THERMAL REORGANIZATIONS OF ISOPROPENYLCYCLOHEPTATRIENES STUDIES OF HOMOCON.
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University of Maryland, Ph.D., 1970
Chemistry, organic

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THERMAL REORGANIZATIONS OF ISOPROPENYLCYCLOHEPTATRIENES. STUDIES OF HOMOCONJUGATION

by
Douglas Warren Reichard

Dissertation submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
1970

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APPROVAL SHEET

Title of Thesis: Thermal Reorganizations of Isopropenylcycloheptatrienes. Studies of Homoconjugation

Name of Candidate: Douglas Warren Reichard
Doctor of Philosophy, 1970

Thesis and Abstract Approved: Stuart W. Staley
Stuart W. Staley
Associate Professor
Organic Chemistry

Date Approved: May 18, 1970

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ABSTRACT

Title of Thesis: Thermal Reorganizations of Isopropenylcycloheptatrienes. Studies of Homoconjugation

Douglas Warren Reichard, Doctor of Philosophy, 1970

Thesis directed by: Dr. Stuart W. Staley
Associate Professor of Organic Chemistry

During the course of this research the relative rates of deuterium exchange of 3-methylbicyclo [3.2.2] nona-2,6,8-triene, 3-methylbicyclo [3.2.2] nona-2,6-diene, and 3-methylbicyclo [3.2.1] octa-2,6-diene were determined to be 750:1:14, respectively, when allowed to exchange in 1 N potassium t-butoxide/dimethyl sulfoxide-d_6 solutions at 25°. The rates strongly suggest that the bicyclo [3.2.2] nonatrienyl anion is bicycloaromatic since field/inductive effects and geometry arguments cannot satisfactorily account for its enhanced rate of exchange relative to 3-methylbicyclo [3.2.2] nona-2,6-diene. The other anions show rates appropriate for them to be bishomoaromatic in character.

The lithium-ammonia reduction of these three bicyclic systems was studied, and, with regard to 3-methylbicyclo [3.2.2] nona-2,6,8-triene and 3-methylbicyclo [3.2.1] octa-

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2,6-diene, the latter was reduced faster when one accounts for statistical factors. This rate of reduction is correlated with the strain energies of the systems and is not compatible with the argument that the energy of the lowest unoccupied molecular orbital always controls the rate of reduction. The relative energies of this orbital have been estimated for these bicyclic systems from their tetracyanethylene charge transfer spectra.

3-Methylbicyclo [3.2.2] nona-2,6,8-triene can be conveniently synthesized by the thermal reorganization of 7-isopropenylcycloheptatriene. The isopropenylcycloheptatriene system was also thermally equilibrated at 170.2°, 202.2°, and 259° and the entropy, enthalpy and free energies of isomerization were obtained. 1-Isopropenylcycloheptatriene is the thermodynamically favored isomer, but 3-methylbicyclo [3.2.2] nona-2,6,8-triene is present at equilibrium and the results show that entropy is the controlling factor in determining its relative stability in this equilibrium mixture. Rehybridization and strain effects can account for much of the observed free energy differences, and the strain energies of several bicyclic systems have been estimated. The high temperature thermal reorganization of 7-isopropenylcycloheptatriene was also investigated, and the products isolated include 1-, 2-, and 3-isopropenylcycloheptatriene,

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methallylbenzene, β,β-dimethylstyrene, cis-2-methyl-8,9-dihydroindene, 2- and 3-methylindene, indene, and o-, m-, and p-allyltoluene. The mechanisms of the formation of these compounds involve the cleavage of substituted norcaradienes and the interconversion of alkyl-substituted cis-dihydroindenes via cis, cis, cis, cis-1,3,5,7-cyclononatetraene intermediates.

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ACKNOWLEDGEMENTS

This thesis was prepared under the direction of Professor Stuart W. Staley and to him I wish to express my sincere appreciation. Professor Staley's helpful advice and guidance have been invaluable to me and have contributed immeasurably to my knowledge of chemistry.

I wish to thank Doctor G. W. A. Milne of the National Heart Institute, National Institutes of Health, Bethesda, Maryland, for his assistance in obtaining several of the mass spectra. I would also like to thank Doctor W. Kraus of the Universität Tübingen, Germany, and Doctor M. Blanchard of the Universite de Poitiers, France, for kindly providing copies of the spectra of 3-methylbicyclo[3.2.1]oct-2-ene. I would also like to express my appreciation to my colleagues, Doctor Frank Wiseman and Mssr. John Erdman, Robert Doherty, Tim Henry, and Joe Rocchio, with whom many fruitful discussions were held in the course of this research.

