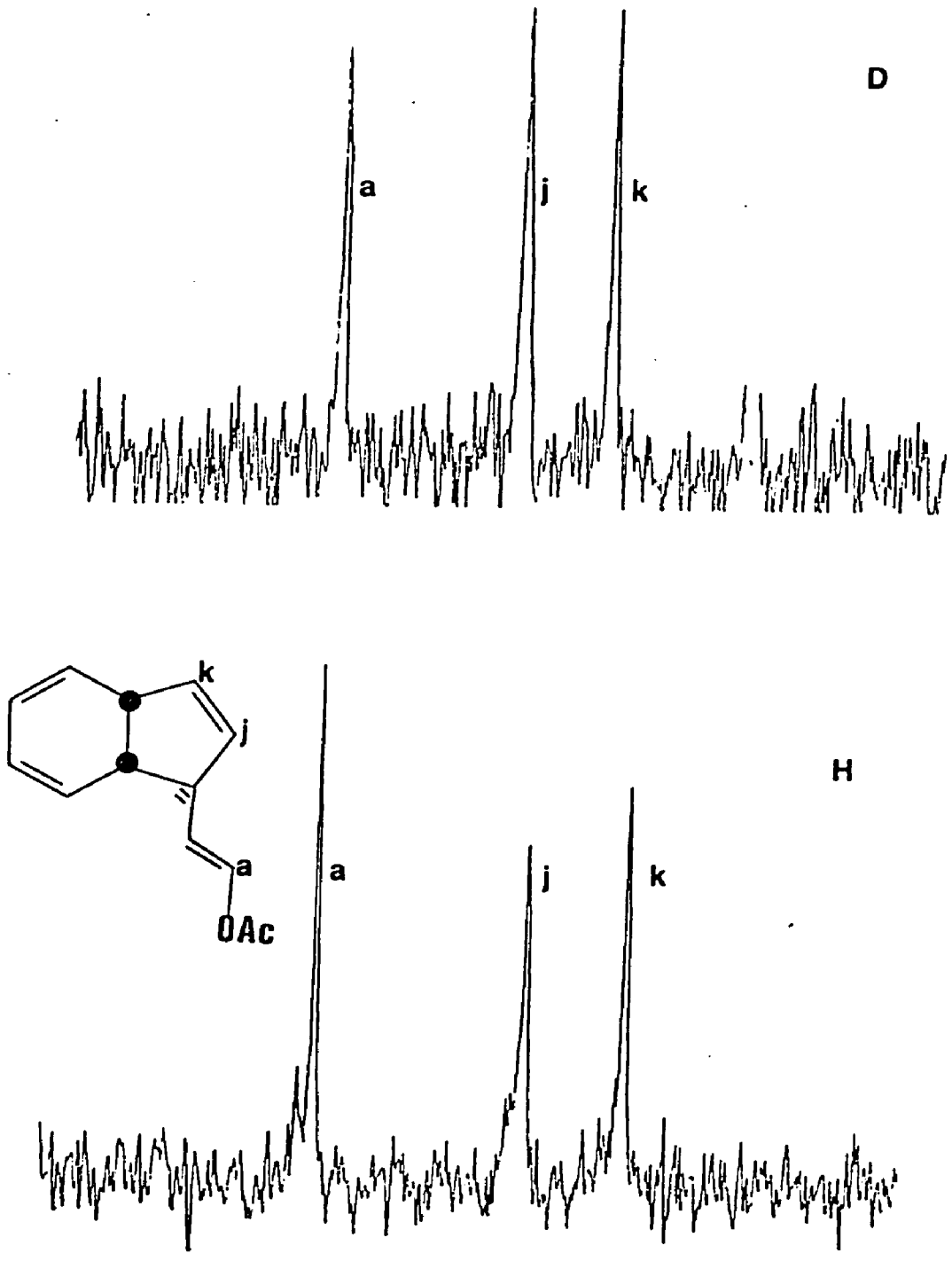


Figure 4: Comparison of C_{13} Spectra of Deutero-and Protio-Enolacetate 39 (200 Hz. width, 135.0-132.8 ppm)

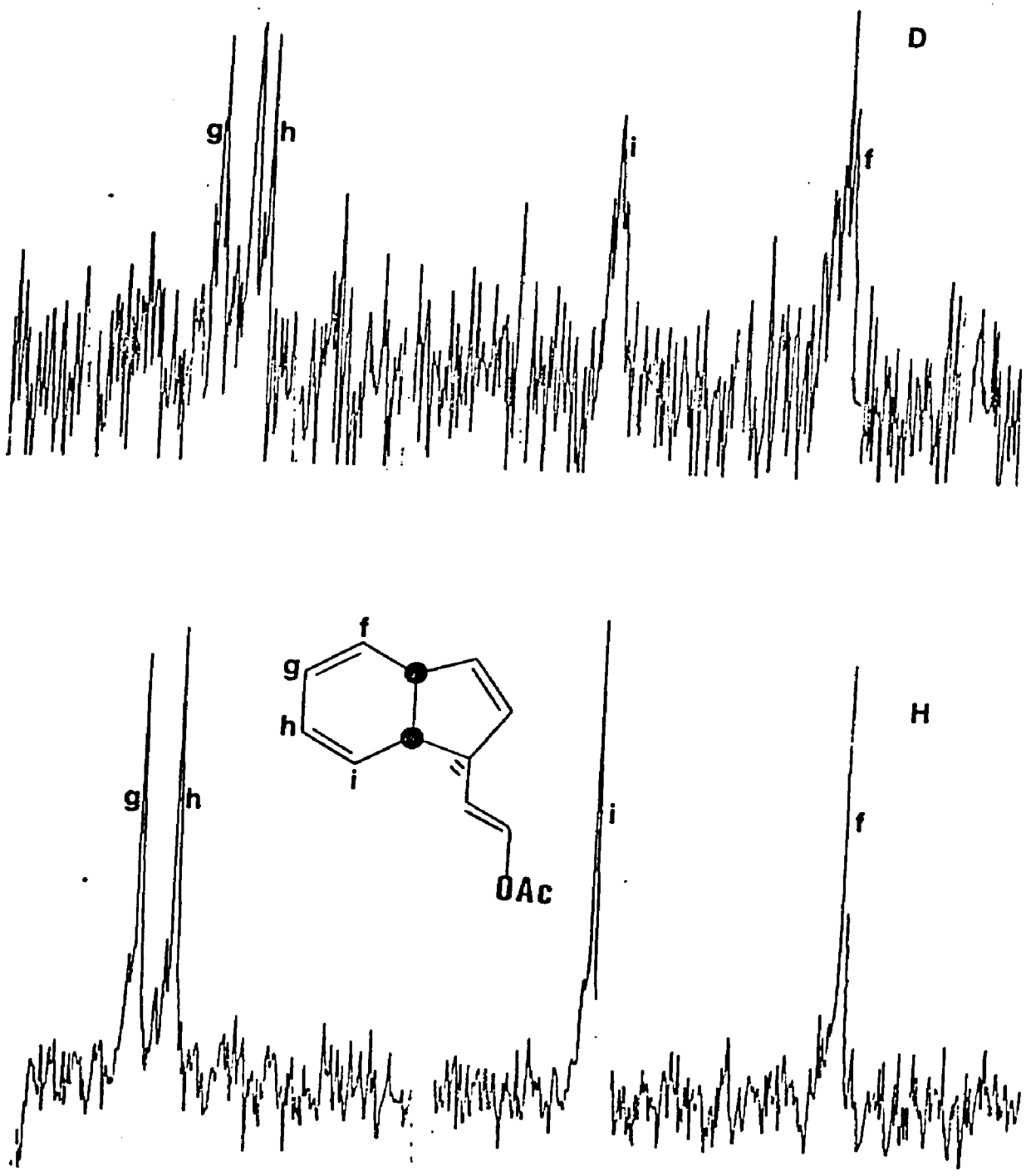


Figure 5: Comparison of C_{13} Spectra of Deutero- and Protio-Enolacetate 39 (200 Hz width, 126.1-120.7 ppm)

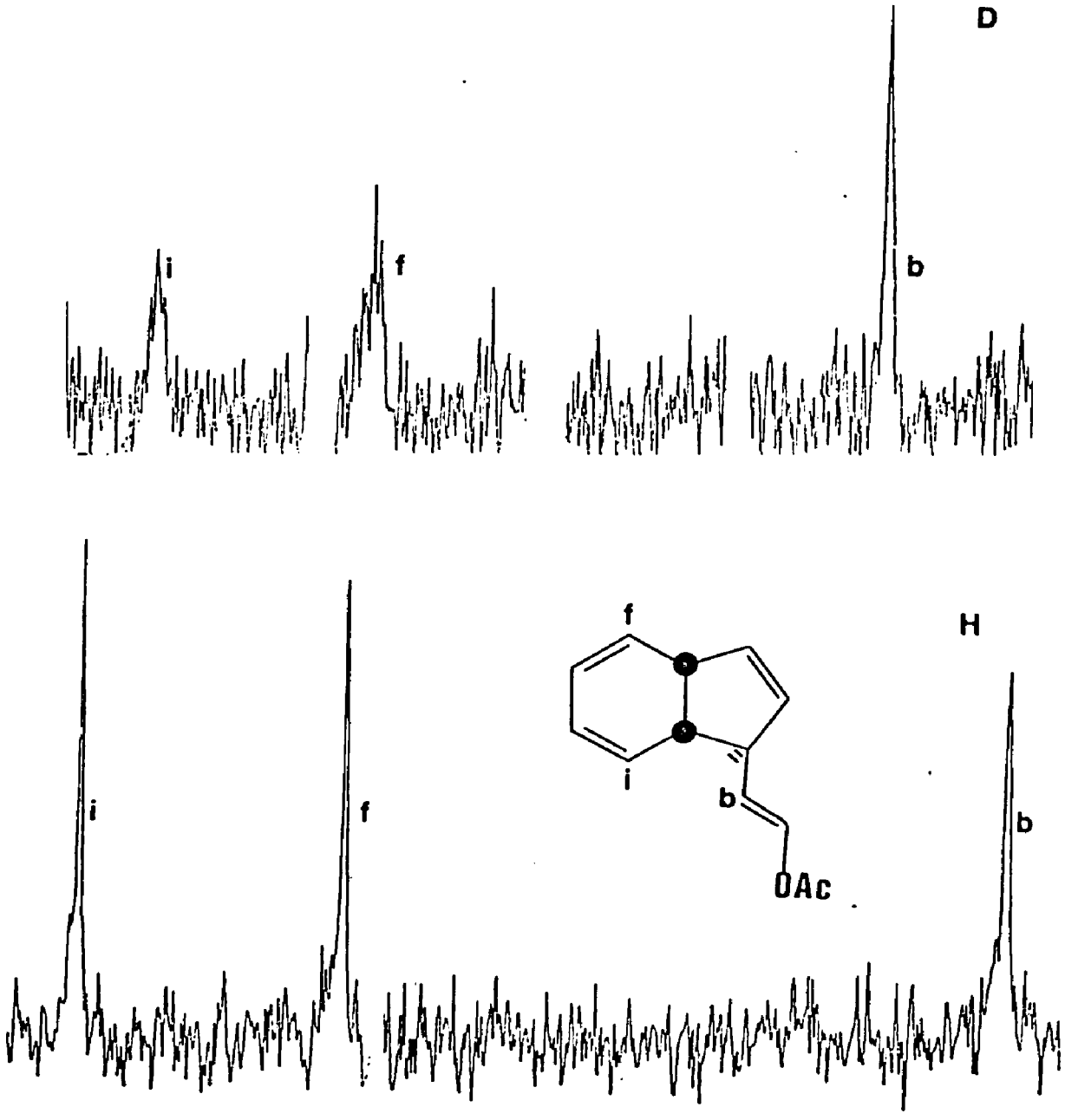


Figure 6: Comparison of C_{13} Spectra of Deutero-and Protio-Enolacetate 39 (200 Hz width, 123.0-116.2 ppm)

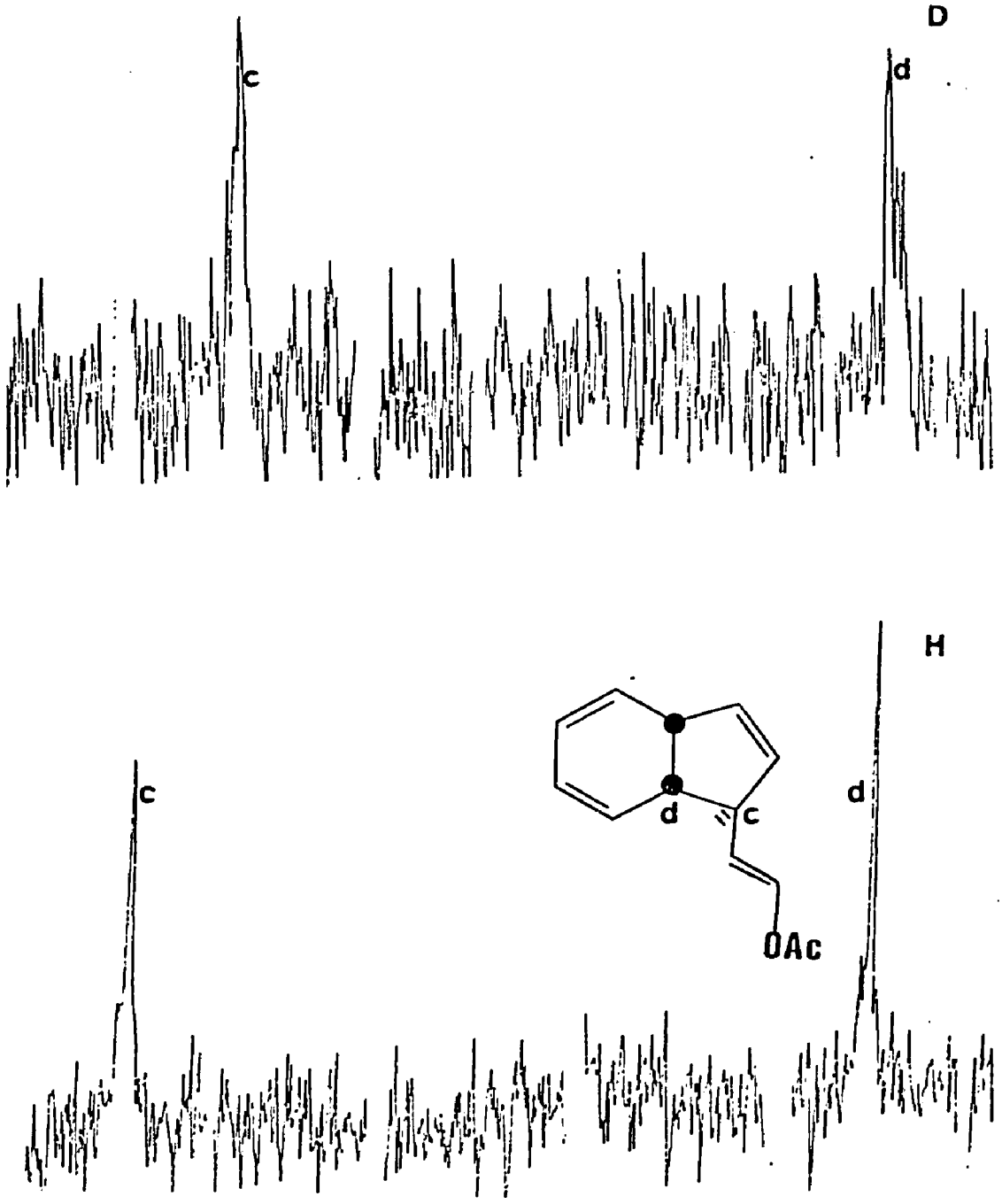


Figure 7: Comparison of C_{13} Spectra of Deutero-and Protio-Enolacetate 39 (200 Hz width, 49.7-43.6 ppm)

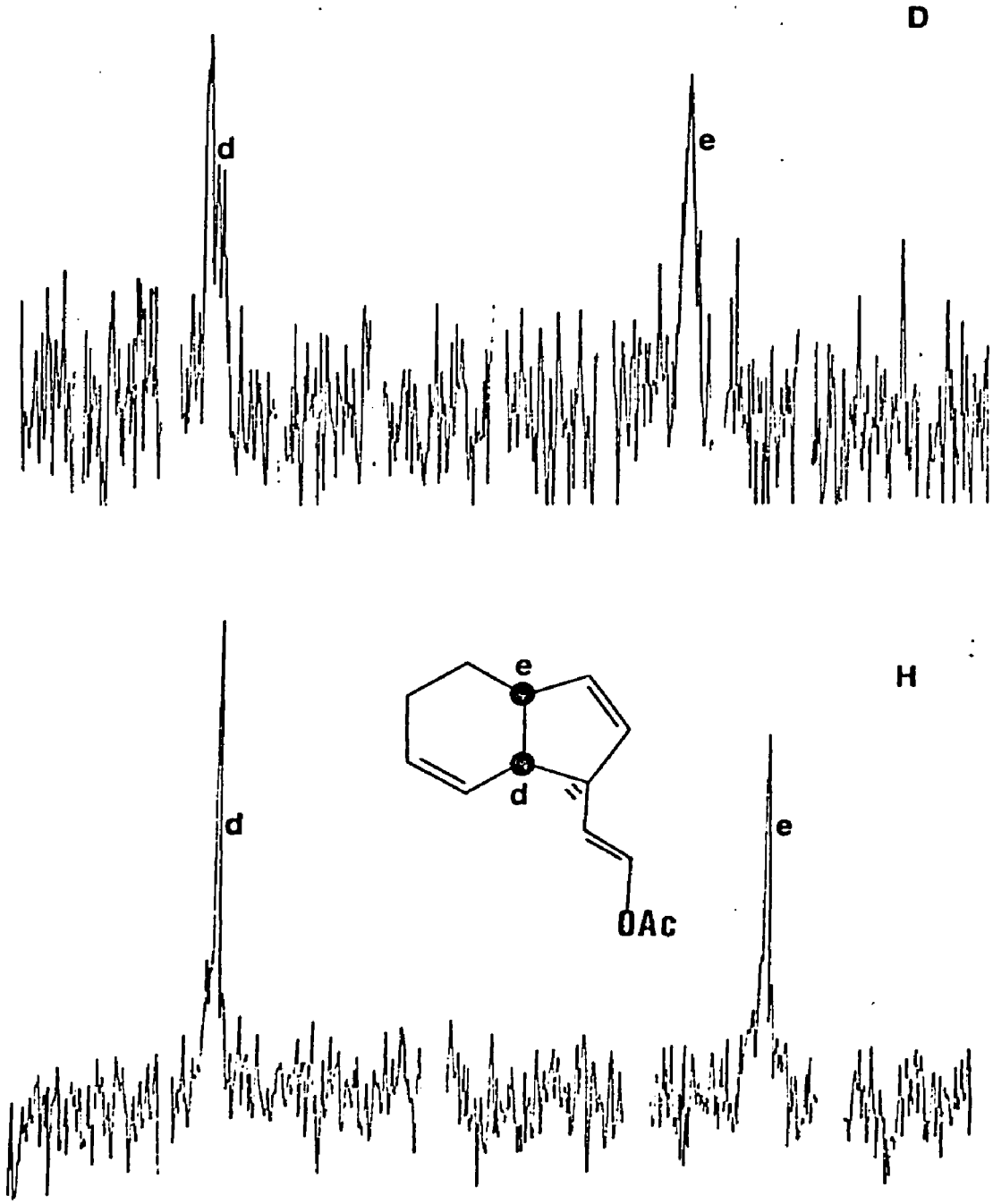


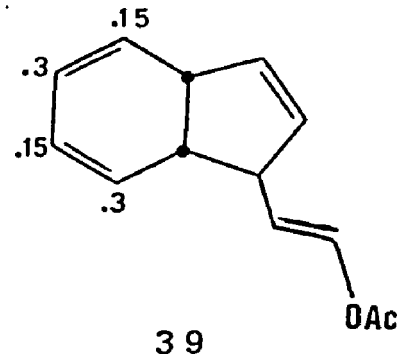
Figure 8: Comparison of C_{13} Spectra of Deutero- and Protio-Enolacetate 39 (200 Hz width, 43.6-38.2 ppm)

Close examination of the cmr spectrum (found in Table XVII) of the deuterium labeled enol acetate 39 reveals an asymmetrical disposition of the deuterium label, in the diene unit, with the bulk of the deuterium located at C_g and C_i with approximately equal distribution of over those two carbons.