This research was supported by the National Science Foundation (Grants GP-8673 and GP-17899).

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DEDICATION

To my wife

for all her patience, understanding, and love

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SECTION I

THERMAL REORGANIZATIONS OF ISOPROPENYLCYCLOHEPTATRIENES

The thermodynamic effects of long-range π-interactions have occupied the attention of this research group for a number of years. The initial studies have dealt with diene and triene equilibrations,[1] for which the results have been somewhat difficult to interpret. The current study focuses attention on the energetic effect of long-range interactions in anions, commonly called "homoconjugation."[2] Recently this idea has been extended further to include "bicyclo-aromaticity"[3] which may be considered to be a special type of "Mobius"[4] aromaticity.

In the work reported herein, several bicyclic systems and their rates of deuterium exchange were investigated. The data provided a better understanding of the factors that influence and determine long-range interactions in these bicyclic anions. These systems also provided an opportunity to study the destabilizing "inductive effect" of a methyl group.[5]

In a closely related study, the systems chosen provided another opportunity to obtain thermodynamic data <u>via</u> equili-

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brations in the hope that the data would allow delineation of the factors which contribute to ground state stabilities.

Isomerization of the Isopropenylcycloheptatriene System

Introduction

Synthesis. The synthesis of 7-substituted cycloheptatrienes has been accomplished by several convenient methods. The basic ingredient is readily available cycloheptatriene which is converted via tropylium ion intermediates to the final product.

When Doering and Knox[6] treated cycloheptatriene with bromine, they isolated an ionic salt, tropylium bromide. Treatment of this compound with phenyllithium yields 7-phenyl-1,3,5-cycloheptatriene.[6,7] Later Vol'pin et al.[8] synthesized the perchlorate and fluoborate salts of cycloheptatriene. Several authors[9,10] have found that treatment of these salts with Grignard reagents also leads to 7-substituted isomers.

Tropylium salts also react with alkoxides[6,10,11] to yield 7-substituted tropyl ethers. For example, treatment of tropylium fluoborate with sodium methoxide yields 7-methoxycycloheptatriene.[6,11] These ethers are also good intermediates, since the action of Grignard reagents on them provides 7-alkylsubstituted cycloheptatrienes in very good yield.[10,11,12]

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Recently McGeachin[13] has found that treatment of tropylium fluoborate with even sterically hindered bases such as triphenylmethyl sodium also yields 7-substituted cycloheptatrienes in moderate to good yields.

Isomerization reactions. The isomerization of cycloheptatriene and substituted cycloheptatrienes has received considerable attention in the last 10 years. Little data are available on the mineral acid-catalyzed isomerizations due to the poor control of experimental conditions. Cairncross[7] has found that phenyl substituted cycloheptatrienes were not isomerized to any extent by 1 N fluoboric acid in dioxane for 20 days. However, Conrow[10] has shown that oxidizing acids or strong mineral acids in the presence of air lead to isomerization. Thus, 7-methylcycloheptatriene isomerizes slowly in perchloric acid or sulfuric acid and acetonitrile at room temperature. The rate increases with time and the extent of rearrangement is greater in an oxygen atmosphere since most of the isomerization probably occurs by oxidation of the 7-methylcycloheptatriene to methyltropylium ion followed by reversible hydride exchange with unreacted 7-methylcycloheptatriene.

Strong bases can also be used to effect isomerization. Thus Gaspar[14] has shown that 7,7-dideuterocycloheptatriene

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is completely scrambled by potassium triethylcarbinolate in triethylcarbinol at 97.5°. Also Eglinton et al.[15] were able to equilibrate the methylcycloheptatrienes in potassium t-butoxide in diglyme at 160°.

Several workers have shown that cycloheptatrienes are isomerized by reversible hydride exchange. Parnes, Vol'pin, and Kursanov[16] have isomerized 7-deuterocycloheptatriene with tropylium ion in glacial acetic acid. The isomerization of 7-methylcycloheptatriene to an equilibrium mixture of methylcycloheptatrienes has also been reported by Conrow.[10] This was accomplished by hydride exchange with tropylium perchlorate or methyltropylium perchlorate in acetonitrile. Cairncross[7] has reported the equilibration of 7-phenylcycloheptatriene with tropylium fluoborate or phenyltropylium fluoborate in acetonitrile or 1 N fluoboric acid in dioxane.