The quantitative relative intensity data in Table XVII for the carbons $C_{f,g,h,i}$ lacks precision as it assumes that the t_1's and the nuclear Overhouser enhancements for those carbons will be equal, which is not necessarily valid. However, the quantitative intensity data is supported by the qualitative effect found in the bridgehead carbons, $C_{c,d,e}$. Of these three carbon resonances, only C_d exhibits significant splitting, with C_e showing only a slight deuterium effect. This places a bulk of the deuterium at C_i, which is adjacent to C_e, with a minimal amount of deuterium at C_b. The identity of the bridgehead carbons, $C_{c,d,e}$, coupled with the observed splitting, defines the origin of asymmetrical deuterium distribution to be C_i, with the remaining location of high deuterium content (C_g) defined by the observed intensity and splitting pattern found in the diene carbons, $C_{f,g,h,i}$. The inner diene carbon, C_h, exhibits no appreciable reduction in intensity, but a significant splitting to a first-order 1:1 doublet. The remaining inner diene carbon, C_g, shows less splitting but a significant intensity reduction. The high intensity of carbon, C_b, with its complicated splitting places it

adjacent to a carbon of high deuterium content which then must be C_g.

Quantitative analysis of the observed splitting of the diene carbons is severely hampered by the relatively high signal to noise ratio found in the expanded spectra. However, a reasonable quantitative distribution over the diene carbons, consistent with the available data, places approximately 0.3 D at C_g and C_i, with 0.15 D at C_f and C_h.



39

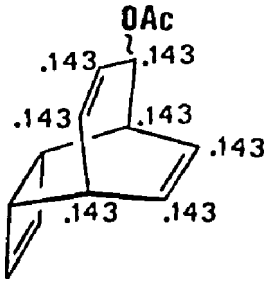
It is worthy of note, that the analysis of the asymmetrical deuterium distribution, based upon the identity of C_d, supports the assigned resonances of C_f, C_g, C_h and C_i.

The deuterium asymmetry is consistent with the fact that the solvolyses of the deuterium labeled allylic acetate 31d and benzoate 30d, producing the deuterium labeled enol acetate 39, were carried out for only one-half life, $t_{1/2}$ 39 = 90 min. The half-life for deuterium scrambling is estimated to be approximately the same as the half life for the formation of the enol acetate, as the two mechanistic processes both involve the participation of the cyclopropyl

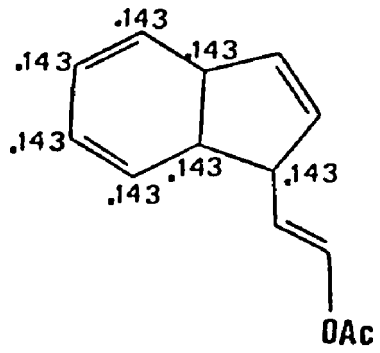
ring in 34 with the allylic carbonium ion 34+. This assumption agrees with the small amount of deuterium scrambling found in all of the solvolysis products at 118°C.

The deuterium asymmetry is consistent with the proposed mechanism (Scheme 4a) for the formation of the enol acetate 39, with one half life and is depicted in Scheme 6.

The predicted deuterium scrambling for t → ∞ is shown in Scheme 7, with the following predicted deuterium distribution:



31 & 32

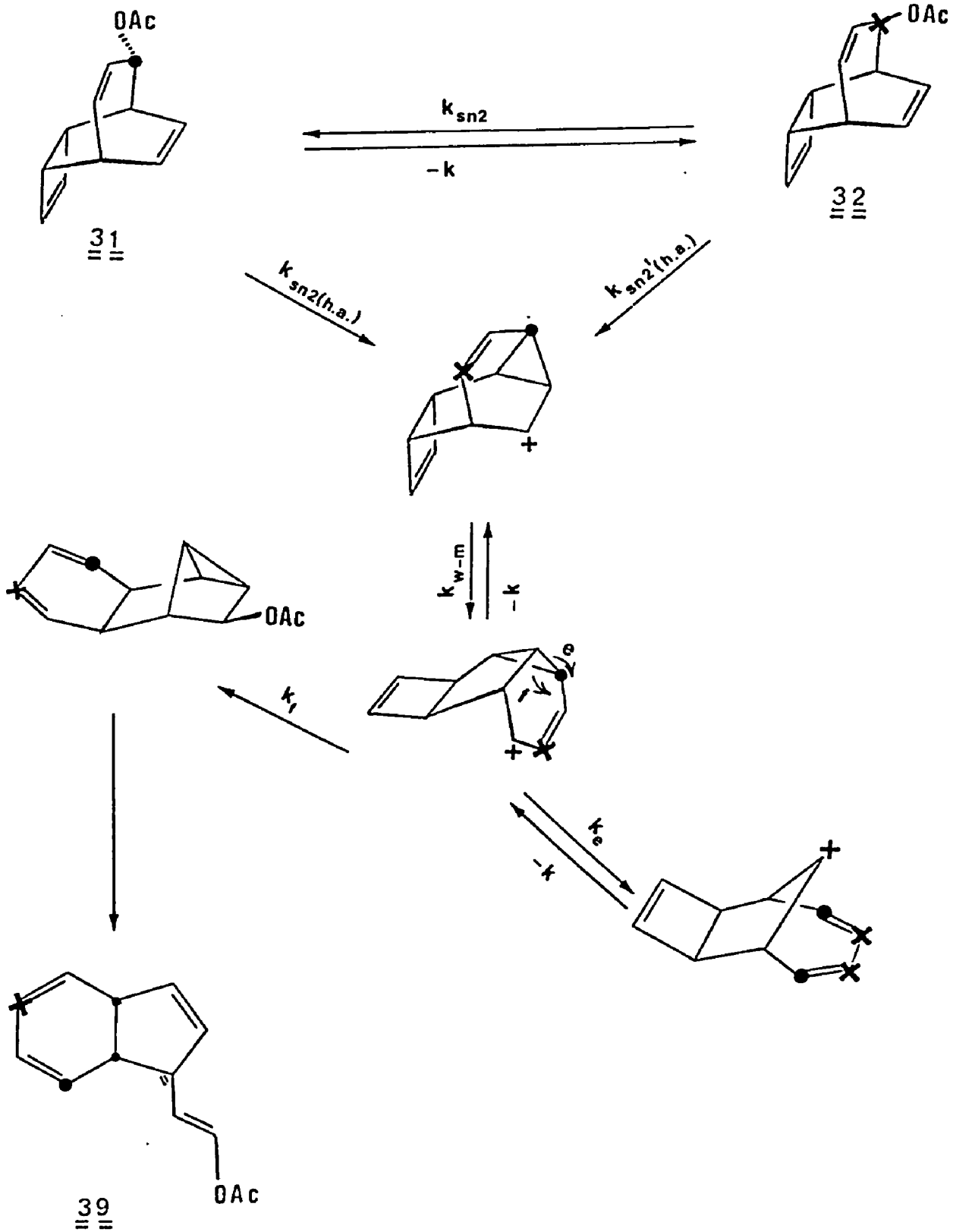


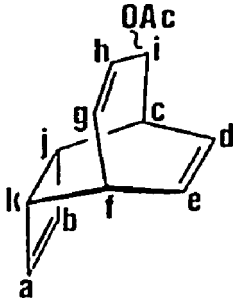
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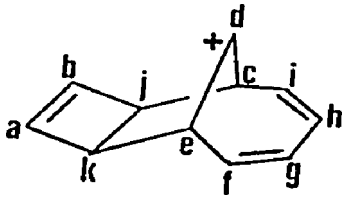
As Scheme 7 indicates, all seven carbons C_{c-i} become equivalent by virtue of the equilibration of g → i, f → c and e → d by rapid Sn2 displacements at C-7 in conjunction with the partitioning of the intermediate cation 41' by Sn2 and Sn2' attacks by solvent and the equilibration of c → e, f → i and g → h in the symmetrical cationic intermediate 42.

Scheme 6

Initial deuterium distribution in enol acetate 39







The seven carbon scrambling C_{c-i} can also be represented by the following logic matrix:

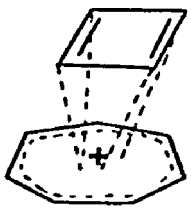
	c	d	e	f	g	h	i
c		O	+	+	O	O	O
d	O		+	O	O	O	O
e	+	+		O	O	O	O
f	+	O	O		O	O	+
g	O	O	O	O		+	+
h	O	O	O	O	+		O
i	O	O	O	+	+	O	

= identity

+ = mechanistic identity

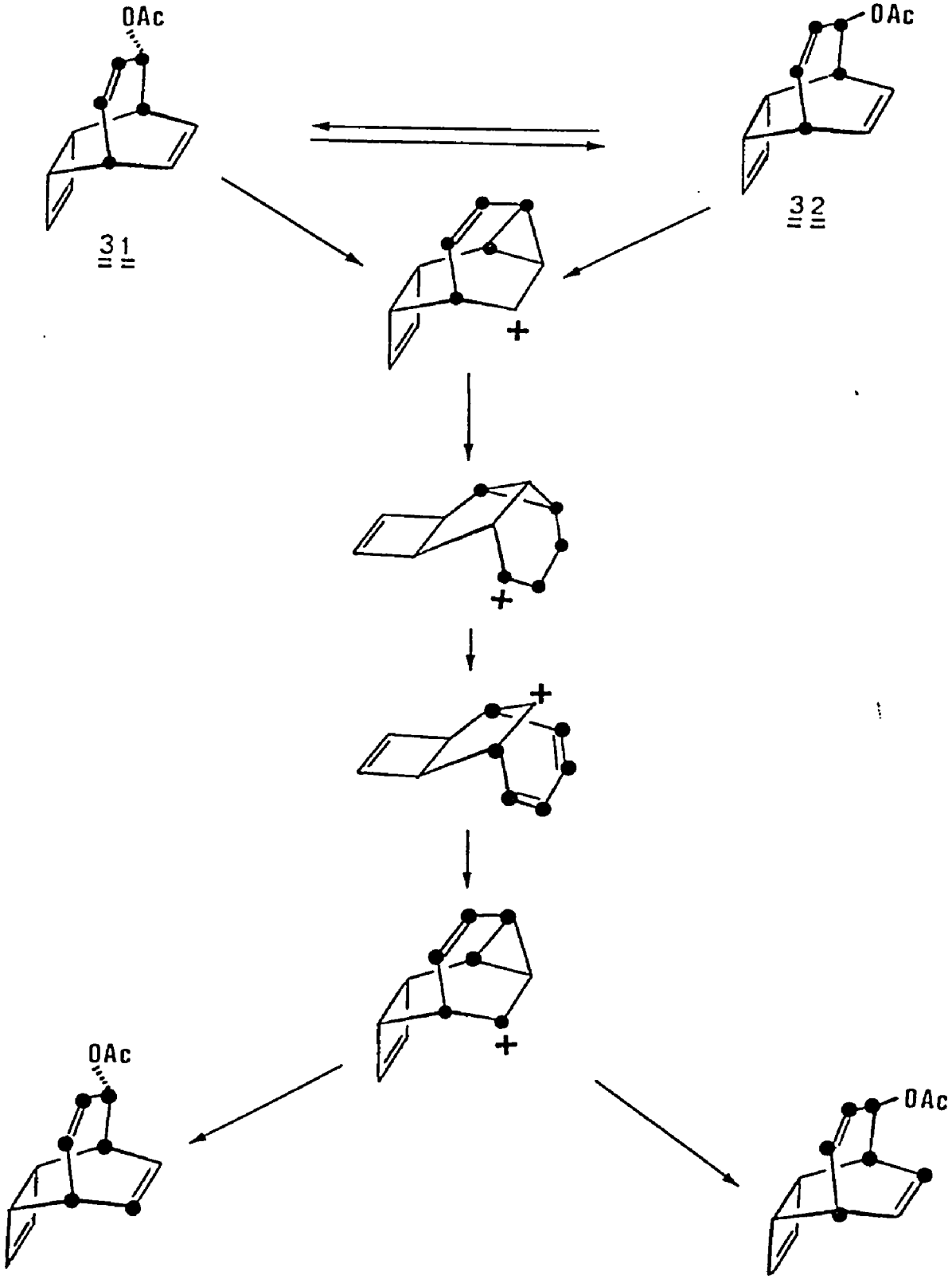
O = logical identity

A chemically equivalent representation of this logic matrix would be the following delocalized sandwich cation:



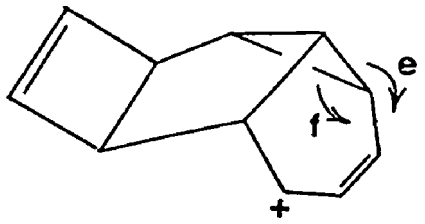
Scheme 7

Deuterium distribution for $t_{1/2} \rightarrow \infty$



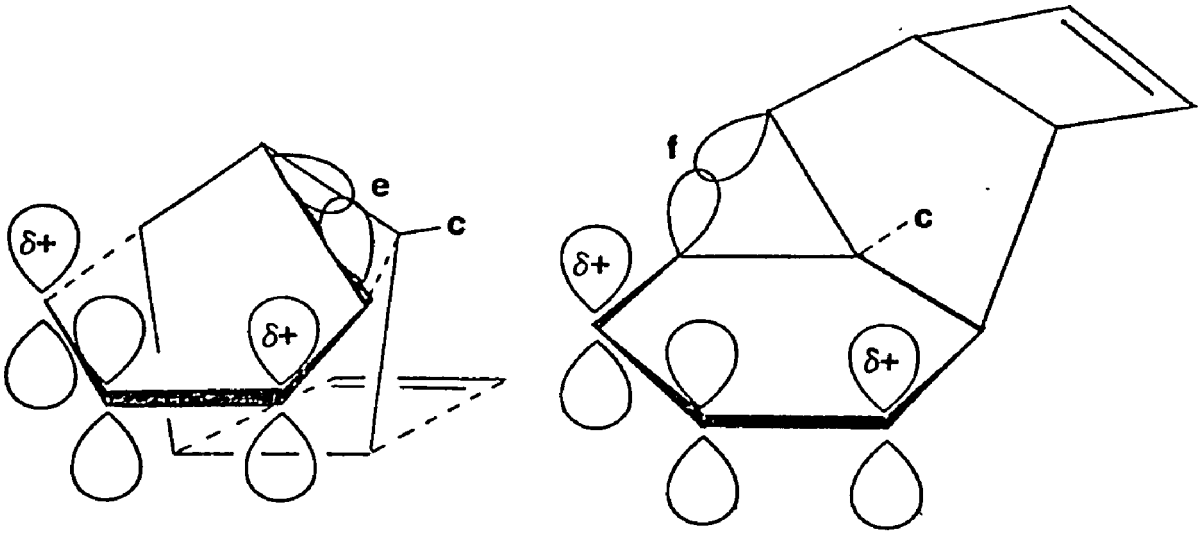
While there is no chemical evidence at all to justify the postulation of the sandwich cation 46, it is an example of how it would be possible to postulate such an intermediate based upon an observed seven carbon degenerary in the recovered acetates 31 and 32 in the absence of the intermediate cyclopropyl acetate 34 and product enol acetate 39. This is perhaps a vivid example of the invalidity of a deuterium scrambling experiment as a probe for a degenerate species, without direct observation of that degenerate species.

The partitioning of the intermediate 34+ to the symmetric cation 42 and cation 46 is of interest.



34+

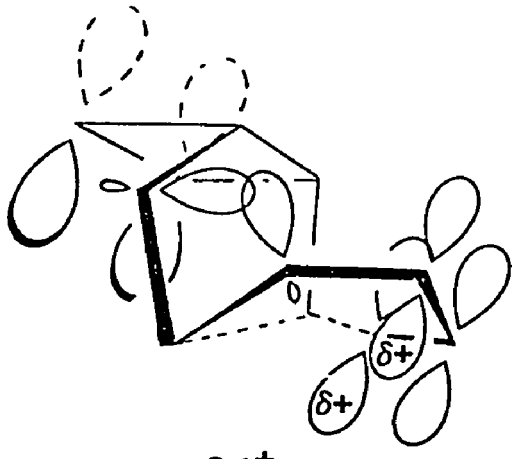
The disposition of the two participating cyclopropyl bonds with respect to the planar allyl cation is such that e is nearly perpendicular to the allylic system while f is almost parallel to the terminus of the allylic system. On the basis of maximum overlap of the cyclopropyl bond for participation, path f would be preferred. In addition, as the f cyclopropyl bond opens to stabilize the positive



42
via e

43
via f

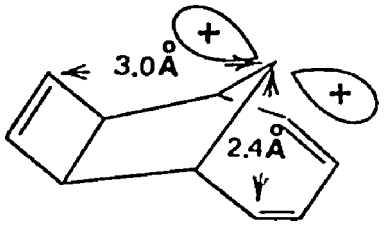
charge, the developing positive orbital at C_c is in the correct geometrical relationship with the π bond of the cyclobutene to be stabilized by that bond.



34+

The π-bond of the cyclobutene could in fact anchimerically assist the ring opening of the f cyclopropyl bond.

The strain energy of the intermediate bicyclo[2.1.0]-pentane (housane) cation $\underline{\underline{44}}^{+}$ would be approximately the same as the cation $\underline{\underline{34}}^{+}$, but somewhat higher in overall energy, as the cyclopropyl allylic cation $\underline{\underline{34}}^{+}$ would be more stable than the cyclobutylcyclopropyl carbinyl cation $\underline{\underline{43}}$. The rigid symmetrical methine cation $\underline{\underline{42}}$, while relieving 28 kcal of cyclopropyl ring strain would experience very little stabilization from the remote cyclobutene π bond and would be destabilized to whatever extent the bishomocyclopentadienyl cation interaction is operative. In addition, in going from $\underline{\underline{34}}^{+}$ to cation $\underline{\underline{42}}$, the cyclopropyl ring strain relief would be compensated for by the thermodynamically unfavorable process of going from allylic cation to a secondary cation.

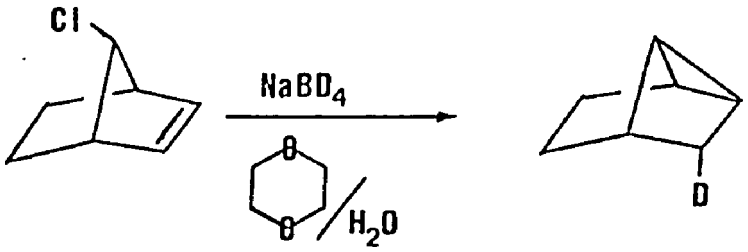


$\underline{\underline{42}}$

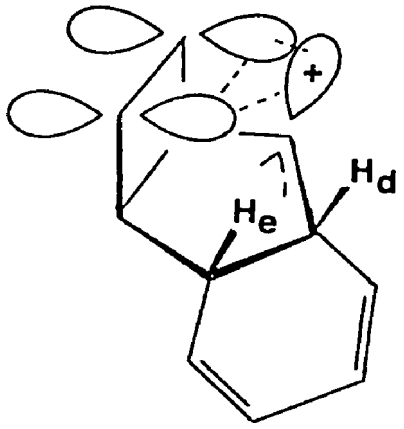
While it is difficult to make an accurate estimate of the difference in the activation energies for cyclopropyl participation <u>via</u> path e or f, analysis indicates that the

energies should be comparable due to: the preference for participation by cyclopropyl bond f *versus* e, a slight increase in ring strain for cation 43 *versus* cation 34; the relief of ring strain from 34+ to cation 42, and the stability of the secondary methine cation 42 *versus* the allylic cation 34+, approximately cancelling each other.

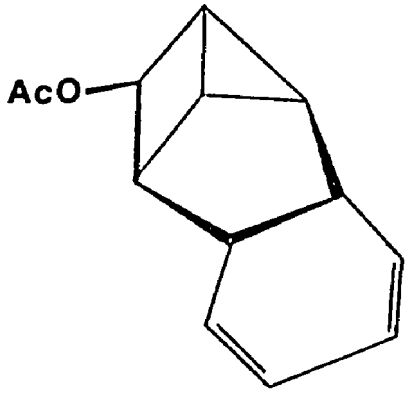
The further mechanistic sequence for the fate of the intermediate housane 44 is in accord with the known chemistry of housanes. Symmetrical bishomocyclopropenyl cations are known to be subject to stereoelectronic control of the addition of external nucleophile.[53]



To whatever extent the cyclobutene π-bond is symmetrically participating in the stabilization of C_c in cation 43, stereoelectronic control would predict the postulated stereochemistry of the intermediate housane acetate 44. In addition, the hydrogens H_d and H_e would exhibit a considerable steric directing effect on the incoming nucleophile, predicting, in accord with stereoelectronic control, the postulated stereochemistry represented in 44.



43



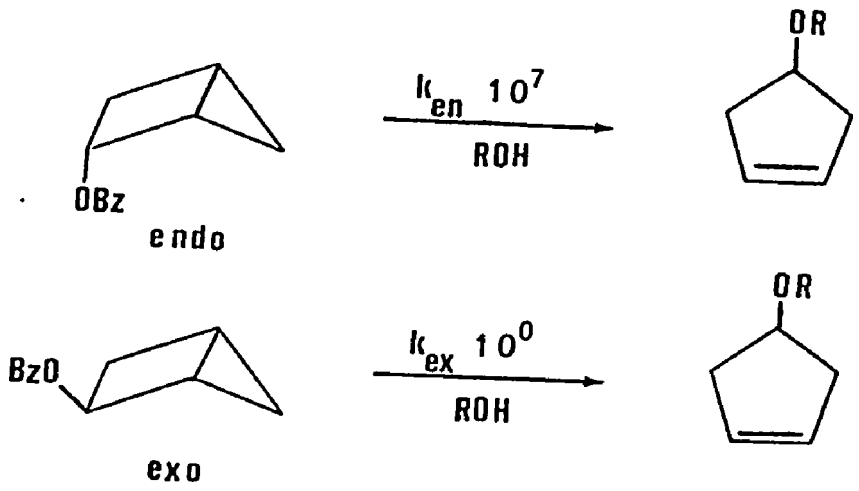
44

III

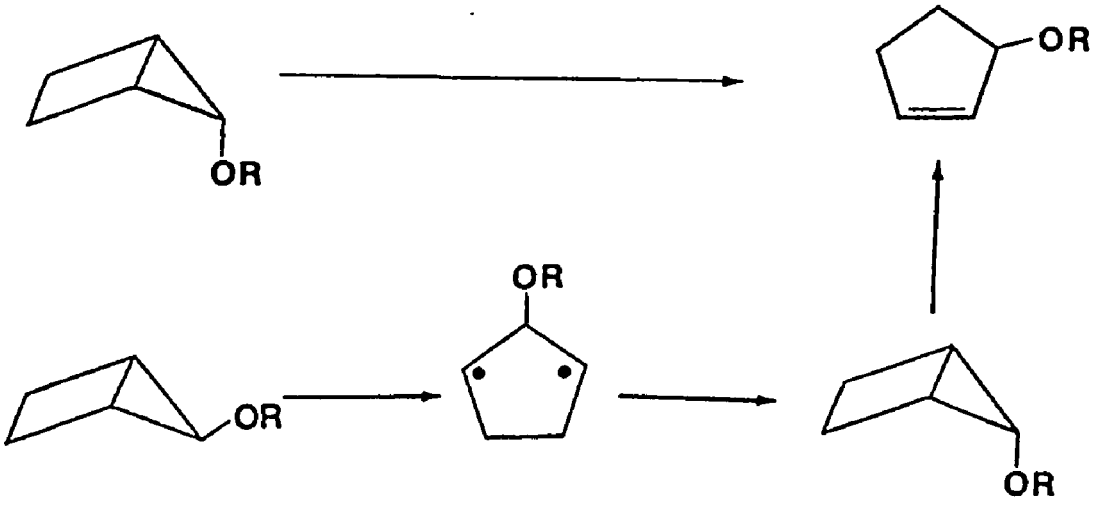


44

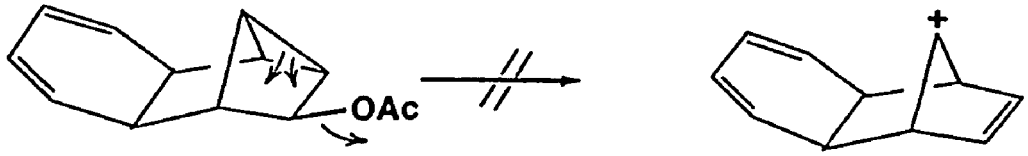
Endo and exo-2 substituted housanes solvolyze with relative rates of 10^{7}.[54] The endo isomer solvolyzes quite rapidly as the allowed motion of the zero bridge anchimerically assists the ionization of the leaving group, with attendant relief of strain.



The exo-2 housane, on the other hand, quite probably solvolyzes by the epimerization of the 2 position via homolytic opening of the zero bridge followed by inversion, with sequential rapid solvolysis of the epimeric endo isomer as was found in the solvolysis of epimeric-5-housanes.[55]

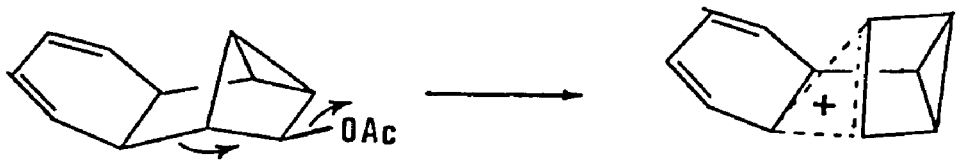


In 44 the acetate is exo to the cyclopropyl ring, so that the assisted solvolysis of 44 to cation 46 does not occur.



44 46

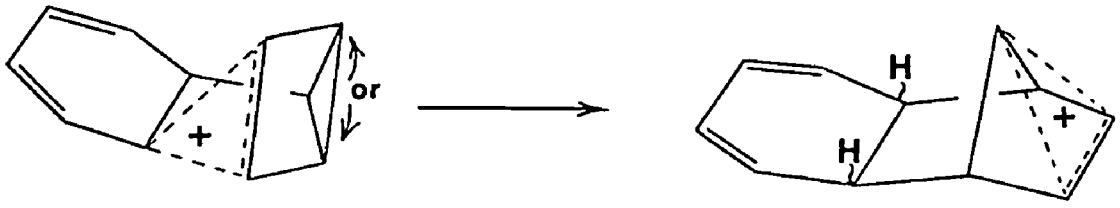
The housane intermediate 44 has another mode of solvolysis available to it, however. The housane 44 could undergo a Wagner-Meerwein shift of the C_{1-2} bond as 44 could be considered to be 5,6 substituted 2-nonbornyl system.



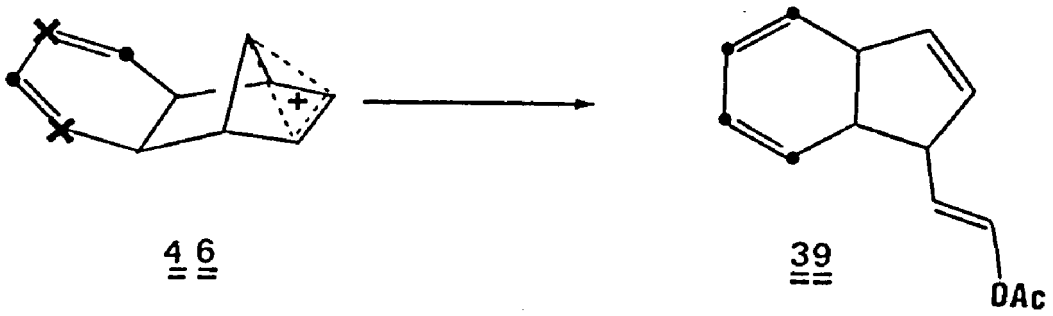
44 47

The intermediate cation 47 then has the correct geometry for the anchimeric disrotatory assistance of the cyclopropyl

bond with the relief of 28 kcal of cyclopropyl ring strain to generate the symmetrical intermediate epimeric cation 46.



If the imagined conversion of the housane 44 to cation 46 were reversible, this process would represent another mode of scrambling the initially formed 2,4-deuterocyclohexadiene from Scheme 6 over the four carbons of the cyclohexadiene-diene unit.

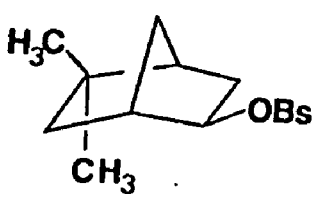


46 39

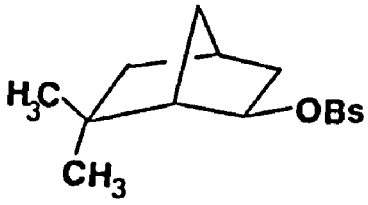
This is not believed to be the case, however, when the reactivity of 2-norbornyl derivatives is considered. When the rates of acetoylsis of 5 and 6 disubstituted 2-norbornyl brosylates were compared with 2-norbornyl brosylate they were found to be 3 and 30 times less reactive,[56] respectively.



30



10

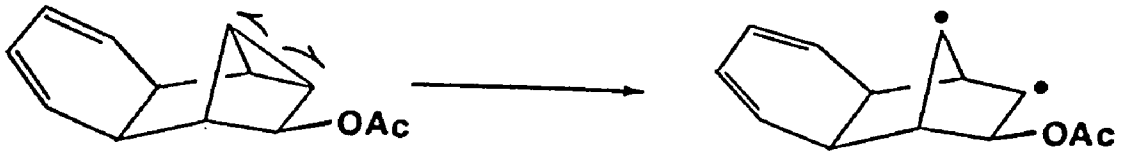


1

The 5,6 substitution in 44 would be expected to decrease the rate 50 fold. In addition, the vinyl and cyclopropyl groups should exhibit a rate-retarding inductive influence of 2-10 fold. The difference in reactivity between a brosylate and an acetate of 10^3-10^4 would also greatly retard the Wagner-Meerwein assisted solvolysis of the housane 44.

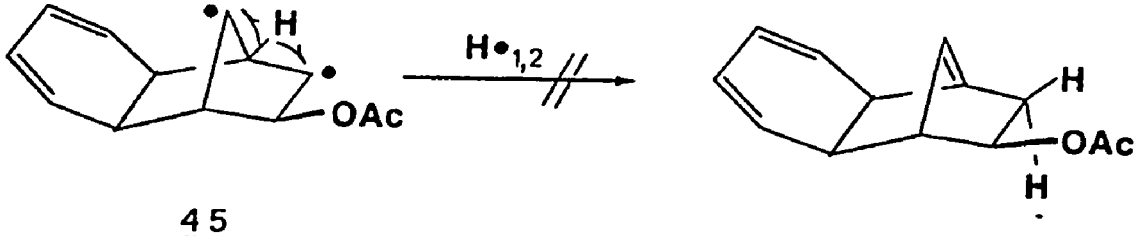
This qualitative argument for the expected suppressed reactivity of the housane 44 in a norbornyl fashion is supported by the 12-14 kcal increase in activation energy (Ea) that these factors would be expected to cause. The $\Delta H^{\dagger}$ for the acetolysis of 2-norbornyl brosylate is 22 kcal,[54] with an expected $\Delta H^{\dagger}$ of 34 to 36 kcal for the acetolysis of the housane 44. The $\Delta H^{\dagger}$ of 31 kcal for the formation of the enol acetate 39 is well below the expected minimal value for the norbornyl type acetolysis of 44.

Instead, it is postulated that the intermediate housane 44 homolytically cleaves the most strained bond in the molecule, the zero bridge to generate the diradical 45, as is the case of exo-4-disubstituted housanes,[57] but in this instance epimerization by ring inversion is not possible due to the bicyclic ring system.



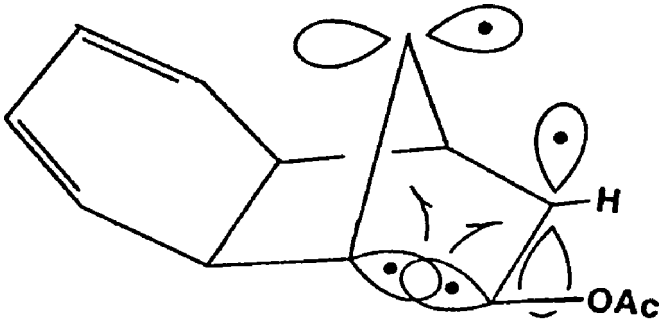
44 45

A 1-2 hydrogen shift in the diradical 45, while known in housane systems,[58] is energetically disfavored as a trans double bond in a five membered ring would be formed.

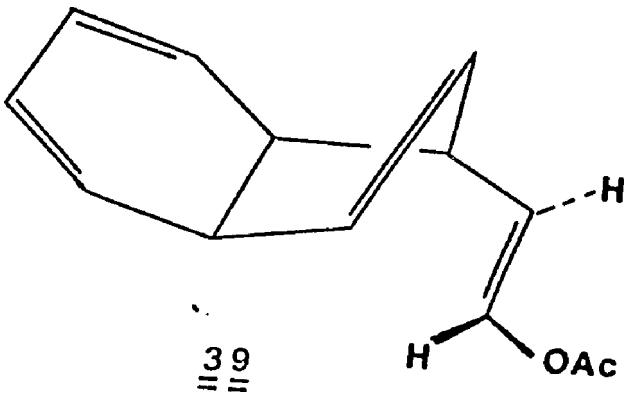


45

With the solvolysis of the housane acetate 44 and a 1-2 hydrogen shift in the diradical 45 energetically disfavored, the diradical 45 then homolytically cleaves the C_c-C_f bond to generate the acetate stabilized radical which leads to the formation of the thermodynamically favored enol acetate 39. The homolytic cleavage of the C_c-C_f bond occurs such that the movement of the orbitals is in agreement with the principle of least motion and the steric interaction of the acetate group is minimal with the 5-membered ring of the dihydroindene ring skeleton.



45



39

It is of interest, at this point, to consider the energy of activation for the formation of the enol acetate 39, via the postulated diradical 45, in relationship to the known activation parameters (Table XVIII) for the epimerization and the 1,4-cleavage of housanes and bicyclohexanes.

It is useful for the discussion of these activation energies to consider the strain energies[58] found in Table XIX.

The Ea for epimerization of housanes, found in Table XVIII, reflects the energy of formation of the 1 cyclopentan-1,3-diyl radical 48. If the relief of ring strain in housane and the heat of formation of the homolytic cleavage of dissoproyl are considered, a value of 28 kcal is expected for the diradical 48. The additional 4-10 kcal that are observed for the epimerization of substituted housanes (Table XVIII), most probably reflects the bond stretching required to effect the ring flip required for epimerization. The calculated value of 28 kcal for the homolytic cleavage of the zero bridge in housane then probably accurately reflects the activation energy for the formation of the diradical 48.

Analysis of the Ea for 1,4 diradical cleavage and the strain energies in Table XIX is revealing. In the housane

Table XVIII

Representative Activation Parameters

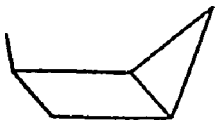
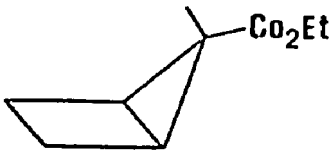
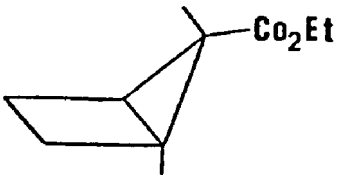
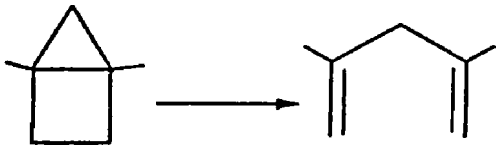
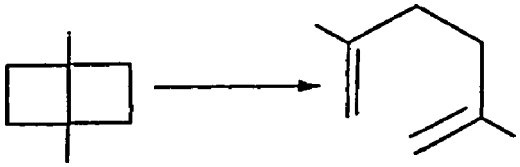
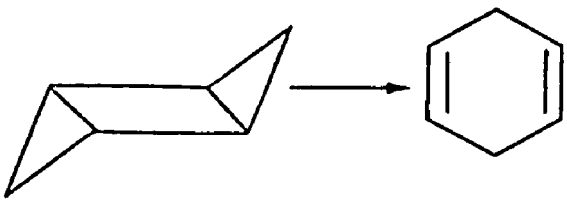
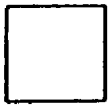
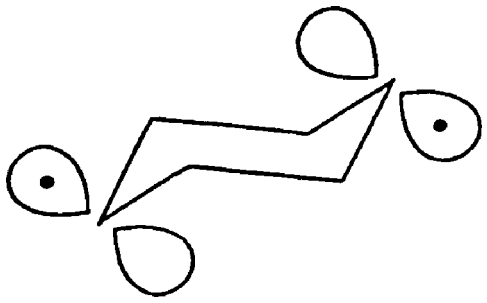
		ref
	Ea (epi) = 38 kcal	59a
	=35.8	59b
	=32.9	59b
	Ea = 57	59c
	=31	57c
	=37	57d

Table XIX

Strain Energies of Selected Ring Skeletons

Compound	S_E (kcal)	Reference
	57	60
	28	
	27	
	7	
	18	

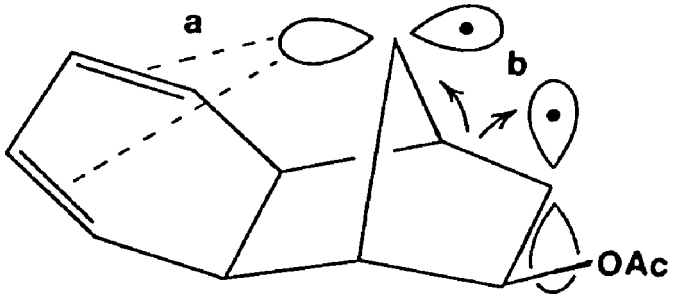
1,4 cleavage, the value of 57 kcal reflects both the 32 kcal of energy required to cleave the zero bridge and an additional 25 kcal of contortional energy resulting from the $\sigma_{2s} + \sigma_{2a}$ cycloreversion which would be predicted, as the 1,3 diradical is still correlated. Berson has provided evidence that the 1,4 cleavage of housanes is a $\sigma_{2s} + \sigma_{2a}$ process.[59] The validity of this analysis is indicated by the Ea for the bicyclo-[2.2.0]-hexane and tricyclohexane cleavages (Table XVIII). The Ea of 31 kcal for the bicyclo hexane cleavage reflects the initial diradical formation, as Paquette[60] has proposed a chair form cyclohexyl 1,3-diradical, which is no longer correlated and thus allows a formally viewed $\sigma_{2s} + \sigma_{2s}$ cycloreversion.



The tricyclohexane cleavage reflects the strain energy released from a cyclopropane to render the $\sigma_{2s} + \sigma_{2a}$ process energetically more accessible.

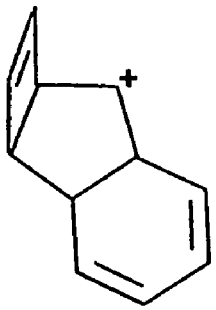
When the E_a of 32 ± 3 kcal for enol acetate 39 formation is considered with this analysis, it appears to be consistent with the intervention of the housane diradical intermediate 45.

The thermal cleavage of the zero bridge of the housane would be expected to require 32-37 kcal of energy. An additional 11-13 kcal of strain energy would be released upon the 1,4 cleavage of the bicycloheptane to the cyclopentane and the enol acetate 39. This calculated strain energy for the bicycloheptane represents a minimal value as the cyclohexadiene substituent would be expected to increase the strain significantly (2-5 kcal) by its interaction with the 7-carbon in the norbornyl skeleton of the housane acetate 44. The additional 8-12 kcal of energy that is to be accounted for, if significant, could readily be compensated by the formation of the resonance stabilized enol acetate and perhaps decorrelation of the 1,3 diradical by thru space interactions of the radical with the diene (a) and a possible springing open of the puckered cyclopentane diradical (b).

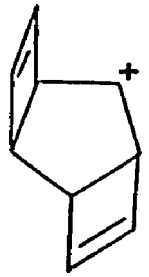


45

Coates[61] has studied the interesting vinylog of the cation 43, the tricyclic cation 49.

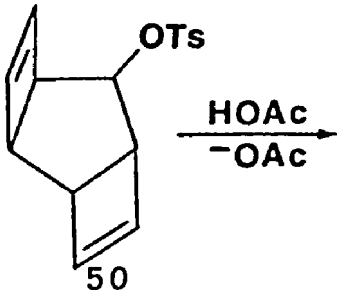


43

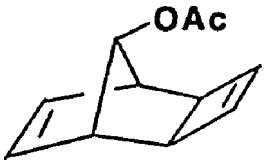


49

The acetolysis of the tricyclic tosylate 50 produced as the only product, the norbornyl derivative 51.