However, the most widely applicable and most practical means of isomerization is the thermal mode. As early as 1903 Buchner and Feldmann[17] reported that methyl cycloheptatriene-7-carboxylate isomerizes to methyl cycloheptatriene-3-carboxylate when heated for 1½ hours at 150°. Similar results have been reported by Grundmann and Ottmann[18] and Doering and Laber.[19] Buchi and Burgess[20] have shown that cyclooctatetraene epoxide rearranges at 260° to cycloheptatriene-3-carboxaldehyde, probably through cycloheptatriene-7-carbox-

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aldehyde as an intermediate. The 3-isomer rearranges to the 1-isomer upon further heating.

Conrow[10] has shown that the thermolysis of 7-ethylcycloheptatriene at 400° results mainly in isomerization to a mixture of ethyl isomers, and Cairncross[7] has shown that 7-phenylcycloheptatriene isomerizes easily to 3-phenylcycloheptatriene at 140°.

During his study, Cairncross[7] was able to show that these isomerizations proceeded via 1,5-hydrogen shifts. Similar results were also obtained at the same time by ter Borg, Kloosterziel, and Van Meurs[21] from their work with 7-deuterocycloheptatriene. Others[22] came to a similar conclusion from their work with other substituted cycloheptatrienes. Later Eggers[23] did a complete kinetic study with the monomethylcycloheptatrienes and came to the same conclusion - that isomerization of cycloheptatrienes proceedes via consecutive 1,5-hydrogen shifts. It has recently been shown[24] by C^{14} labeling that 7-phenylcycloheptatriene isomerizes to 3-phenylcycloheptatriene without intramolecular phenyl migration to give added weight to the mechanism of 1,5-hydrogen shifts.

ter Borg and Kloosterziel,[25,26] Cairncross,[7] Conrow,[10] and Eggers[23] have obtained equilibrium mixtures via thermal isomerization of various isomers; their results will be

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discussed later.

Results and Discussion

7-Isopropenylcycloheptatriene, 1, was synthesized by the extension of the procedure of Dauben et al.,[11] employing isopropenylmagnesium bromide and 7-methoxycycloheptatriene. Proof that the product was the 7-isomer was shown by a triplet at δ = 2.12 ppm integrating for one proton at C_7. This isomer was then thermalized under varying conditions (i.e. high temperature flow system, refluxing nonane) until it was found that heating a 30% solution in dimethylacetamide (DMA)* at reflux gave excellent results and allowed a convenient workup procedure (see Experimental Section). Analysis of the reaction mixture showed four products in addition to a small amount of unchanged starting material. These were collected by glpc and identified by spectral methods.

The first product after the 7-isomer on column C0880-2 had an nmr spectrum similar to that reported[27] for bicyclo-[3.2.2]nona-2,6,8-triene, with the differences being an additional peak at δ 1.42 (singlet, 3 H, methyl) and no vinyl peak at δ 4.8. Also the C_4 methylene peak at δ 1.93 is a broad singlet instead of a quartet. This evidence along

---

* Diglyme may be substituted as the solvent with similar results.

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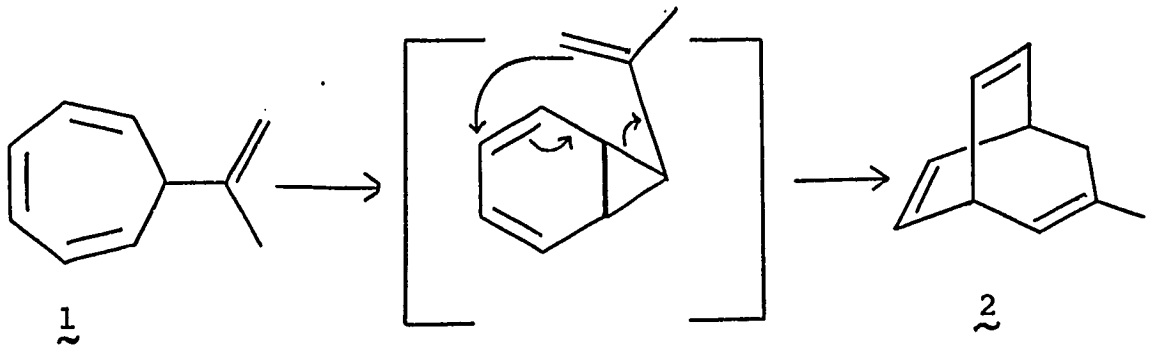
with a uv spectrum which exhibits only end absorption ($\epsilon^{\text{hexane}}_{220\text{nm}}$ 3400) showed this compound to be 3-methylbicyclo-[3.2.2]nona-2,6,8-triene, 2. This compound probably arises via the following mechanism which is analagous to that proposed for several other thermal reorganizations.