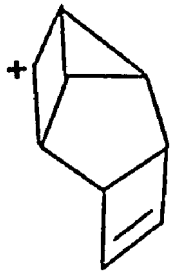


50

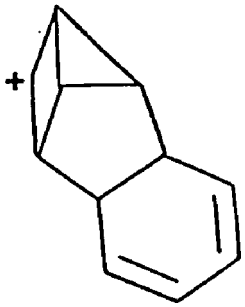


51

The conversion of 50 to 51 apparently involves the vinylogous housane cation 52, which is closely related to the housane cation 44.

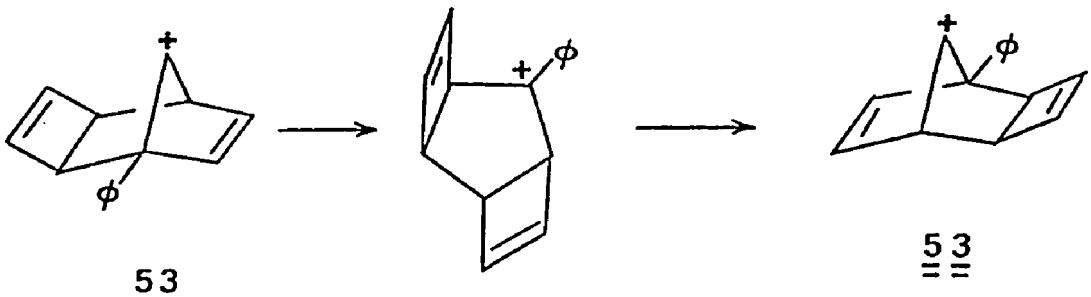


52

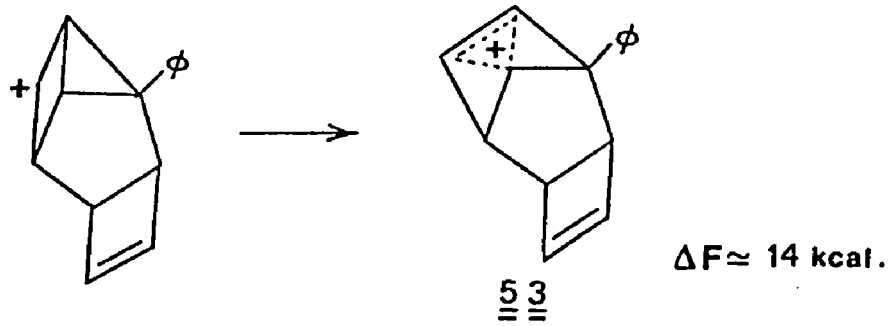


44

The $\Delta F^{\dagger}$ for the equilibration of the protons in a super acid solution of the phenyl derivative of 52, the phenyl housane 53 is approximately 14 kcal, which apparently closely represents the $\Delta F^{\dagger}$ for the opening of the housane cation to the bishomocyclopropenyl species 53.

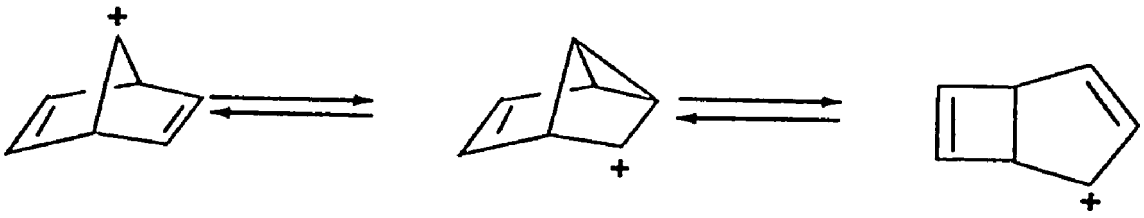


53 53



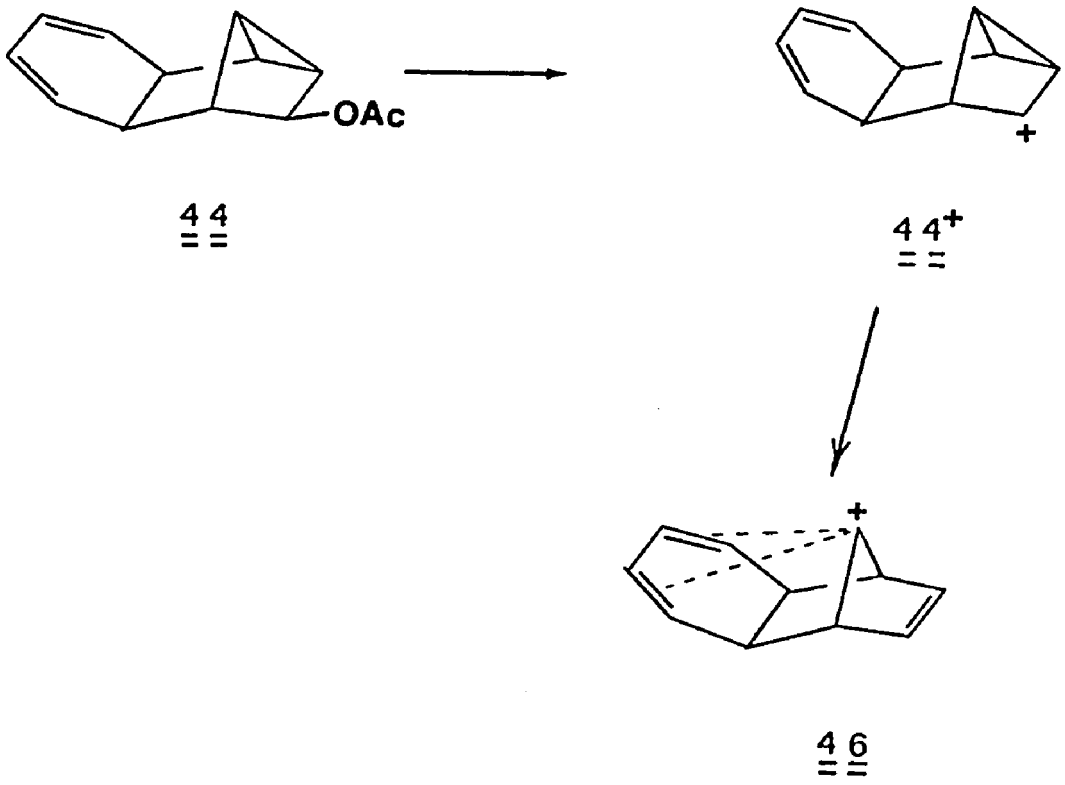
53 $\Delta F \simeq$ 14 kcal.

A similar $\Delta F^{\dagger}$ (16.7 kcal) was found by Winstein[66] for the 5 carbon scrambling in the 7-norbornadienyl cation 54 through the housane 55.



54 55

The lack of rearrangement of the housane acetate 44 could be due to the destabilization that the cation 46 experiences with a bishomocyclopentadienyl cationic interaction from the diene unit of the six-membered ring in 46.



44 44^+ 46

A more reasonable explanation of the lack of this rearrangement is that the total energy from the ground state of 44 to the housane cation 44^+, followed by rearrangement to the symmetrical cation 46 exceeds the 32 kcal from the ground state of the allylic acetate 31 to the housane diradical 45.

An energy profile which embodies the entire mechanism for the interconversion of the allylic acetate 31 to the enol acetate, accounting for the deuterium distribution in recovered products, is found in Figure 9 , which summarizes the conclusions of this mechanism.

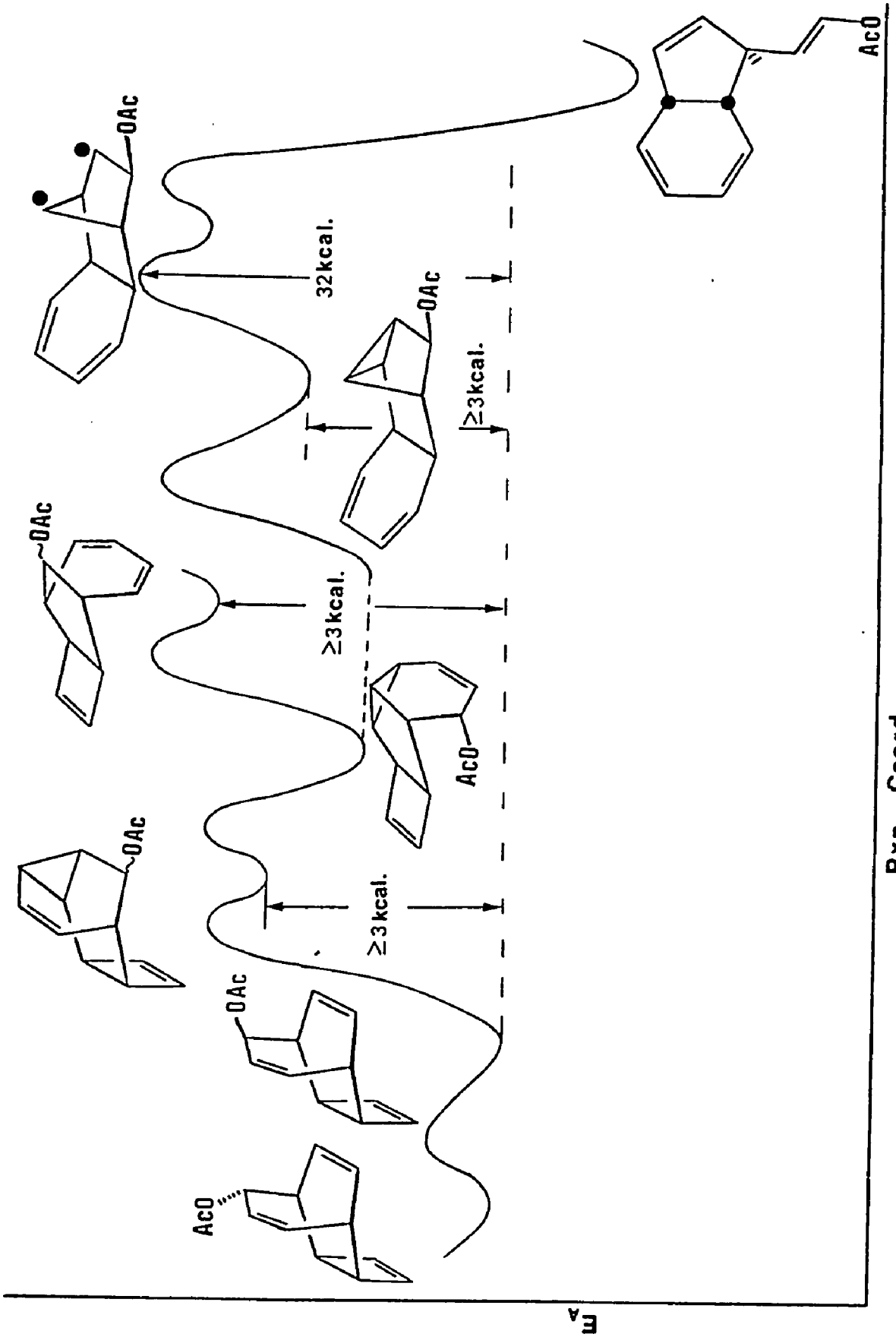


Figure 9. Summary of mechanistic conclusions for the solvolysis of ester derivatives of 6.

IV. Nomenclature discussion:

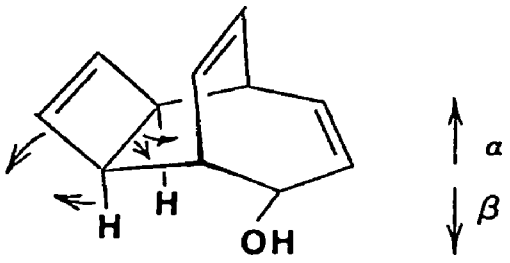
While the relative stereochemistry of the alcohol 21 is now known, the problem of the correct name which specifies the relative stereochemistry of the stereogenic centers remains. The terms exo, endo and syn and anti are not applicable in this case as the molecule is not a bicyclic system. There are two systems which apply in this case, the α and β descriptors and the R^* and S^* descriptors.

In the α and β system the reference plane is chosen so that it passes through the largest ring. The α side is then defined as that side of the plane where the preferred substituent at the position of highest priority lies. Since carbon is preferred over hydrogen and the ring junction at carbon 1 is the position of highest priority, the two bridge defines the α side of the plane.

A point of ambiguity arises, however, when the stereogenic 2 and 5 positions are considered. At these positions, while it is not readily apparent, the zero bridge is the preferred substituent.

At first glance, it appears that the zero bridge lies on the α side of the plane as the protons lie on the β side. This is not the case, however. In order to determine the relative stereochemistry of the zero bridge, the zero bond must be broken and the cyclobutene moved down so that it lies in the plane of a flat nine-membered ring. When this is done the hydrogens rotate up into the α plane and

the zero bridge rotates into the β plane, thus defining the zero bridge as 2β, 5β.

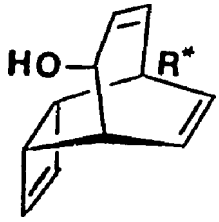


21

The C_6 and C_7 positions readily follow from the definition of the α and β plane, generating the following stereogenic name:

(1α, 2β, 5β, 6α, 7β)-tricyclo-[4.3.2.$0^{2,5}$]-andeca-3,8,10-trien-7-ol.

To apply the R^* and S^* descriptors the first cited stereogenic center is assigned the R^* configuration which is:



From this arbitary configuration, the remaining stereogenic centers then assume the following configurations, using the Cahn, Ingold, Prelog sequence rules.

$1R^*$, $2S^*$, $5R^*$, $6S^*$, $7S^*$

With the relative stereochemistry defined the allylic alcohol 21 would then be named:

Racemic ($1R^*$, $2S^*$, $5R^*$, $6S^*$, $7S^*$)-tricyclo-[$4.3.2.0^{2,5}$]-undeca-3,8,10-trien-7-ol.

While both of these nomenclature systems are adequate to define the relative stereochemistry of the cyclobutene and alcohol, their use is quite cumbersome. The primary goal of any nomenclature system should be communication between the largest number of chemists.

If the tricyclic ring system were named as a bicyclic derivative, then the familiar terms endo, exo, syn and anti could then be correctly applied. With this system of nomenclature, the name for the allylic alcohol 7 would then be:

bicyclo-[3.2.2]-nona-5,6-exo-etheno-2,7-diene-endo-7-ol.

While this name is incorrect for the tricyclic system, it would be readily understood by the largest number of chemists.

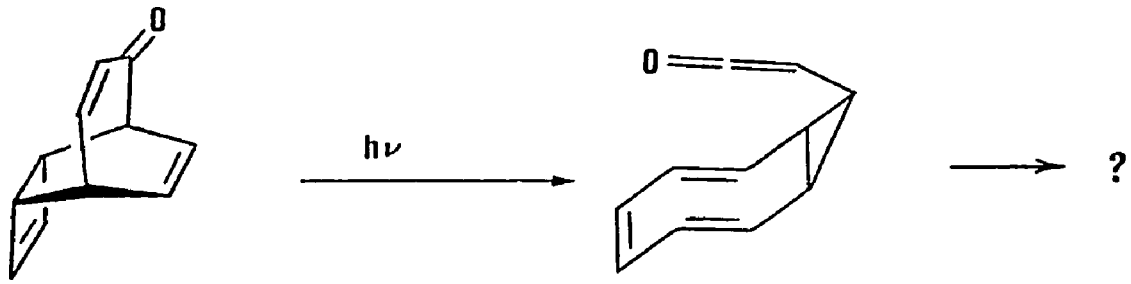
It is suggested that if the terms exo and endo were allowed to be used for a tricyclic system, a much greater population of organic chemists would then be able to generate the correct structure for the allylic alcohol 21 from its name. A name which would serve this function would be the following:

tricyclo-[$4.3.2.0^{2,5\ exo}$]-undeca-3,8,10-trien-endo-7-ol.

Of course, the validity of such a nomenclature system would be its unambiguous application to all cyclic systems greater than bicyclic. In the absence of this name, the least confusing name for the alcohol 21 would be that which employed the α and β stereodescriptors.

V. Photolysis of enone 16.

The enone 16 was photolyzed in an effort to discern the reactivity of the cyclobutene sigma bond under photolytic conditions.

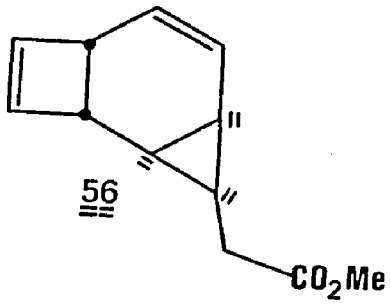


16

When the enone 16 was photolyzed in either ether or acetone through pyrex, no compound other than the starting enone 16 was detected by analytical glpc. However, when the enone was photolyzed in the presence of methanol, two esters, 56 and 57 (6:1) were formed with 100% conversion after 2 hr. The esters 56 and 57 were identified on the basis of their ir and pmr spectra (Table XX).

Table XX

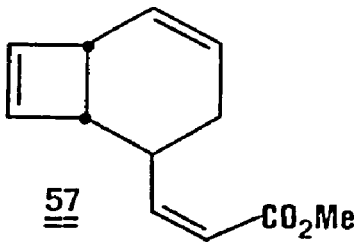
Spectral Data of Esters 56 and 57



56

pmr, CCl_4, δ: 6.14 (1H, d, 7 Hz); 6.06 (1H, d, 7 Hz); 5.65 (2H, br d, 2 Hz); 3.60 (3H, s); 3.20 (2H, m); 3.02 (2H, br s); 2.22 (2H, t, 3 Hz); 1.35 (3H, br m).

ir, CCl_4: 3030, 3000, 2960, 2890, 1735, 1435, 1370, 1320, 1280, 1200, 1175, 1050 cm^{-1}.

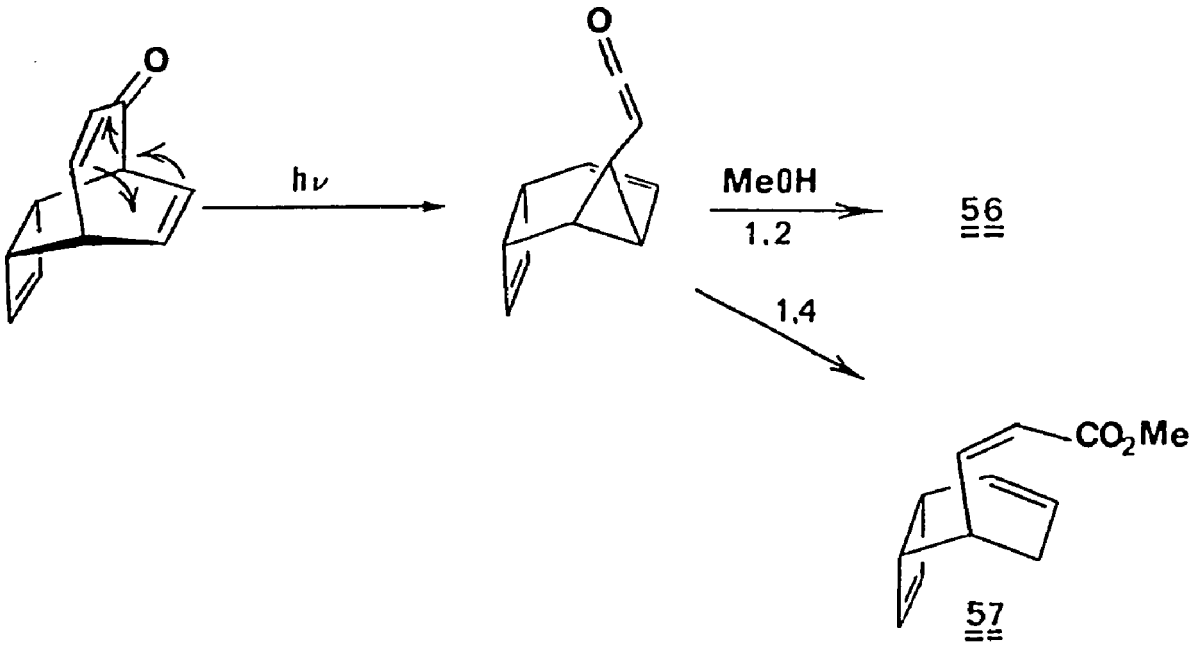


57

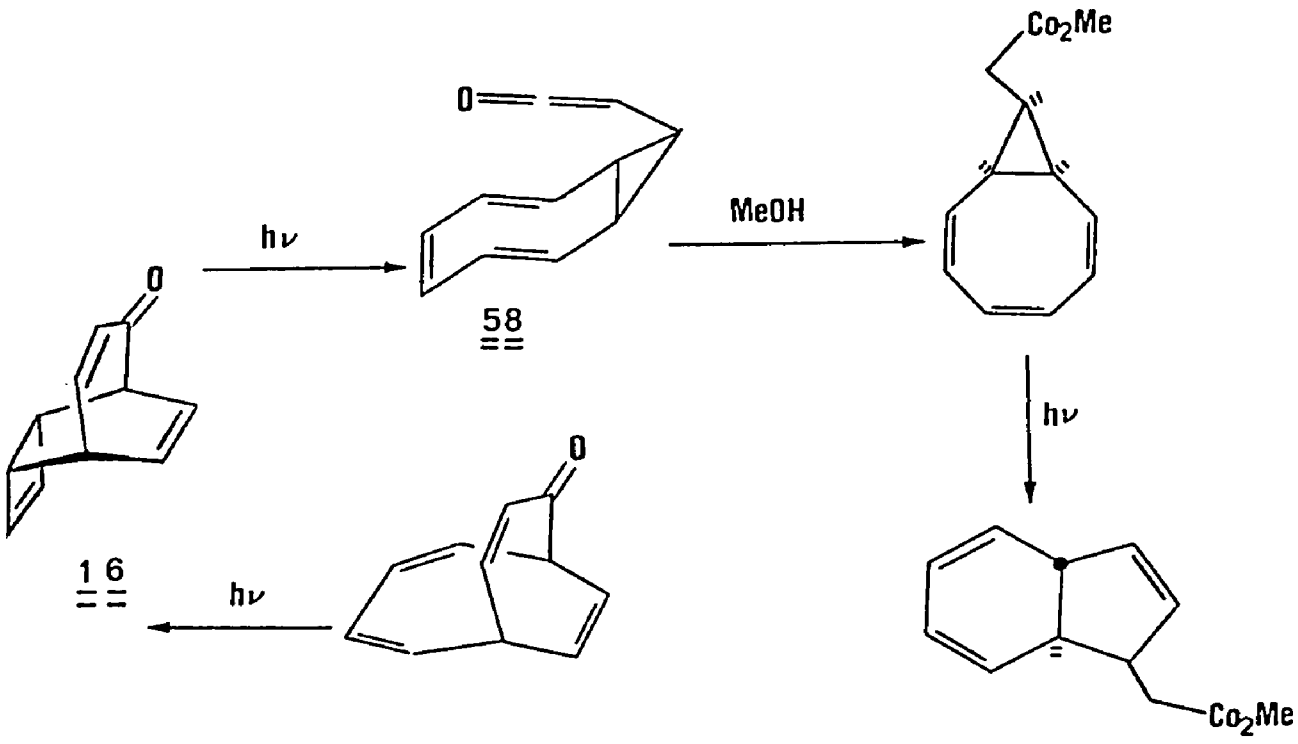
pmr, CCl_4, δ: 6.65 (1H, d, 8 Hz); 5.95 (2H, br d); 5.7 (3H, m); 3.65 (3H, s); 3.00 (3H, m); 2.1 (2H, m).

ir, CCl_4: 3040, 2960, 2900, 1720, 1280, 1250, 1170, 1050 cm^{-1}.

The photochemistry of the enone 16 apparently involves the exclusive participation of the π-bond of the two bridge, as was seen to be the case for the solvolysis of its derivatives.



The possibility of masked participation by the sigma bond in the formation of an intermediate ketene, appears to be eliminated due to the absence of the expected trapped esters derived from the likely 58.



VI. Attempts with superacid media:

Several attempts were made to generate the cation derived from the allylic alcohol 21 in super acid media. The only medium that did not yield red precipitates was $FSO_3H:SO_2Cl:CD_2Cl_2$ (1:4:1), utilizing the parfait method of Winstein.[62] The pmr spectra of the clear yellow solutions generated by this method, showed a broad, low intensity adsorption between 3.5 and 1.7 δ which reversibly increased with temperature as the temperature was increased from -120°C to -60°C. This behavior is typical of polymeric solutions.[63]

All attempts to quench the product generated in the super acid media resulted in the isolation of non-volatile polymeric material, characterized by its broad pmr adsorptions between 4.0 and 1.0 δ.

The failure of these super acid experiments is not understood at this time.

EXPERIMENTAL

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on either a Perkin-Elmer Grating Spectrophotometer, Model 237B or Model 457. Ultraviolet spectra were obtained on a Cary 14 Recording Spectrophotometer. Either a Varian T-60 or Joel PS-100 Nuclear Resonance Spectrometer were used to obtain the pmr spectra and the Joel PS-100 Nuclear Resonance Spectrometer and Digilab software were used to obtain the F.T. cmr and F.T. pmr spectra.

Analytical glpc data were obtained with a Varian Aerograph gas chromatograph Model 1200, equipped with a flame ionization detector and a Leeds and Northrup strip chart recorder. A Varian-Aerograph 90-P gas chromatograph equipped with a thermal conductivity detector and Leeds and Northrup strip chart recorder, was used for preparative glpc. Brinkman thin layer plates precoated with silica gel (0.25 mm and 2 mm) and fluorescent indicator were used for analytical and preparative thin layer chromatography, respectively. Woelm silica gel and basic alumina (0.05-0.2 mm) activity I was used for column chromatography and dry column chromatography was done with Woelm silica gel with fluorescent indicator, "dry-column chromatography grade."

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

Unless otherwise indicated, the term "stirring" refers to the use of a Teflon coated magnetic stirring bar and a magnetic stirrer.

The F.T. cmr and pmr spectra were calculated using box car apodization. Unless otherwise indicated, cmr data was obtained using proton noise decoupling.

The format for the presentation of pmr data is as follows:

pmr, δ, solvent: Chemical shift [apparent multiplicity, integrated area, coupling constant(s) (where appropriate)].

The abbreviations used to indicate the apparent multiplicity are:

m - complex multiplet	t - triplet
br - broad	d - doublet
s - singlet	d,d - doublet of doublets
q - quartet	

I. Synthesis of tricyclo-[4.3.2.$0^{2,5}$]-undeca-3,8,10-triene-7-one (16) and some derivatives:

1. Oxidative decomposition of cyclobutadiene-iron tricarbonyl in the presence of tropone:

a) Excess tropone:

A solution of 1.3 g (0.0068 mole) of freshly distilled cyclobutadieneiron tricarbonyl[64] and 0.78 g (0.074 mole) of freshly distilled tropone[65] in 250 ml of reagent grade acetone was cooled to -5°C using an ice-salt bath. The system was maintained under an argon atmosphere. An elenmeyer flask containing 6.3 g (0.012 mole) of ceric ammonium nitrate was attached to the reaction system by the use of a piece of gooch tubing. The solution was stirred rapidly while the ceric ammonium nitrate was added in several small portions over a period of 30 min.

After stirring for an additional 2 hr, the dark brown reaction mixture was poured into 400 ml of a 1:1 saturated sodium chloride-water solution and washed with 3 x 200 ml portions of ether. The combined organic layers were washed with 250 ml distilled water and 200 ml saturated sodium chloride. The ether layer was dried over anhydrous sodium sulfate, filtered, and the ether removed under reduced pressure to yield 0.51 g of a dark brown oil.

The crude product was then chromatographed on 50 g of silica gel; eluting with 300 ml benzene, followed by 2% ether-benzene. The fractions were monitored by analytical glpc, Column A, 130° (isothermal). The fractions containing

the enone 16 (retention time, 3.5 min) were combined and the solvent removed under reduced pressure to yield 0.08 g (7.4%) of enone 16 as a pale yellow oil.

ir (CCl_4): 3040, 2920, 1680, 1640, 1565, 1385, 1300, 1260, 1240, 1200, 1165 cm^{-1}.

uv (ether): λ_{max} 229 (ε = 4850), 256, (ε = 1950), 290 nm (ε = 266).

Mass. Spec. (70 ev): P = 158 (100), P + 1 (13.4), P + 2 (0.89), 158 (55.9); 157 (32.0); 129 (83.2); 128 (41.2); 115 (44.4); 103 (34.5); 78 (100).

pmr, δ, $CDCl_3$: 7.0 (d,d, 1H; 11, 8 Hz), 6.2 (t; 1H, 8 Hz), 6.0 (s; 2H), 5.9 (t; 1H, 8 Hz), 5.7 (d,d; 1H; 11, 2.2 Hz), 3.44 (d; 1H, 8 Hz), 3.25 (t; 1H, 8 Hz), 3.18 (br, s, 2H).

cmr, δ, $CDCl_3$: 196.5, 152.0, 139.0, 136.0, 133.5, 130.0, 124.0, 55.9, 48.0, 42.4, 39.5.

Anal. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37.
Found: C, 83.41; H, 6.36.

b) Excess cyclobutadieniron tricarbonyl:

The reaction conditions for the synthesis of enone 16 as described on page 124 were modified so that 2.86 g (0.015 mole) of cyclobutadieneiron tricarbonyl, 0.86 g (0.01 mole) of tropone and 13.9 g (0.025 mole) of ceric ammonium nitrate were used. Other than the change in the molar ratios of the reactants, the reaction conditions and workup were identical to that described in Section 1a. Enone 16 was isolated in a 14.5% yield (0.23 g).

c) Addition of cyclobutadieneiron tricarbonyl to a mixture of tropone and ceric ammonium nitrate:

A solution of 0.78 g (0.074 mole) of tropone and 250 ml of acetone was cooled to -5°C in a 3-neck 500 ml round bottom flask, maintained under argon. A solution of 1.3 g, (0.0068 mole) of cyclobutadieneiron tricarbonyl in 20 ml of acetone was added dropwise over a period of 15 min, to the stirred reaction mixture, just after 6.3 g (0.012 mole) of ceric ammonium nitrate had been added to the tropone solution. The tropone solution turned dark red immediately after the addition of the ceric salt. The reaction mixture was subjected to an aqueous workup identical with that described in Section 1a. Analysis of the viscous dark brown oil by analytical glpc showed the absence of 16 or any other volatile compound.

2. From the chemical modification of tricyclo-[4.3.2.$0^{2,5}$]-undeca-3,4,7,7,8,9-hexachloro-8,10-diene (22):

a) Tricyclo-[4.3.2.$0^{2,5}$]-undeca-3,4,7,7,8,9-hexachloro-8,10-diene 22:

A stirred neat solution of 300 g (1.69 moles) of tetrachlorocyclopropene[66] and 58 g (0.34 mole) of 7,8-dichlorobicyclo-[4.2.0]-octa-2,4-diene was degassed by bubbling a fine stream of argon through the solution for 0.5 hr. After the stirred reaction mixture had equili-

brated, the system was stoppered and maintained at 75°C, while stirring, for three weeks.

The reaction mixture was then allowed to cool to room temperature and the unreacted tetrachlorocyclopropene removed by flash distillation, bp 35-80°C/0.1 mm.

Hexahalide 22 could be partially purified by tituration with pentane and crystallized from petroleum ether, mp 120-36°C (mixture of epimers at C-3 and C-4).

Analytical glpc showed that crude 22 consisted of two major components with retention times of 11 and 12 min (Column A, 100-200°C/6°/min).

After the removal of tetrachlorocyclopropene, 100 g of crude 22 was isolated as a pale tan viscous oil, 83.5% yield.

b) Tricyclo-[4.3.2.$0^{2,5}$]-3,4,8,9-tetrachloro-8,10-diene-7-one (23):

A 2 ℓ 3-neck round bottom flask was equipped with a stirring rod and Teflon paddle, thermometer and reflux condenser. One hundred grams (0.6 mole) of silver nitrate was dissolved in 200 ml of distilled water and 700 ml of p-dioxane. This solution was then maintained at 55-65°C, while stirring and 100 g (0.28 mole) of hexahalide 22 dissolved in 100 ml of p-dioxane was added at once to the silver nitrate solution. The reaction mixture was then maintained at 55-65°C, while stirring, for 20 hr.

The reaction mixture was then cooled and the silver chloride removed by suction filtration and washed with 3 x 150 ml portions of 95% ethanol. Saturated sodium chloride was then added to the clear filtrate until the silver chloride precipitation ceased. The reaction mixture was then filtered by suction filtration and used without purification for the sodium borohydride reduction.

Tetrachloroketone 23 could be purified, after removal of solvent, by dry bag chromatography (CH_2Cl_2, rf 0.3), with 2% recovery, but the results of the sodium/t-butanol reduction of tetrachloroalcohol 24 derived from pure 23, as discussed in the Results and Discussion Section, indicated that nothing was gained by this purification.

Sixty-two grams of dry silver chloride was isolated (78%):

ir, film: 3050, 2980, 2940, 1715, 1615, 1590, 1265, 860, 780, 740 cm^{-1}.

pmr, $CDCl_3$, δ: 6.65 (t, 1H, 8 Hz); 6.3 (t, 1H, 8 Hz), 3.9 (m, 4H), 3.2 (m, 2H).

c) Tricyclo-[4.3.2.$0^{2,5}$]-3,4,8,9-tetrachloro-8,10-diene-7-ol (24).

The clear yellow dioxane-water-ethanol solution of 23 (described in Section 2b) was cooled to 0°C in a 3 ℓ three neck flask, equipped with an addition funnel, stirring rod with Teflon paddle and a reflux condenser. A solution of 38 g (1.0 mole) of sodium borohydride in one liter of 95%

ethanol was added dropwise over a period of one hour while stirring. After the addition of the sodium borohydride was complete, the reaction mixture was allowed to warm to room temperature. The reaction mixture was then heated at 80°C for an additional 4 hr.

The cooled tan reaction mixture was then reduced to approximately 500 ml under reduced pressure. The oily two-phase residue was then washed with 3 x 300 ml of chloroform. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and the solvent removed under reduced pressure. The last traces of solvent were removed under reduced pressure (0.1 mm) for a period of 24 hr, to yield 60 g (71.5%, calcd from hexahalide 22)of a viscous tan oil.

Analysis of this oil by analytical glpc (Column A, 100-200°/6°/min) showed that it consisted of three major components (10.5, 11.0, 12.0 min).

Tetrachloroalcohol 24 could be purified by column chromatography (30:1 basic alumina, activity III, benzene as the eluant, monitored by analytical glpc). Pure 24 was isolated with 50% recovery. Analysis by glpc showed that purified 24 consisted of a major and a minor component (retention time 10.5 and 12.0 min, respectively).

Due to the results of the sodium/t-butanol reduction of crude tetrachloroketone 23 and purified 23, crude 23 was used for all preparative scale reductions.

ir, film: 3400, 2950, 2900, 2885, 2850, 1650, 1630, 1300, 1265, 1130, 880 cm^{-1}.

pmr, CCl_4, δ: 6.4 (m, 2H), 4.2 (m, 3H), 3.3 (m, 2H), 2.9 (m, 3H).

d) Tricyclo-[4.3.2.$0^{2,5}$]-3,8,10-triene-7-ol (21) from reduction of tetrachloroalcohol 24.

Several different reducing systems as well as several modifications of each system were explored. The conditions that were found to be most efficient will be described in detail.

The results from the attempts to improve upon the reduction of 24 will be indicated.

(1) Modified procedure of Gassman and Pape.[24]

A 3-neck 1 ℓ round bottom flask, equipped with a 250 ml addition funnel, Herschberg stirrer, a reflux condenser and gas bubbler, was flame dried under a nitrogen atmosphere. A suspension of 15 g of finely cut (approximately 2 cm^3) of fresh sodium (0.66 g-atom) and 400 ml of dry tetrahydrofuran was heated to reflux while stirring rapidly. Five grams of dry t-butanol was added to the refluxing suspension just prior to the addition of tetrachloroalcohol 24. A solution of 5.0 g (0.017 mole) of crude 24, 25 g of t-butanol (total 30 g, 0.66 mole) and 100 ml of tetrahydrofuran was added dropwise over a period of 1 hr. The vigorously stirred solution was maintained at reflux for an

additional 8 hr, or until the sodium formed a large shiny lump. (Caution: the reaction cannot be left unattended after the first two hours of reaction time as the sodium ball can destroy the reaction vessel with rapid stirring).

The reaction was then cooled in an ice bath and methanol added slowly while stirring gently, until the sodium was completely destroyed.

The reaction mixture was poured into 400 ml of water and extracted with 3 x 100 ml portions of ether. The combined organic extracts were washed with 250 ml 5% hydrochloric acid; 250 ml water and 2 x 250 ml saturated sodium chloride. The ether layer was then dried over anhydrous sodium sulfate, filtered, and the solvent removed under reduced pressure to yield 2.4 g of a dark brown oil.

Analysis of the product by analytical glpc (Column A, 100-200°C/6°/min) showed three major components; 0.3, 1.5 and 2.3 min, and three minor components; 0.8, 1.9 and 3.3 min with variable relative ratios. The peak at 0.3 min was identified as a mixture of isomeric olefins (26)[68] analogous to the carbon skeleton of the enone 16. The peak at 2.3 min coinjected with previously prepared allylic alcohol 21. The remaining peaks were unidentified.

After purification of the crude product [see Section 2f(1)], 0.34 g (13%) of enone 16 was isolated.

(2) Reduction of pure tetrachloroalcohol 24.

When pure 24, (one major component--85%) obtained from the column chromatography of crude 24 was reduced under conditions identical with those described in Section 2d(1), the product obtained was identical, by analytical glpc, with that produced from reduction of crude 24, with the exception of the disappearance of the peak at 1.9 min (exocyclic alcohol 25, page 20).

(3) Reduction of pure tetrachloroalcohol 24 derived from pure tetrachloroketone 23.

When pure 23, obtained from dry-bag chromatography (Section 2b) was reduced by sodium borohydride to afford pure 24 and then reduced by the procedure described in Section 2d(1), the product was identical, by analytical glpc, with that produced from crude 24, with the exception of the disappearance of the minor peak at 1.9 min (exocyclic alcohol 25).

(4) Use of sodium dispersion.

When the procedure 2d(1) was repeated using an equivalent amount of a sodium dispersion, which had been washed with 4 x 200 ml portions of refluxing dry tetrahydrofuran, the product was identical by analytical glpc to that found in 2d(1). The only difference between the use of a sodium dispersion and sodium chunks was that the reaction was complete (by analytical glpc) after 1.5 hr when a sodium dispersion was used.

(5) Sodium sand from mineral oil.

When a sodium sand prepared *in situ* from hot mineral oil which was washed with 3 x 300 ml portions of dry tetrahydrofuran, was used as in 2d(1), the product was identical by analytical glpc with that described in 2d(1).

(6) Sodium sand from *p*-xylene.

When a sodium sand was prepared *in situ* from hot *p*-xylene and 90% of the xylene removed and procedure 2d(1) repeated, the product was identical with that from 2d(1), with one exception. The enone **16** (CH_2Cl_2, rf 4) was isolated from a dry-bag chromatography, as shown by its pmr spectrum and glpc retention time.

(7) Sodium-ammonia-THF reduction.

A 100 ml 3 neck round bottom flask was equipped with a dry-ice condenser, addition funnel and gas inlet tube. Twenty-five milliliters of ammonia was condensed into the flask, which contained a solution of 3 g (0.066 mole) of dry *t*-butanol in 25 ml of dry tetrahydrofuran. One- and one-half grams (0.066 g-atom) of finely cut sodium was added cautiously to the ammonia solution under a nitrogen atmosphere. A solution of 0.5 g (0.0017 mole) of crude tetrachloroalcohol **24** in 20 ml of tetrahydrofuran was added dropwise over a period of 0.5 hr to the stirred deep blue reaction mixture. Stirring was continued for an additional 2 hr, then the ammonia was removed by allowing the reaction

mixture to warm to room temperature. The reaction mixture was then subjected to an aqueous workup identical with that described in 2d(1). One-tenth of a gram of a dark brown oil was isolated which contained less allylic alcohol 21 (by analytical glpc) than that obtained in 2d(1).

(8) Sodium amide-sodium-ammonia-THF reduction.