1 2

The next isomer eluted by glpc was collected despite its small concentration (ca. 4%) and an nmr spectrum was obtained. The spectrum along with experience in the cycloheptatriene field (i.e. knowing that, in general, the isomers have retention times in the order 7, 2, 3, and 1) suggested that this compound was 2-isopropenylcycloheptatriene, 3. Therefore, the 2-isomer, along with several other products, was obtained by photolysis* of the 7-isomer. The nmr spectrum and retention time of the photolysis product were identical with those of the compound which was obtained thermally.

---

* Dr. Paul Mazzocchi of this department has investigated the photolysis of the 7-isomer and graciously provided the uv spectrum of the 2-isomer.

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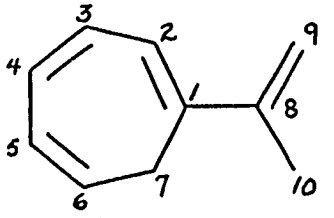
The fourth compound was identified as 3-isopropenylcycloheptatriene, 4, primarily on the basis of its nmr spectrum which exhibited signals at δ = 2.00 ppm (s, 3 H, methyl), 2.21 ppm (t, 2 H, allylic), 5.00 ppm (s, 1 H, vinyl), 5.10 ppm (s, 1 H, vinyl), 5.37 and 5.42 ppm (d's of t's, 2 H, vinyl), 6.14 ppm (d of d, 1 H, vinyl), 6.23 and 6.58 ppm (d's, 2 H, vinyl). (See Experimental Section for detailed analysis).

The fifth and final compound was 1-isopropenylcycloheptatriene, 5, and was identified by its nmr spectrum which showed signals at δ = 1.94 ppm (s, 3, allylic methyl), 2.53 ppm (d, 2, allylic), 4.99 ppm (broad s, 1, terminal vinyl), 5.30 ppm (broad s, 1, terminal vinyl), 5.03-5.62 ppm (m, H_6, vinyl), 5.87-6.33 ppm (m, H_2 and H_5, vinyl), 6.38-6.65 ppm (m, H_3 and H_4, vinyl).



The ultraviolet spectra of the various isomers in this system parallel the phenylcycloheptatriene system quite well and may be used as additional physical evidence.

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Isopropenyl System			Phenyl System[7]		
Isomer	λ(nm)	ε	Isomer	λ(nm)	ε
7	257.5	3140	7	256	3650
2	229	19000	2	239	----
3	225	10600	3	232	17000
	276.5	9600		285	10000
1	222	21100	1	233	13500
	296	7330		300	9600

All the isomers having been separated by glpc and identified, the thermodynamic equilibrium values of the various isomers were obtained in order to investigate whether the bicyclic isomer formed kinetically would manifest itself at equilibrium.

An attempt was made to equilibrate the isomers by reversible hydride exchange by the method of Conrow.[10] This has been successful with methyl-[10] and phenylcycloheptatrienes.[7] Treatment of 7-isopropenylcycloheptatriene with tropylium[28] or trityl fluoborate[29] in dry acetonitrile resulted in the formation of a single compound of longer glpc retention time than the starting material on column C0880-4 at 90°. From a large-scale reaction this product was collected and identified as β,β-dimethylstyrene by comparison

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of the infrared spectrum with that of an authentic sample.* A rearrangement had definitely occurred, but what had caused the reaction? When the 7-isomer was treated with aqueous fluoboric acid, β,β-dimethylstyrene was again the only product of the reaction. Thus it seems plausible that the reaction is acid-catalyzed, and that the fluoborate salts decomposed to form a slightly acidic solution to initiate styrene formation.

A second attempt with potassium t-butoxide in dimethylsulfoxide (DMSO), or hexamethylphosphoramide (HMPA) led only to material loss and no equilibration.

Equilibrium was finally obtained thermally with pentane solutions of isopropenyl isomers sealed in tubes and suspended in the vapors of various refluxing solvents for constant temperature control. Equilibrium was obtained at three temperatures starting from both sides of the equilibrium. The results are listed in Tables I through IV.

The percentages at equilibrium, the equilibrium constants (K_{eq}) with respect to the 1-isomer which is the most stable, and the free energies of isomerization (ΔG_{isom}) are listed in Tables I through IV.

---

* Authentic β,β-dimethylstyrene was provided by G. Craig.

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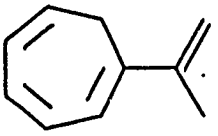
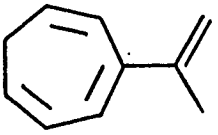
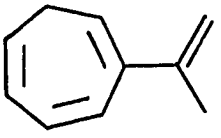
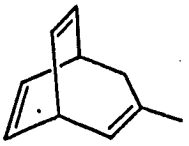
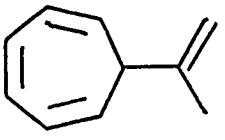
Table I. Composition of the Isopropenylcycloheptatriene System at Equilibrium (%)

Isomer	170.2°	202.2°	259°
	64.5 ± 1.0	65.0 ± 0.3	62.1 ± 1.0
	18.1 ± 0.4	18.2 ± 0.3	20.1 ± 0.4
	13.3 ± 0.8	14.3 ± 0.4	15.9 ± 0.4
	4.2 ± 0.4	2.5 ± 0.3	1.9 ± 0.2
	0.6 ± 0.3	---------[a]	--------[a]

[a] The 7-isomer could not be detected at equilibrium at these two temperatures.

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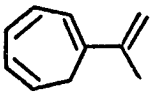
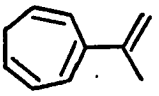
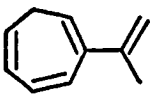
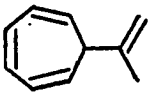
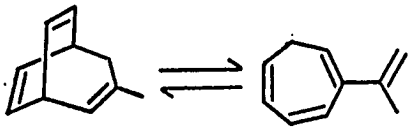
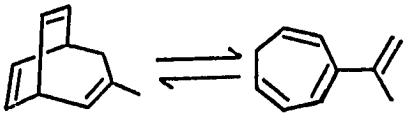
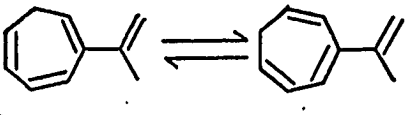
Table II. Equilibrium Constants and Free Energies for the Isopropenylcycloheptatriene System at 170.2°

Compound(s)	K_{eq}	ΔG_{isom} (kcal/mole)
	1.00	0.00
	3.56 ± 0.14	1.12 ± 0.04
	4.85 ± 0.37	1.39 ± 0.07
	15.36 ± 1.35	2.41 ± 0.07 1.80 ± 0.07[a]
	107.5 ± 71.7	4.12 ± 0.50 3.51 ± 0.50[a]
	3.17 ± 0.54	-1.02 ± 0.14 -0.41 ± 0.14[a]
	4.31 ± 0.51	-1.29 ± 0.11 -0.68 ± 0.11[a]
	1.36 ± 0.11	-0.27 ± 0.07

[a] Corrected for entropy of mixing of the dl forms of the 1-, 2-, or 3- isopropenyl isomer

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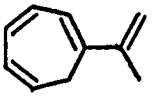
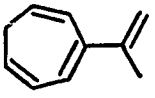
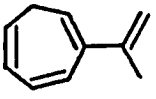
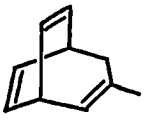
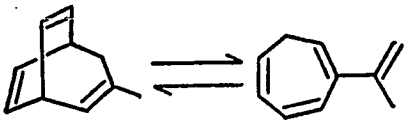
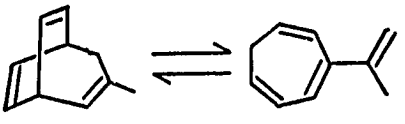
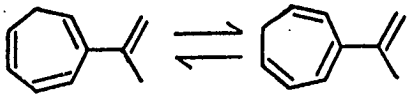
Table III. Equilibrium Constants and Free Energies for the Isopropenylcycloheptatriene System at 202.2°