The method of Nieuwland[69] was adapted for the preparation of sodium amide. Twenty-five milliliters of ammonia was condensed in a 100 ml 3 neck round bottom flask, equipped with a dry-ice condenser and a gas inlet tube. While stirring, 0.1 g (0.0043 g-atom) of sodium was added to the ammonia. A fine stream of air was passed through the solution for 15 min. After the blue color had discharged, a solution of 0.5 g (0.0017 mole) of tetrachloroalcohol 24 in 25 ml of tetrahydrofuran was added dropwise over a period of 15 min to the grey solution. Stirring was continued for an additional 0.5 hr. Finely cut sodium (1.5 g, 0.066 g-atom) was added over a period of 0.5 hr and the turbid blue reaction mixture stirred for an additional hour. The ammonia was removed by warming the reaction mixture to 0°C and the dark brown solution was washed as described in 2d(1). Analysis of the viscous brown oil (0.16 g) by analytical glpc showed only trace amounts of allylic alcohol 21 present.

e) Tricyclo-[4.3.2.$0^{2,5}$]-undeca-3,4,8,9-tetrachloro-8,10-diene-7-(1,3-dioxalane) (28):

A solution of 30.2 g (0.086 mole) of hexahalide 22 in 100 ml of dry methylene chloride was added in one portion to a stirred solution of 35 g (0.18 mole) of silver fluoroborate and 26.5 g (0.42 mole) of dry ethylene glycol in 200 ml of methylene chloride. The reaction mixture was stirred for an additional 2 hr at room temperature.

The silver chloride was removed by suction filtration and washed with 2 x 100 ml portions of methylene chloride. The methylene chloride solution was then washed with 4 x 200 ml portions of water, and 2 x 200 ml of saturated sodium chloride dried over anhydrous sodium sulfate, filtered, and the solvent removed under reduced pressure.

The crude oil (31.6 g) was chromatographed on 500 g of basic alumina, eluting with 200 ml of carbontetrachloride, 400 ml of 2% ether and 600 ml of 5% ether. When the 5% ether aliquots were combined and the solvent removed under reduced pressure, 23.5 g (79%) of tetrachloroketal 28 was isolated.

Analytical glpc: 1 peak (with shoulder), retention time--12.0 min, Column A, 100-200°C/6°/min.

ir (film): 3050, 2970, 2960, 2880, 1620, 1290, 1160, 1140, 1125, 1105, 1020, 950, 870, 785, 765 cm^{-1}.

pmr, δ, CCl_4: 6.55 (t, 1H, 8 Hz), 6.15 (t, 1H, 8 Hz), 4.6-3.9 (m, 6H), 3.45 (br, s, 1H), 3.3 (br, s, 1H), 3.6-3.1 (m, 1H), 2.9 (br, d, 1H, 8 Hz).

Mass spectrum (70 ev): m/e 342.

(1) Tricyclo-[4.3.2.$0^{2,5}$]-undeca-3,10-diene-7-one (29) from the reduction of tetrachloroketal 28.

Of the several reducing systems explored, the sodium-t-butanol-tetrahydrofuran reaction mixture was found to be the most efficient in terms of total yield and lack of complexity of the products produced. The other reducing systems investigated were: sodium-ammonia; sodium-ammonia-tetrahydrofuran; sodium-ammonia-tetrahydrofuran-t-butanol; sodium-ammonia-ethanol-tetrahydrofuran; sodium-ammonia-diethylamine-tetrahydrofuran; lithium-ammonia; lithium-ammonia-tetrahydrofuran and lithium-ammonia-tetrahydrofuran-t-butanol. All of these reductions were carried out and analyzed as described in Section 2d(7).

When tetrachloroketal 28 was reduced in sodium-t-butanol-tetrahydrofuran as described in Section 2d(1), the crude product isolated after aqueous workup was a mixture of seven components with one major component, as shown by analytical glpc (Column A, 100-200°C/6°/min, major component retention time 7.0 min). When the crude ketals were hydrolyzed to the ketones, analysis by analytical glpc (Column A) indicated that enone 16 was not a product of the reaction. Ketone 29, the major component, was isolated in 25% yield by column chromatography, silica gel-carbontetrachloride.

ir (CCl_4): 3040, 2900, 1705, 1455, 1425, 1300, 1230, 1150 cm^{-1}.

pmr, δ, $CDCl_3$: 6.3-5.7 (m, 4H); 3.3 (br, s, 2H); 3.0 (br d, 1H, 8 Hz); 2.5 (m, 3H); 2.0 (m, 2H).

Mass spectrum (70 ev): m/e 161 (2.9); 160 (21.0); 132 (10.4); 118 (26.7); 117 (56.1); 116 (23.5); 104 (73.7); 91 (51.9); 78 (100).

f) Isolation of enone 16 from reduction [2d(1)] of tetrachloroalcohol 24.

A series of control experiments was conducted on the crude oil obtained in 2d(1). When 100 mg of the crude oil was purified by preparative TLC (silica, benzene), three bands were isolated, rf 0.2, 0.3, and 0.5. Band 2, rf 0.3, when extracted with 5% methanol-chloroform and the solvent removed under reduced pressure gave 30 mg of a yellow oil which was a mixture of three components, including the allylic alcohol 21 (by analytical glpc, Column A). When this purified material was subjected to another identical preparative tlc, the same three bands were again isolated with band 2 yielding 9 mg of an oil which contained 21 and the same two other compounds.

When a similar set of control experiments was conducted on the acetates obtained from acetylating the crude oil from 2d(1), the identical behavior of decomposition was observed, with sequential loss of material.

(1) Oxidation of crude oil 2d(1).

The method of Radcliffe and Rodehorst[19] was employed for the oxidation of the crude alcohols to their respective ketones. A 500 ml 3-neck round bottom flask was equipped with a Hershberg stirrer and maintained under a nitrogen atmosphere. One- and one-half grams of chromium trioxide (0.015 mole) was added to a stirred solution of 2.37 g (0.03 mole) of pyridine in 200 ml of methylene chloride. After stirring for 15 min, 2.4 g (0.015 mole) of the crude oil from 2d(1) in 50 ml of methylene chloride was added in one portion to the deep red, clear solution. Stirring was continued for an additional 15 min, followed by the addition of isopropanol until the red color of the chromium oxide-pyridine complex was completely discharged.

The reaction mixture was decanted and the tarry residue washed with 3 x 100 ml portions of ether. The combined organic layers were then washed with 3 x 200 ml of 5% sodium hydroxide, 100 ml of 5% hydrochloric acid, 100 ml of 5% sodium bicarbonate, and 200 ml of saturated sodium chloride. The organic layer was then dried over anhydrous sodium sulfate, filtered, and the solvent removed under reduced pressure to yield 2.3 g of a dark brown oil.

When this oil was chromatographed as described in Section 1a, 0.34 g (13%) of enone 16 was isolated.

3. Oxidation of tricyclo-[4.3.2.$0^{2,5}$]-undeca-3,8,10-triene 26.

The method of Sondheimer[71] was used for the oxidation of the tricyclic olefin to the enone 16. A solution of 0.2 g (0.0014) of 26[72] (mixture of isomers) and 0.2 g of selenium dioxide in 50 ml of p-dioxane was heated at reflux for 12 hr.

The reaction mixture was cooled, taken up in 200 ml of ether and washed with 2 x 100 ml of 5% hydrochloric acid, 100 ml of 5% sodium bicarbonate, 3 x 100 ml of water and 100 ml of saturated sodium chloride. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure. The oil was dissolved in methylene chloride, filtered and purified by preparative tlc (silica, benzene).

The enone 16, as identified by its pmr spectrum, was isolated in .23% yield (0.005 g).

4. Reduction of the enone 16 to the allylic alcohol 21:

a) Attempts with sodium borohydride.

The following sodium borohydride reducing systems were investigated: sodium borohydride (methanol, 0°C; dioxane-water, 0°C; ethanol, 0°C and dimethylfurmamide, 0°C). Each system gave appreciable amounts of 1,4 reduction as shown by the pmr of the crude oil obtained after aqueous workup, with significant adsorptions from 2.5 to 0.8 δ.

b) Lithium aluminum hydride reduction.

A clear lithium aluminum hydride-ether (LAH) solution was prepared by heating a reflux for 0.5 hr, 0.24 g (0.064 mole) of LAH and 50 ml of dry ether under a nitrogen atmosphere. The cooled solution was filtered under nitrogen with a Schlenk tube into a dry 100 ml 3 neck round bottom flask. The clear LAH-ether solution was cooled to -78°C and a solution of 1 g (0.064 mole) of the enone 16 in 10 ml of dry ether was added to the stirred LAH solution dropwise over a period of fifteen minutes. The reaction mixture was maintained at -78° for an additional hour at which time 5 ml of water was added dropwise over 5 min. The dry-ice-acetone bath was then removed and the stirred reaction mixture was allowed to warm to room temperature. The mixture was then filtered and the aluminum oxide salts were washed with several portions of hot methanol.

The filtrate was then washed with 3 x 50 ml of water, 50 ml of 5% hydrochloric acid, 50 ml of 5% sodium bicarbonate and 50 ml of saturated sodium chloride. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure to yield 1.0 g (99%) of the allylic alcohol 21.

glpc: Column B, 130°, 5.3 min.

ir, CCl_4: 3580, 3400, 3030, 2900, 1640, 1390, 1305, 1190, 1025 cm^{-1}.

pmr: See Table III and Figure 12.

Mass spectrum: m/e 160.

P (100); P + 1 (14.8); P + 2 (2.6); 160 (15.7); 142 (33.5); 141 (27.6); 131 (47); 117 (43.5); 104 (90.5); 91 (95); 82 (100).

c) 7-Deuteroallylic alcohol (21-d) from the lithium aluminum deuteride reduction (LAD) of the enone 16.

When the procedure 4b was repeated using LAD, a 97% yield of 21-d was obtained.

glpc: Column B, 130°, 5.3 min.

pmr: See page 14, adsorption at 4.25 absent, and Figure 14.

Mass spectrum (70 ev): m/e 161.

5. Tricyclo-[4.3.2.$0^{2,5}$]-undeca-3,8,10-triene-7-acetate (31).

A solution of 0.5 g (0.0032 mole) of allylic alcohol 21 and 5 ml of acetic anhydride in 25 ml of dry pyridine was heated at reflux for 1 hr. The reaction mixture was cooled and the pyridine removed by flash distillation. The brown oil was dissolved in 50 ml of ether and washed with 3 x 100 ml of water, 100 ml of 5% hydrochloric acid, 100 ml of 5% sodium bicarbonate and 2 x 100 ml of saturated sodium chloride. The organic layer was dried over anhydrous sodium sulfate, filtered, and the solvent removed under reduced pressure to yield 0.6 g (93%) of the allylic

acetate 31 as a tan oil.

glpc: Column A, 100-200°/6°/min, 5.8 min.

ir, CCl_4: 3020, 2900, 1720, 1370, 1225, 1025 cm^{-1}.

pmr, $CDCl_3$, δ: 6.0 (m, 5H), 5.4 (m, 2H), 3.4 (d, 1H, 3 Hz), 3.2 (t, 1H, 3 Hz), 2.6 (m, 2H), 2.05 (s, 3H).

Mass spectrum (70 ev): m/e 202 (2.7): 160 (35); 142 (100); 115 (58.5); 104 (57); 91 (89.2).

6. 7-Deuteroallylic acetate (31-d).

When 7-deuteroallylic alcohol 21-d was acetylated as in Section 5, 31-d was isolated in a 90% yield.

pmr, CCl_4: Adsorption at 5.4 integrated for 1H.

Mass spectrum (70 ev): m/e 203.

7. Tricyclo-[4.3.2.$0^{2,5}$]-undeca-3,8,10-triene-syn-7-(3,5-dinitrobenzoate) (30):

A solution of 1.43 g (0.0064 mole) of 3,5-dinitrobenzoyl chloride (recrystallized from carbon tetrachloride, as pale yellow needles, mp 73.5-74.0°C, and 1.0 g (0.0064 mole) of allylic alcohol 21 in 50 ml of dry pyridine was heated at reflux for 1 hr. The reaction mixture was cooled and the pyridine removed by flash distillation. The yellow oil was dissolved in 100 ml of ether, after an aqueous workup, as described in Section 5, 2.05 g (93%) of the allylic benzoate 30 was isolated as a light tan solid.

Anal. Calcd: C, 61.10; H, 3.96; N, 7.92.

Found: C, 61.10; H, 4.06; N, 7.91.

mp, (acetone-water): 142-3°C, irridescent plates.

ir, CCl_4: 3080, 3030, 2900, 1730, 1640, 1550, 1350, 1270, 1170 cm^{-1}.

pmr, $CDCl_3$, δ: 8.05 (s, 3H), 6.2 (m, 2H), 6.0 (m, 4H), 5.5 (m, 1H0, 3.4 (m, 2H), 2.8 (m, 2H).

8. 7-Deuteroallylic benzoate 30-d:

When the benzoate of 7-deuteroallylic alcohol 21-d was prepared as described in Section 7, a 90% yield of 7-deuteroallylic benzoate 30-d was isolated.

pmr, CCl_4: Adsorption at 6.2 δ integrated for 1H.

II. Solvolyses of derivatives of the allylic alcohol 21:

The glacial acetic used for the solvolyses was distilled from acetic anhydride under an argon atmosphere.

1. Solvolysis of benzoate 30 at reflux:

A solution of 0.5 g of the benzoate 30 in 50 ml of glacial acetic acid was heated at reflux for 2 hr under an argon atmosphere. The reaction mixture was cooled to room temperature and dissolved in 100 ml of ether. The organic layer was washed with 4 x 100 ml of water, 100 ml of 5% soxium bicarbonate and 100 ml of saturated sodium chloride. The ether layer was dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure.

The epimeric allylic acetates, 31 and 32, were separated from the cyclopropyl allylic acetate 34 by preparative glpc (Column A, 130°).

The epimeric acetates were then reduced to their corresponding alcohols (21 and 33) as described in 4b and separated by preparative glpc (Column C, 125°C).

2. Solvolysis of the benzoate 30 at 190°C.

A solution of 0.5 g of the benzoate 30 in 50 ml of glacial acetic, in a combustion tube, was degassed by bubbling a fine stream of argon through the solution for 1 hr. The tube was cooled to -78°C and sealed under vacuum. The reaction mixture was then warmed to room temperature and then maintained at 190°C for 2 hr.

The reaction mixture was then cooled to 0°C and then to -78°C. After the combustion tube was cracked open, the reaction mixture was dissolved in 100 ml of ether and subjected to an aqueous workup as in II(1).

The epimeric allylic acetates, 31 and 32, were separated from the enol acetate 39 by preparative glpc (Column B, 120°C). The epimeric acetates were then reduced to their corresponding alcohols as in 4b, and separated by preparative glpc (Column C, 125°C). The cyclopropyl allylic acetate 34, while present, could not be successfully isolated due to the very low amount present and the close proximity of its retention time to that of the enol acetate 39.

3. Solvolysis of other derivatives of allylic alcohol 21:

The deuterobenzoate 30-d, allylic acetate 31, deuteroallylic acetate 31-d, the epimeric allylic acetate 32, and the cyclopropylallylic acetate 34 were solvolyzed in the same manner as just described in II(2d), with the observed generation of the enol acetate 39 (analytical glpc, co-injection with authentic material).

4. Exploration of other solvolytic conditions with the benzoate 30:

At low temperatures (-78°-0°C), trifluoroacetic acid, trifluoroacetic acid-methylene chloride, aluminum trichloride-ether, and sulfuric acid-water all showed (by analytical glpc) the formation of the allylic alcohol 21, epimeric allylic alcohol 33, and the cyclopropylallylic alcohol 37 and no other products.

At elevated temperatures (25-100°C), 80% acetone, 80% dioxane and 80% acetone-2,6-lutidine gave 21, 33 and 37 as the only products (by analytical glpc). Formic acid and trichloroacetic acid at 100°C gave only three products (by analytical glpc), after aqueous workup which were not further characterized.

III. Thermal stability of solvolysis products.

One milligram of the allylic acetate 31, a mixture of the epimeric allylic acetates 31 and 32, and a mixture of 31, 32 and the cyclopropylallylic acetate 34 were each dissolved in 30 µl of benzene and sealed under vacuum in a capillary tube. The tubes were maintained at 180°C for 2 hr, cooled and analyzed by analytical glpc.

They all were unchanged after 2 hr.

IV. Kinetics.

1. 118°C.

A solution of 0.77 g of the benzoate 30 in 50.0 ml of glacial acetic acid was immersed in a bath at 130°C. Aliquots, taken at various intervals, were quenched by plunging into a dry-ice-acetone bath. The rate of product formation was analyzed by analytical glpc (Column B, 125°C).

2. Elevated temperatures.

A solution of the allylic acetate 31 and biphenyl in glacial acetic acid was sealed under vacuum in a series of capillary tubes. Eight tubes were immersed in an oil bath at temperatures ranging from 165°C to 190°C. Samples were quenched at various times by rapid cooling to -78°C. The rate of disappearance of the acetates 31, 32 and 34 was then analyzed by analytical glpc (Column B, 125°C). See page 61.

V. Photolysis of the enone 16.

All photolyses were done through pyrex with a rayonette apparatus.

1. Photolysis in ether.

A solution of 3 mg of the enone 16 in 10 ml of ether was irradiated for 24 hr. No reaction occurred as shown by analytical glpc.

2. Photolysis in acetone.

A solution of 3 mg of the enone 16 in 10 ml of acetone was irradiated for 24 hr. Analysis by analytical glpc showed that no reaction had occurred.

3. Photolysis in ether-methanol.

A solution of 20 mg of the enone 16 in 10 ml of 1:1-ether-methanol was irradiated for 4 hr. Two products were isolated by preparative glpc (Column B, 120°C). See page 118.

VI. Super acid experiments:

1. Attempts at generation of allylic cation 21^{+}:

The procedure of Winstein[62] was used for the attempted generation of the cation from the allylic alcohol 21. Two-hundred micro liters of a 1:3-fluorosulfonic acid-fluorosulfuryl chloride solution was cooled to -120°C, as moni-

tored by a copper-constantan couple. A buffer layer of 3-4 mm of fluorosulfuryl chloride was condensed on top of the acid layer in a parfait fashion by a bulb-to-bulb distillation. A solution of 30 mg of the allylic alcohol 21 in 50 µl of deuteromethylene chloride was carefully added on top of the cold fluorosulfuryl chloride layer with a drawn out capillary pipette, so as not to disturb the parfait.

Just before the methylene chloride layer froze, the three layers were rapidly mixed with a stirring rod to give a clear yellow solution. The solution was cooled rapidly to below -150°C and the pmr tube sealed under vacuum.

The sealed pmr tube was then quickly transferred to a liquid nitrogen bath. The frozen pmr solution was then quickly transferred to the precooled (-120°C) pmr prode and the spectrum recorded after the solution had melted.

2. Quenching of super acid solution:

The pmr solution (see above) was cooled to -198°C and the sealed tube cracked open. The solution was then warmed to -78°C and quickly poured in a fine stream, into a rapidly stirred solution of saturated sodium bicarbonate at 0°C.

The bicarbonate solution was then washed with 2 x 20 ml portions of ether. The combined ether layers were washed with 50 ml of water and 50 ml of saturated sodium chloride. The ether layer was then dried over anhydrous

sodium sulfate, filtered, and the ether removed under reduced pressure.

The gummy residue was analyzed by glpc and pmr, both of which indicated the lack of monomeric products.

glpc: Column B, 100-200°C/6°/min. No volatile peaks were observed.

pmr, $CDCl_3$: Broad adsorptions, 4.0-1.0 δ.

3. Enone 16 in fluorosulfonic acid.

A solution of 5 mg of the enone 16 in 5 ml of carbontetrachloride was cooled to 0°C. While stirring rapidly, 0.5 ml of distilled fluorosulfonic acid was added to the carbontetrachloride solution. The dark brown acid layer was then removed and the pmr spectrum recorded at room temperature. The resolution was very poor but adsorptions were present at 7.0, 5.5, 4.0, 3.5 and 3.0 δ.

When this acid solution was quenched as described in VI 2, analytical glpc (Column A, 100-200°C/6°/min) revealed one peak which did not coinject with authentic enone 16.

The pmr spectrum of the quenched material was very poorly resolved but it was not identical with that of enone 16.

VII. Attempts to trap an intermediate from high temperature solvolysis of the benzoate 30.

The benzoate 30 was solvolyzed at 180°C in glacial acetic acid (as in II 2) in the presence of both dimethyl acetylenedicarboxylate and tetracyanoethylene. After aqueous workup, analysis by glpc (Column B*, 140°C) showed the absence of any new volatile products, other than those previously reported.

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* Column A: 3% SE30/100-120 varaport/AW-DMCS.

Column B: 3% SE52/100-120 varaport/AW-DMCS.

Column C: 20% Carbowax/60-80 Chrom W.