Compound(s)	K_{eq}	ΔG_{isom} (kcal/mole)
	1.00	0.00
	3.57 ± 0.08	1.20 ± 0.02
	4.54 ± 0.15	1.43 ± 0.03
	26.00 ± 3.30	3.07 ± 0.12 2.42 ± 0.12[a]
	5.72 ± 0.86	-1.65 ± 0.14 -1.00 ± 0.14[a]
	7.28 ± 1.01	-1.87 ± 0.14 -1.22 ± 0.14[a]
	1.27 ± 0.06	-0.23 ± 0.04

[a]Corrected for entropy of mixing of the dl forms of the 1-, 2-, or 3- isopropenyl isomer

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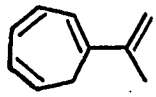
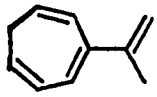
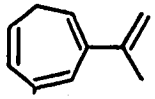
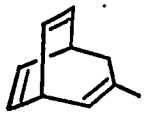
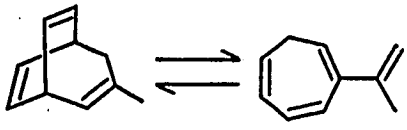
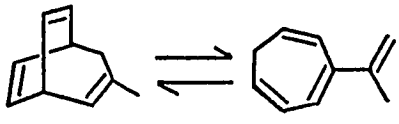
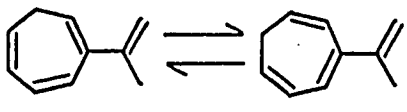
Table IV. Equilibrium Constants and Free Energies for the Isopropenylcycloheptatriene System at 259°

Compound(s)	K_{eq}	ΔG_{isom} (kcal/mole)
	1.00	0.00
	3.09 ± 0.11	1.19 ± 0.04
	3.91 ± 0.16	1.44 ± 0.05
	32.68 ± 4.01	3.69 ± 0.13 2.96 ± 0.13[a]
	8.37 ± 1.10	-2.25 ± 0.15 -1.52 ± 0.15[a]
	10.58 ± 1.34	-2.50 ± 0.14 -1.77 ± 0.14 [a]
	1.26 ± 0.06	-0.24 ± 0.05

[a]Corrected for entropy of mixing of the dl forms of the 1-, 2-, or 3- isopropenyl isomer

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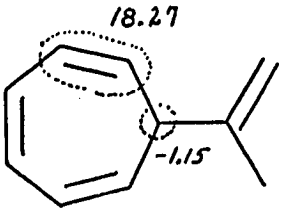
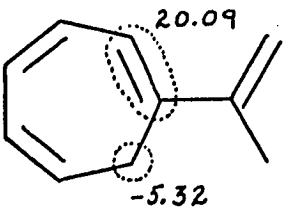
The results of these experiments are quite interesting. The 7-isomer is present to only a very small extent at equilibrium, being detectable only in the reaction at 170°. The 7-isomer lacks interaction between the isopropenyl group and the π-system of the ring. This is clearly shown in the ultraviolet spectrum where the 7-isomer absorbs at λ = 257.5 nm and cycloheptatriene has λ = 261 nm.[30] However, the noninteraction of the π orbitals probably affects its equilibrium value very little, as will be shown later.

The stability of all the other positional isomers with regard to the 7-isomer can be attributed in part to a sp^2 C-H bond becoming sp^3 hybridized and a sp^2-sp^3 C-C bond becoming a sp^2-sp^2 bond. When the Franklin[31] group equivalents method of calculation is used, it can be seen that the isomers differ only in the groups circled.* By using the





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* The 1-isomer is shown, but there is no gross rehybridization between the 1-, 2-, and 3-isomers.

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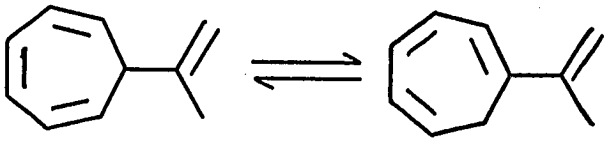
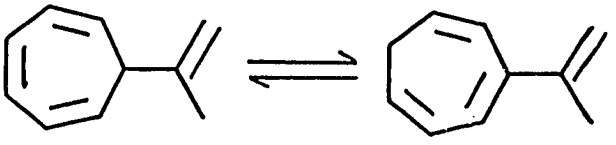
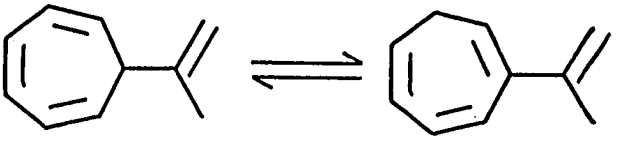
Franklin values the difference in ΔH between the 7- and 1-isomers at 500° K is ca. 2.3 kcal/mole. As can be seen from Table V, this can account for much of the free energy differences between the 7-isomer and the other positional isomers. The Franklin method, as used above, does not contain a key parameter (i.e. a parameter for resonance interaction of a trisubstituted double bond), and therefore the calculations do not take into account this resonance consideration.[32]

Table V. Free Energies for the Isopropenylcycloheptatriene System at 170.2°

	ΔG_{isom} (kcal)
	-3.5 ± 0.5
	-2.4 ± 0.6
	-2.1 ± 0.6

Therefore the methods of Dewar and Schmeising,[33] Cox,[34] and Bloor and Gartside[35] have also been used to calculate ΔH_f for these compounds. The results are listed in Table VI.

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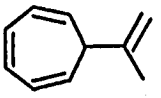
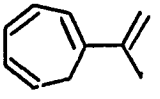
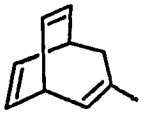
Table VI. Differences in Heats of Formation from Bond Energy Calculations for Isopropenylcycloheptatriene Equilibrium

Compound	Franklin[31]		Dewar[33]	Cox[34]	Bloor and Gartside[35]
	0°	298°	0°	298°	
	0.0	0.0	0.0	0.0	0.0
	-3.08	-2.53	-1.18	-6.30	-6.08
	-20.90	-21.60	-20.25	-13.5	-12.88

Just how useful are these bond energy schemes? An idea of their predictive power in a similar system can be seen in Table VII.

In general the agreement is quite acceptable, the calculated values varying less than 0.5 kcal from the experimental values. The equilibria between the 1-, 2-, and 3-isomers involve no gross rehybridization and correspondingly have much smaller free energy differences (see Table VIII).

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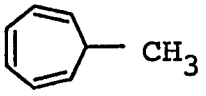
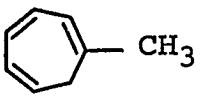
Table VII. Heats of Formation from Bond Energy Calculations for Methylcycloheptatrienes

Compound	ΔG_{isom}	Franklin	Dewar	Cox	Gartside
	0.0	0.0	0.0	0.0	0.0
	-3.02[a] -2.75[b] -1.61[c] -2.91[d]	-2.53	-0.81	-2.40	-2.70

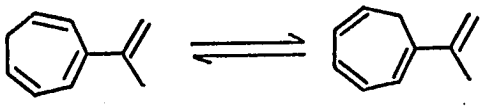
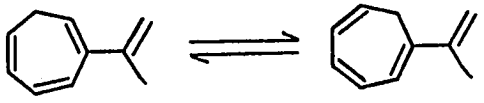
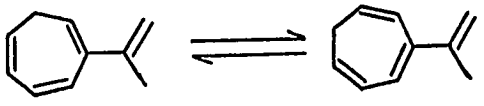
[a] K. Eggers, ref. 23, gas phase shows ΔH_{isom} = 1.9 kcal at 414°.

[b] ter Borg and Kloosterziel, ref. [26], solution at 140°.

[c] K. Conrow, ref. 10, hydride exchange at 25°.

[d] G. Eglinton et al., ref. 15, potassium t-butoxide in diglyme at 160°.

Table VIII. Selected Free Energies and Enthalpies in the Isopropenylcycloheptatriene System

	ΔG[a]	ΔH
	-1.20	-0.82
	-1.40	-1.17
	-0.25	-0.35

[a] Constant within experimental error at all temperatures studied.

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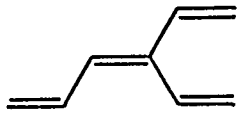
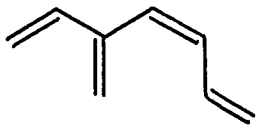
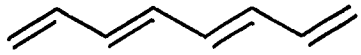
An explanation for the stability of the 1-isomer could be that it has a linearly conjugated tetraene system versus the cross-conjugated systems in the 2- and 3-isomers. Streitwieser and Brauman[36] give the following HMO values for various linear and cross-conjugated tetraenes; in all cases the linear system is more stable than the cross-conjugated. (Table IX).