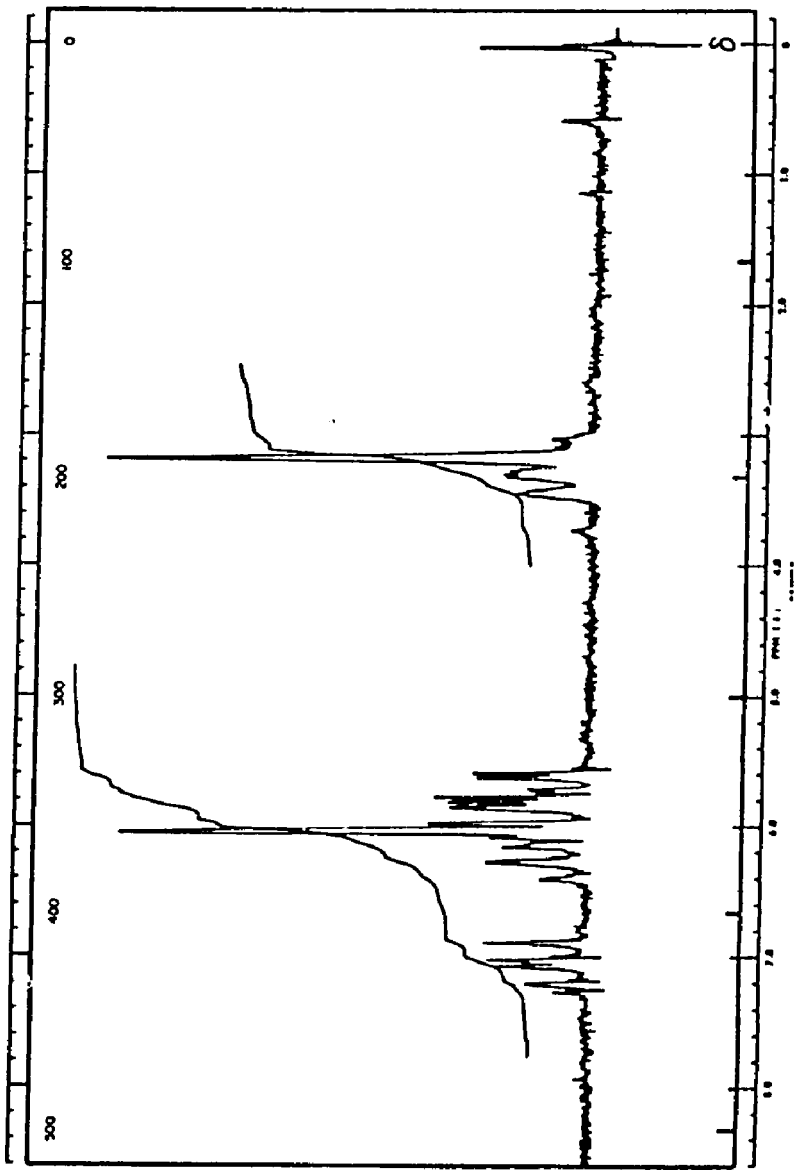


Figure 10: 60 MHz pmr Spectrum of Enone 16

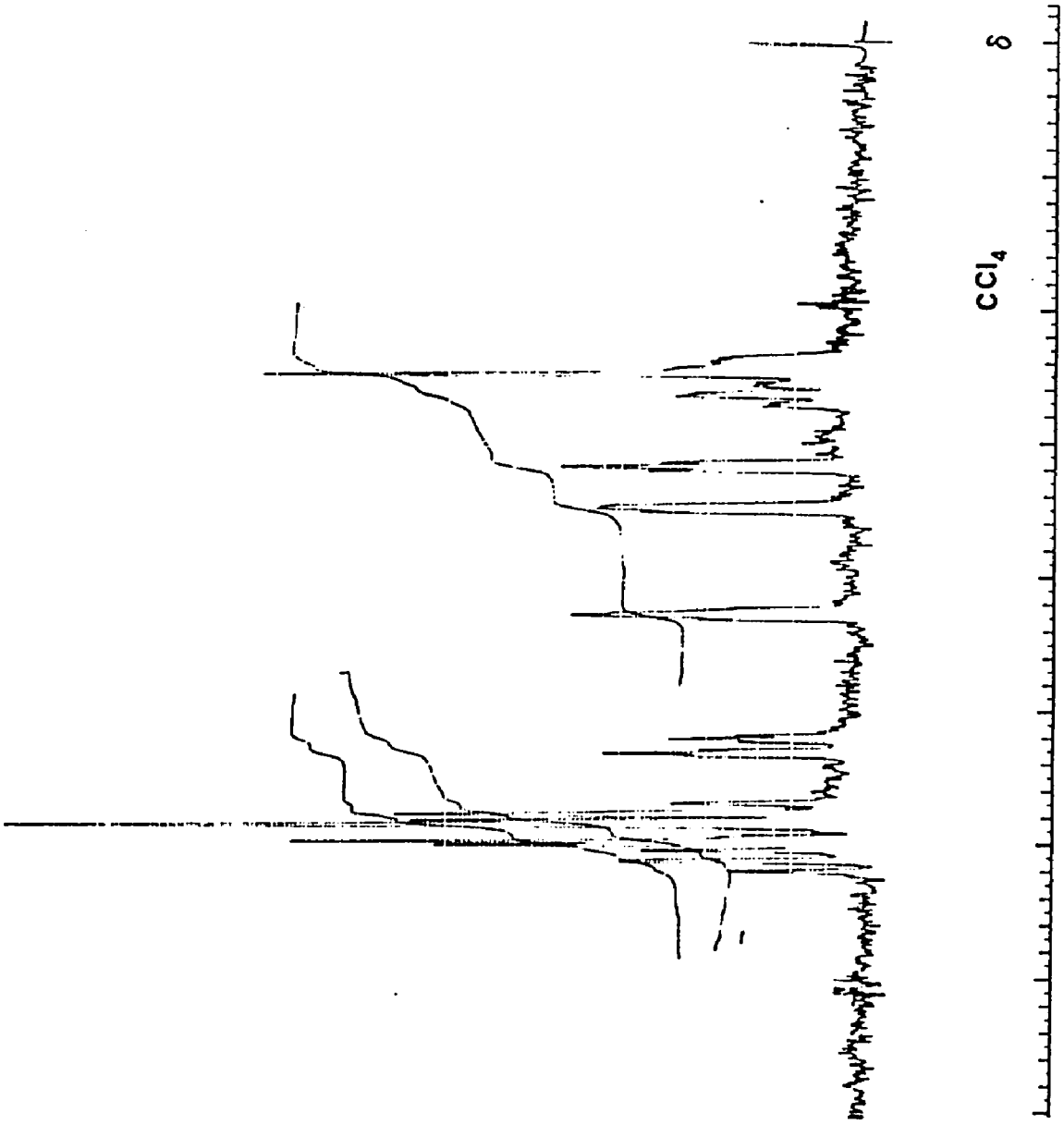


Figure 11: 100 MHz pmr Spectrum of Allylic Alcohol 21

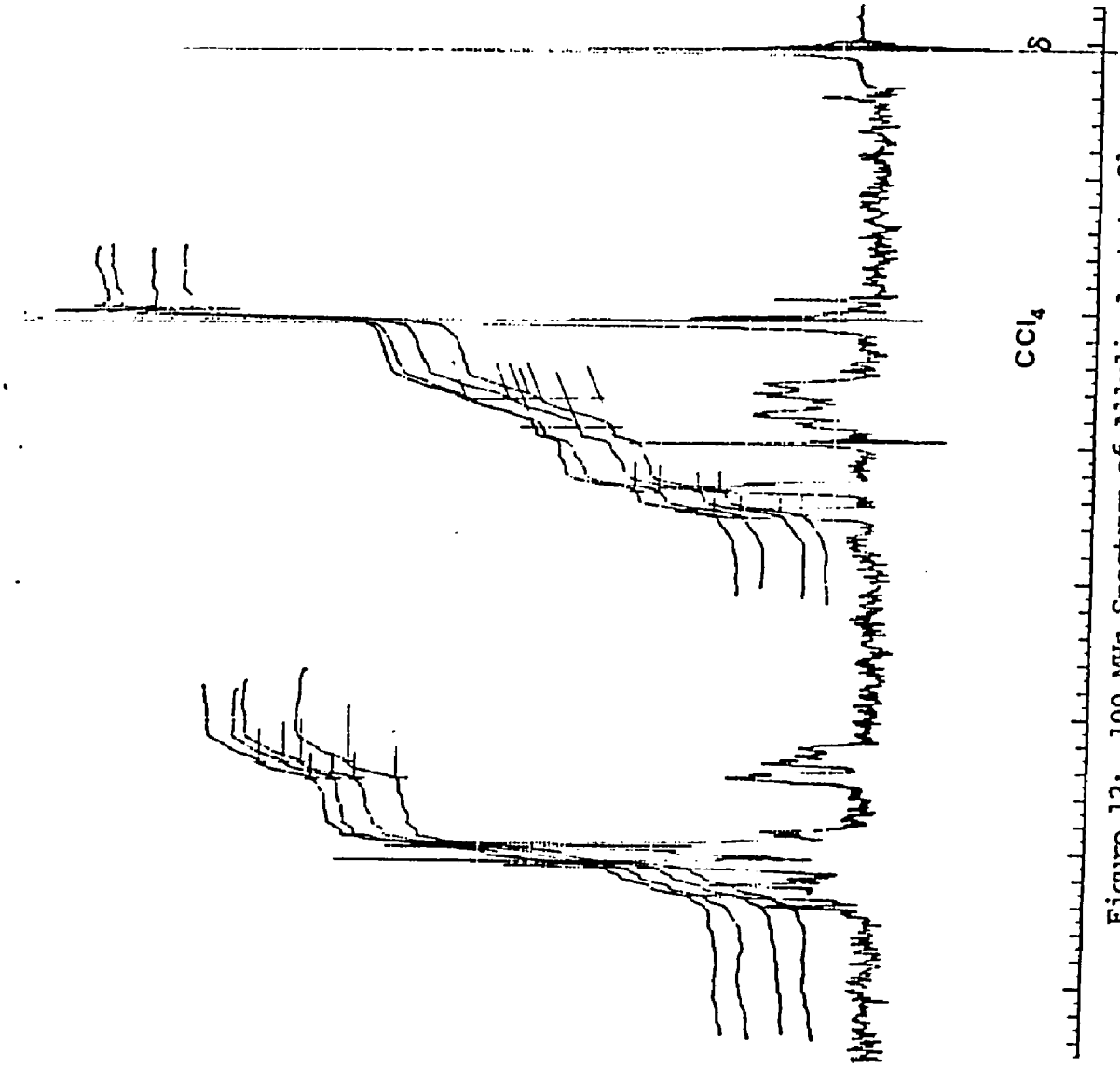


Figure 12: 100 MHz Spectrum of Allylic Acetate 31

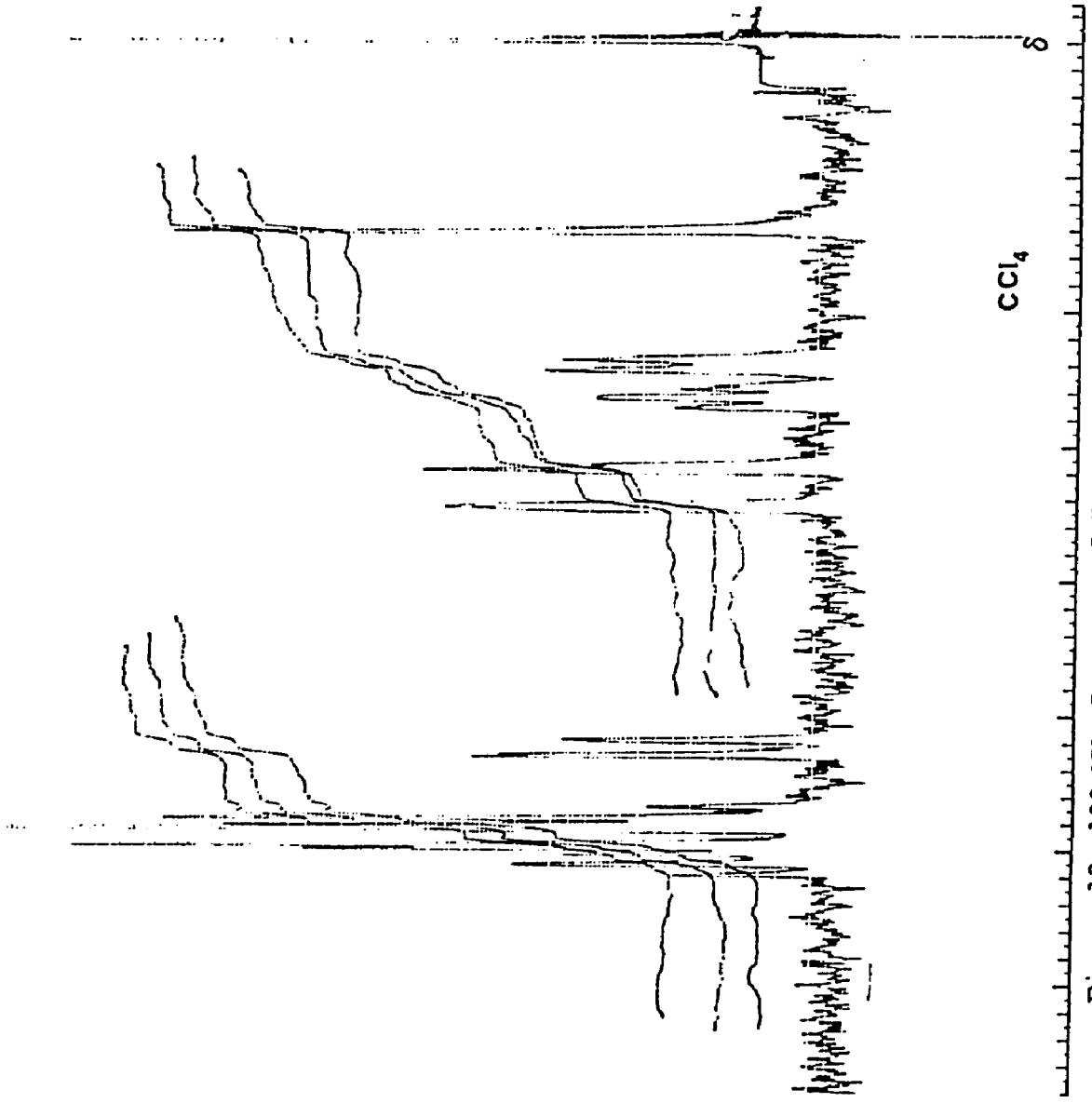


Figure 13: 100 MHz Spectrum of 7-Deuteroallylic Alcohol 21-D

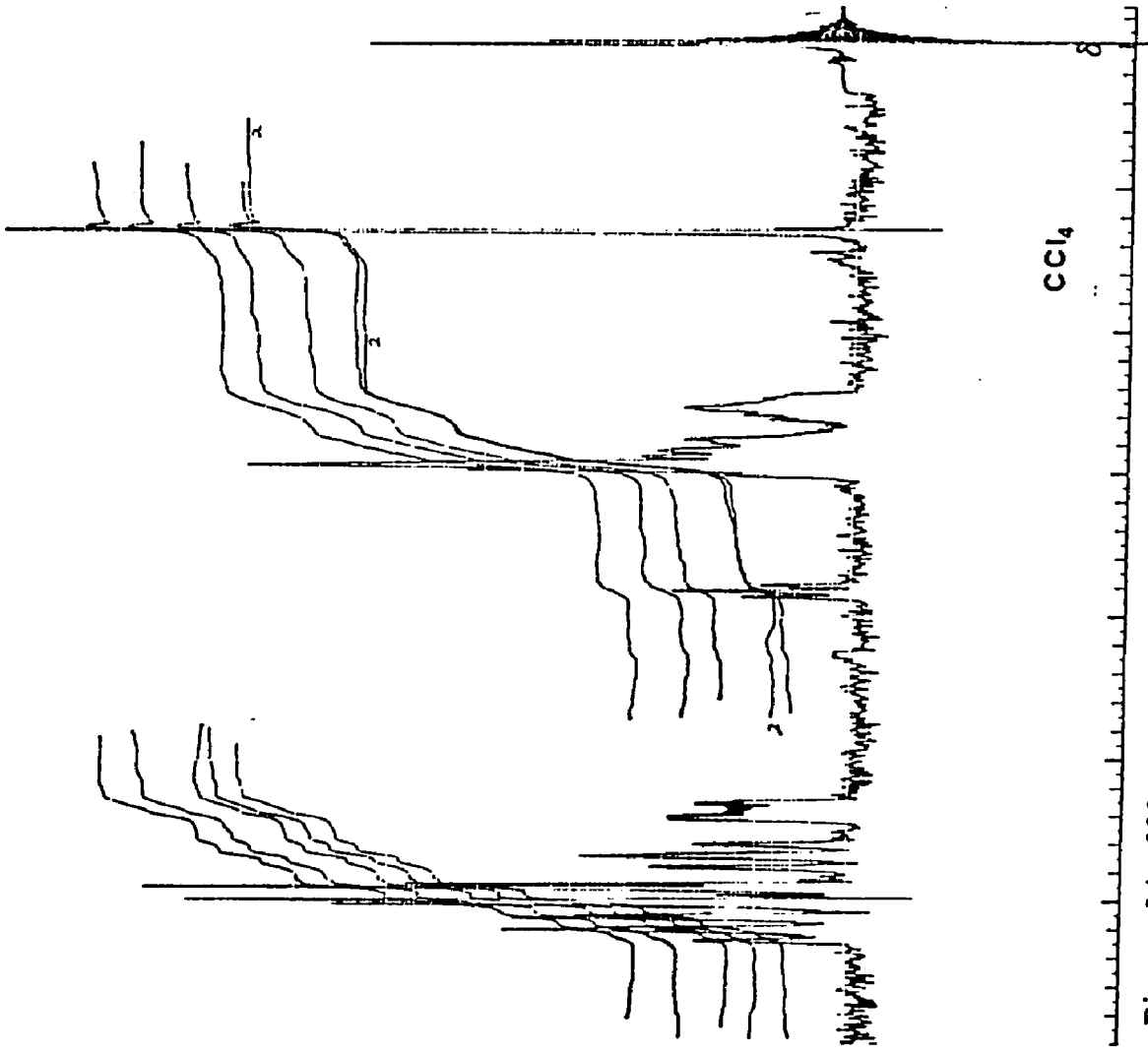


Figure 14: 100 MHz pmr Spectrum of Epimeric Allylic Alcohol 33

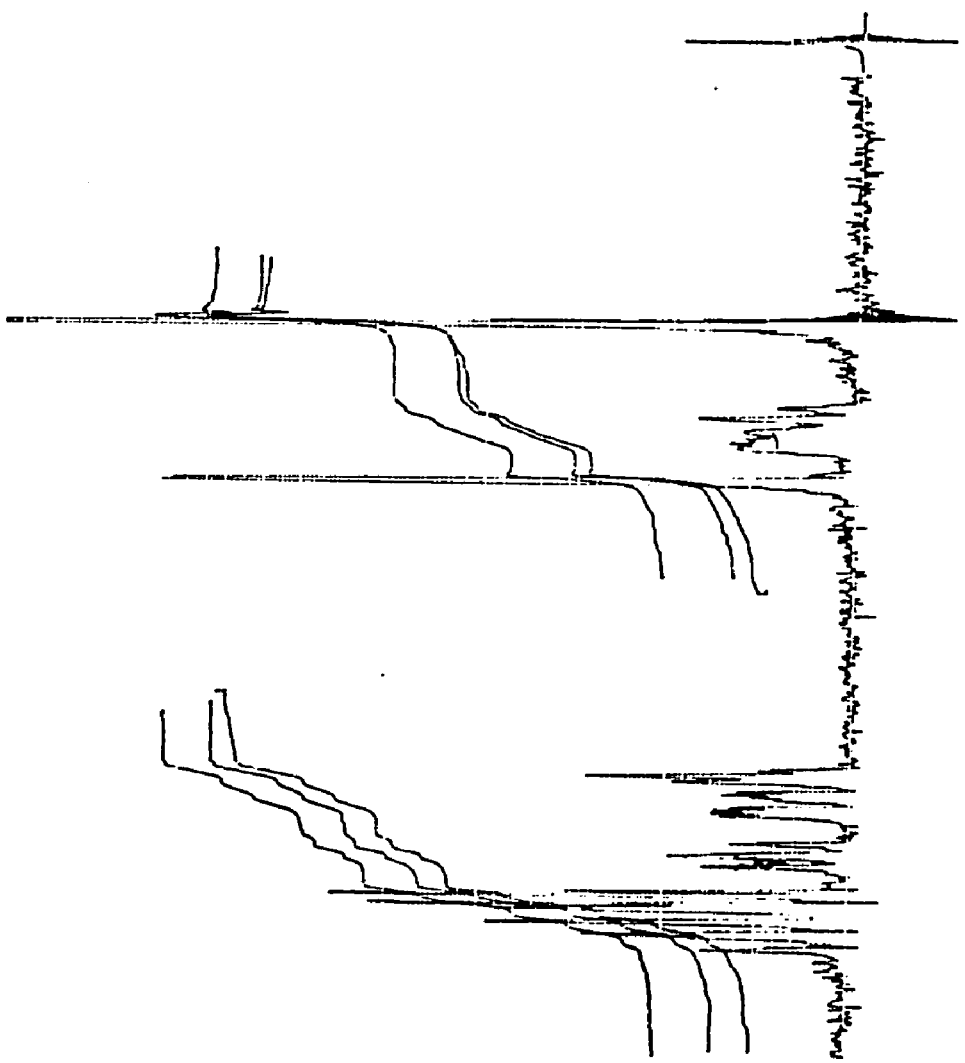


Figure 15: 100 MHz Spectrum of Epimeric Allylic Acetate 32

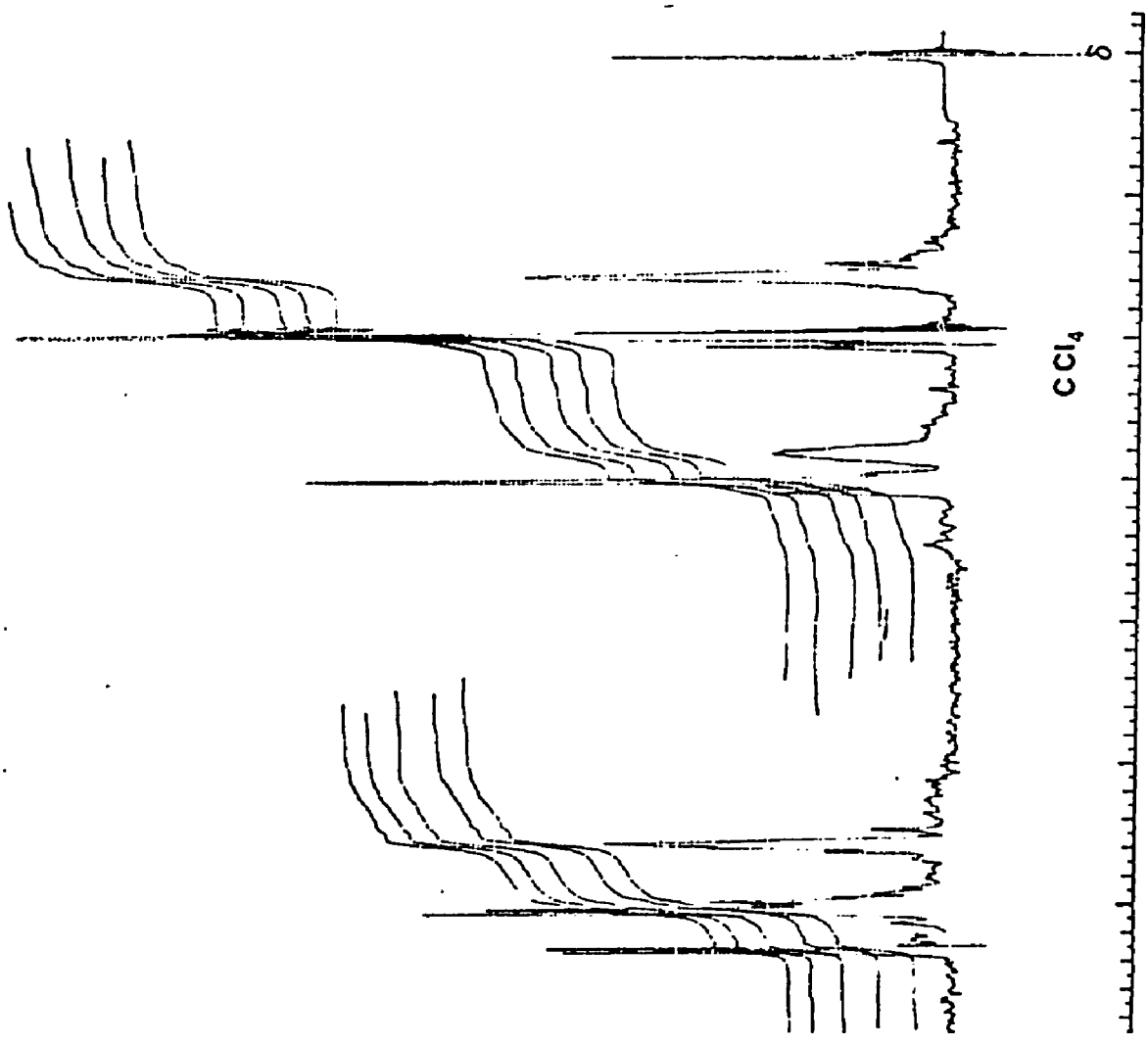


Figure 16: 100 MHz pmr Spectrum of Cyclopropylallylic Acetate 34

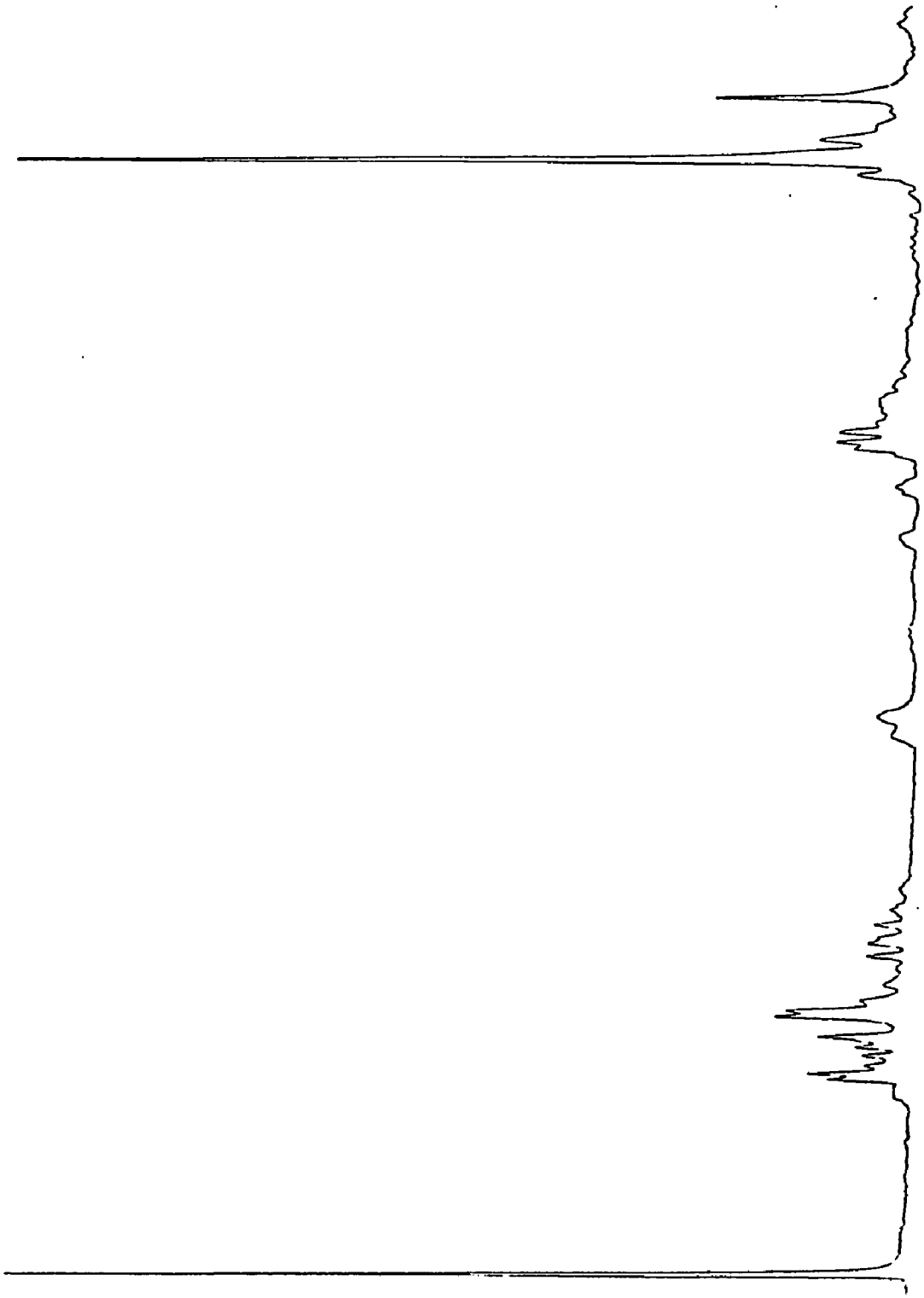


Figure 17: 100 MHz FT pmr Spectrum of Cyclopropylallylic Alcohol 37

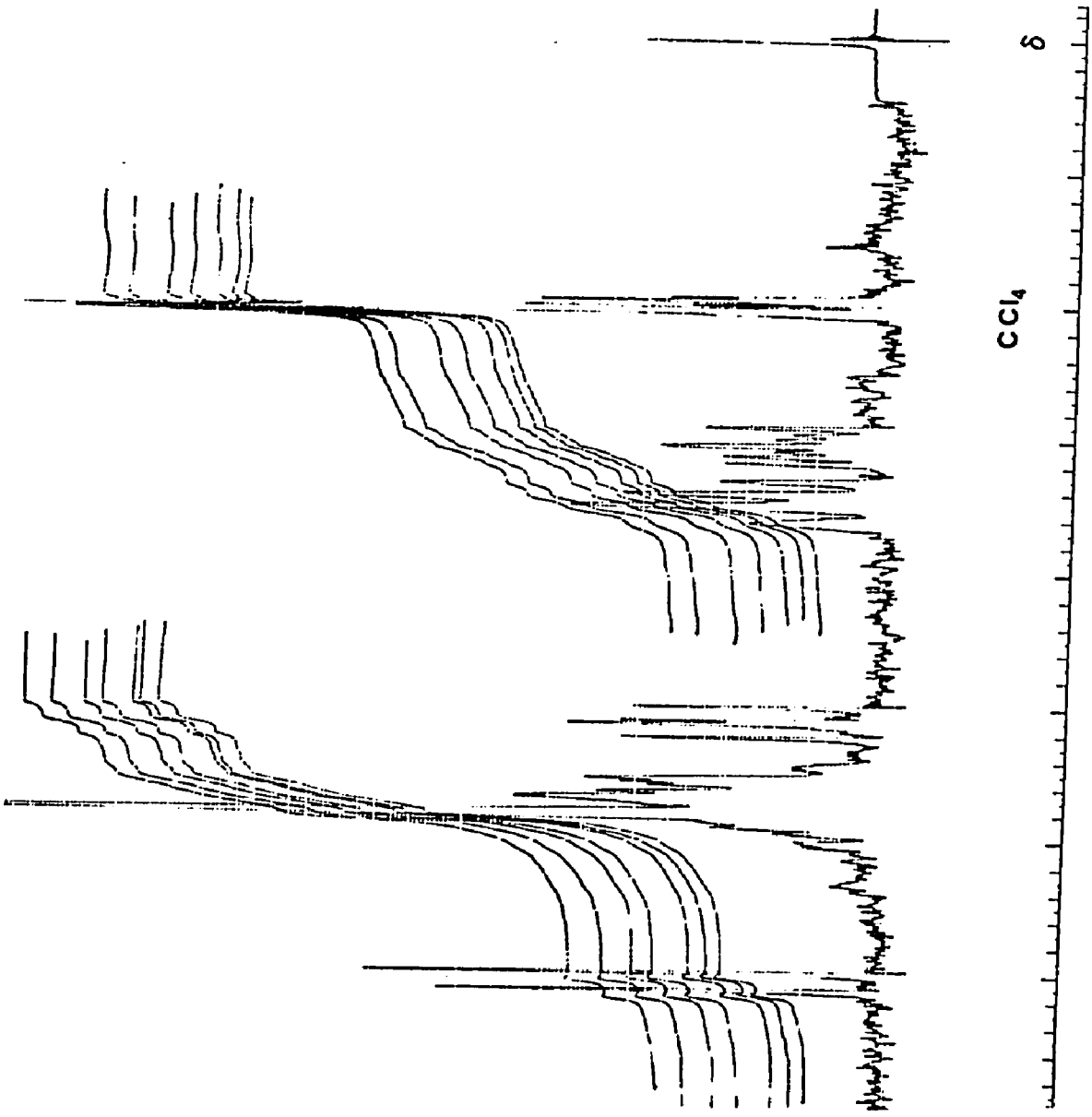


Figure 18: 100 MHz pmr Spectrum of Enol Acetate 39

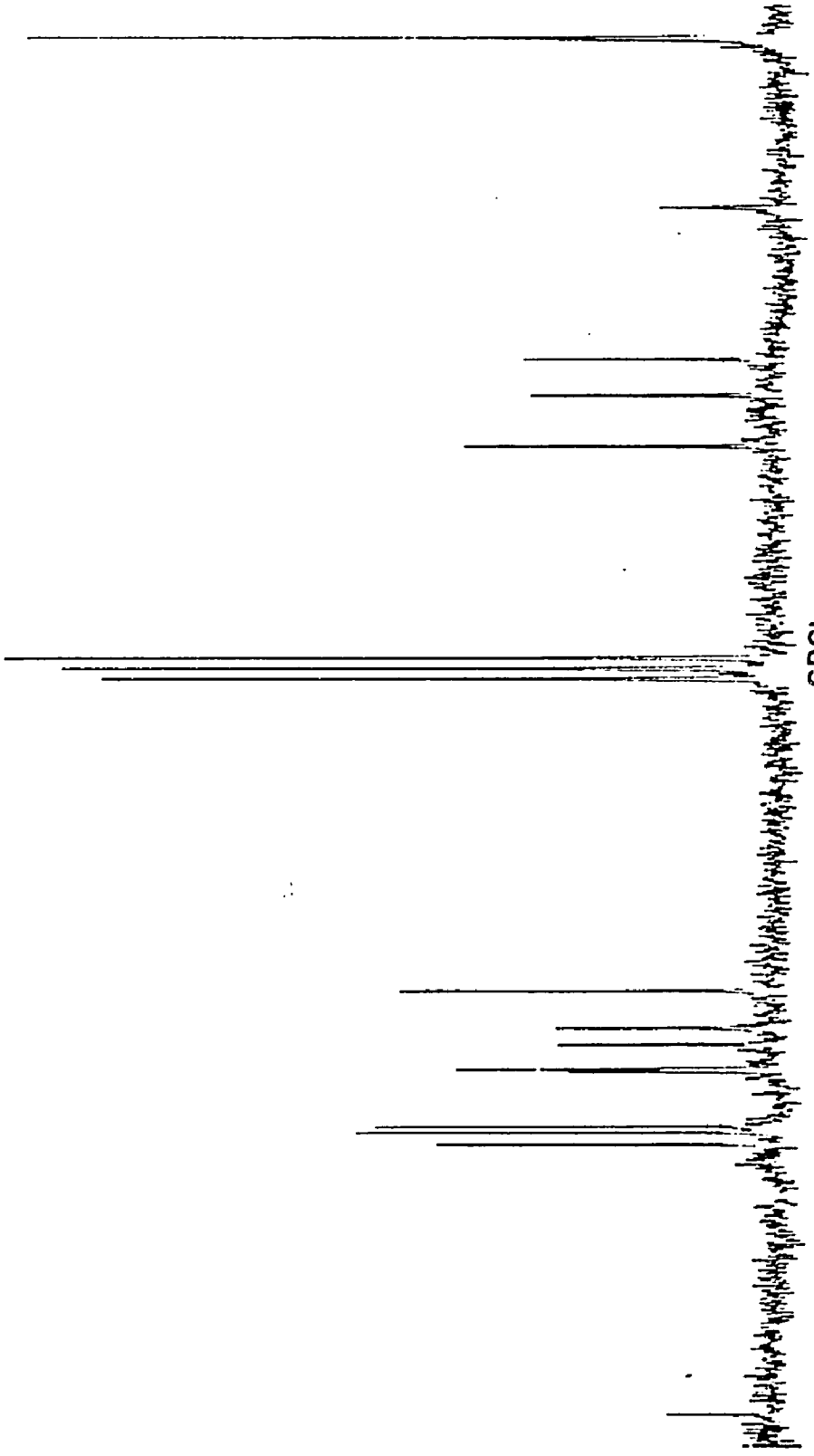


Figure 19: cmr Spectrum of Enol Acetate 39

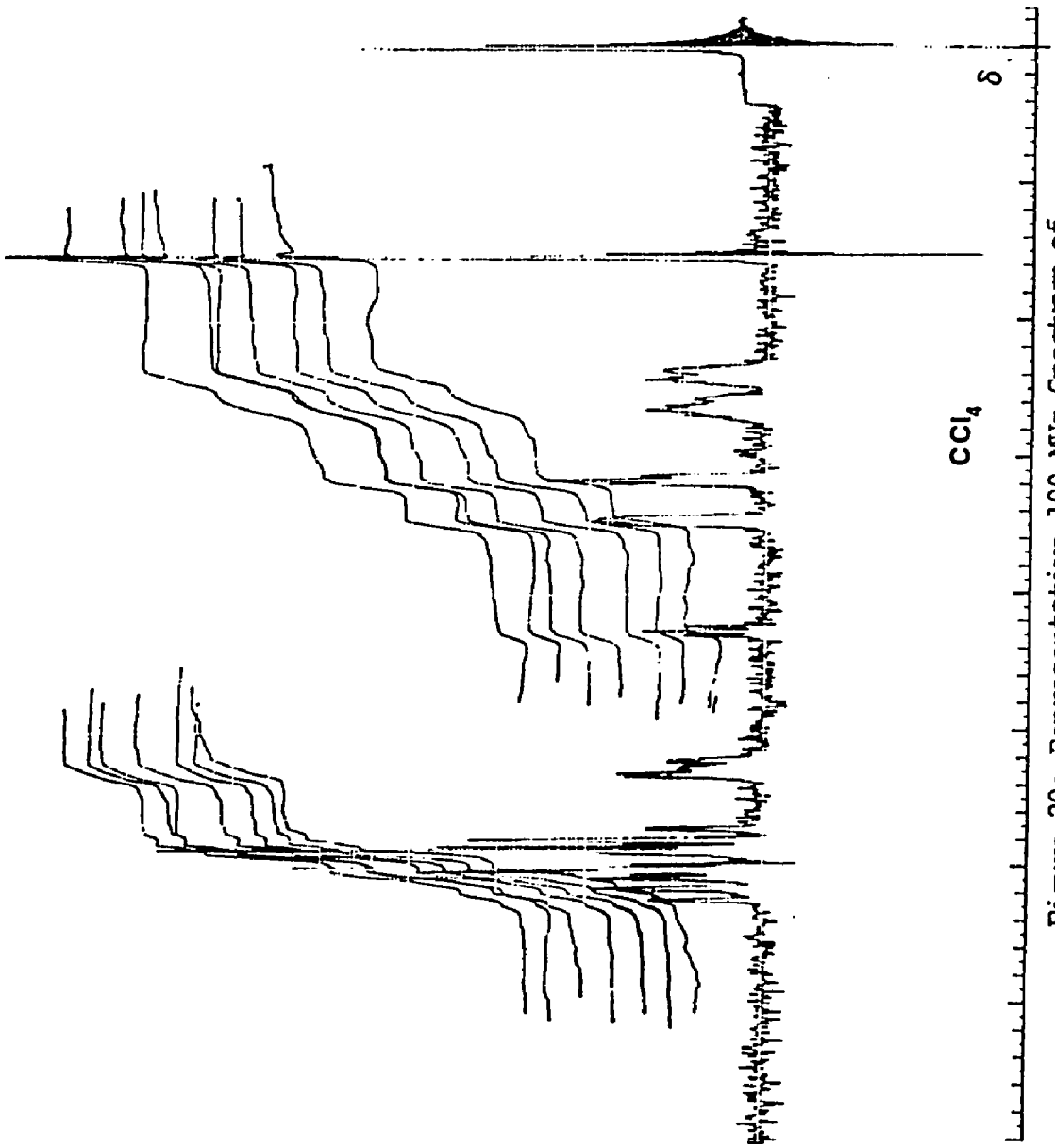


Figure 20: Representative 100 MHz Spectrum of Deuterium Scrambled Allylic Alcohol 22

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