Table IX. Resonance Energies of Various Tetraene Systems

Compound	Resonance Energy	
	β	kcal/mole[a]
	1.446	-8.68
	1.408	-8.45
	1.517	-9.10

[a] for β = -6 kcal/mole.[37]

ter Borg and Kloosterziel[26a] have also reported that electron-donating species show a preference for the 1-position at equilibrium. Thus, with a dimethylamino group, the 1-isomer is the only isomer observed at equilibrium (see Table X). However, even the cyano group, which is strongly electron-withdrawing, favors the 1-position but not nearly to

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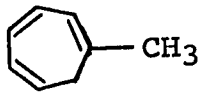
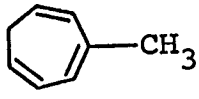
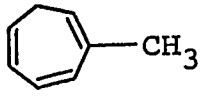
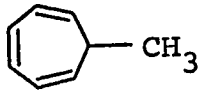
the extent of an electron-donating species.

Table X. Composition of Cycloheptatriene Systems at Equilibrium[26a]

Substituent	%1	%2	%3	%7	Temperature
$N(CH_3)_2$	100	--	--	--	100
OCH_3	88	9	3	--	120
SCH_3	76	16	8	--	114
CH_3	57	24	17	2	140
ø	64	18	18	--	136
CN	52	24	24	--	142

Table XI. Composition of Methylcycloheptatriene Equilibrium at Various Temperatures (%)

Compound	25°[a]	140°[b]	160°[c]	414°[d]
	69.7	57	59	45.5
	16.1	24	21	27.5
	9.6	17	15	22.0
	4.6	2	2	5.0

a Ref. 10
b Ref. 26a
c Ref. 15
d Ref. 23

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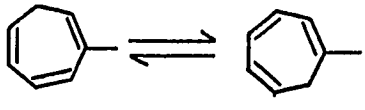
However, the methylcycloheptatriene system gives a different insight into this problem. The results in Tables VIII, XI and XII show that although the free energies differ for the isopropenyl- and methylcycloheptatriene systems, ΔH's are nearly identical and, therefore, the isopropenyl moiety acts like a methyl group. Similar results have also been obtained from the phenylcycloheptatriene system,[7] showing that the conjugative ability of methyl and phenyl groups

Table XII. Selected Free Energies and Enthalpies of Isomerization for Methylcycloheptatriene System at Various Temperatures

Equilibrium	ΔG_{25}[a]	ΔG_{140}[b]	ΔG_{160}[c]	ΔG_{414}[d]	ΔH[d]
	-0.9	-0.7	-0.9	-0.7	-0.8
	-1.2	-1.0	-1.2	-1.0	-1.1
	-0.3	-0.3	-0.3	-0.3	-0.3

[a] Ref. 10, hydride exchange at 25°.

[b] Ref. 26a, solution at 140°.

[c] Ref. 15, potassium t-butoxide in diglyme at 160°.

[d] Ref. 23, gas phase at 414°.

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is about the same. Thus conjugation considerations probably play only a small part in the observed stabilities of these hydrocarbon substituents.

Models show that an isopropenyl group in the 1-position is more easily accommodated (i.e. the nonbonded interactions are less severe) than at C_2 or C_3. This same result has been reported[23] in the methylcycloheptatriene system. However, it seems unlikely that these steric considerations can account for all of the ΔH and ΔG of $1 \rightleftharpoons 3$ and $1 \rightleftharpoons 2$.

The difference in free energy (ca. -250 cal) for the 2-isomer vs. 3-isomer might be due to several different effects. Models show little if any steric difference between an isopropenyl group at either position. In each case the isopropenyl moiety must be twisted to relieve nonbonded interactions. Secondly, the resonance effect must be considered. However, as shown before, the conjugative ability of methyl, phenyl, and isopropenyl are nearly equal and, therefore, conjugation effects will be very small if they appear at all.

Thirdly, although there is no gross rehybridization change between the 2- and 3-isomers, there may be a small change due to changes in bond angles. Figure 1 shows the structures of cycloheptatriene[38] and thujic acid[39] as determined by electron diffraction and x-ray crystallography,

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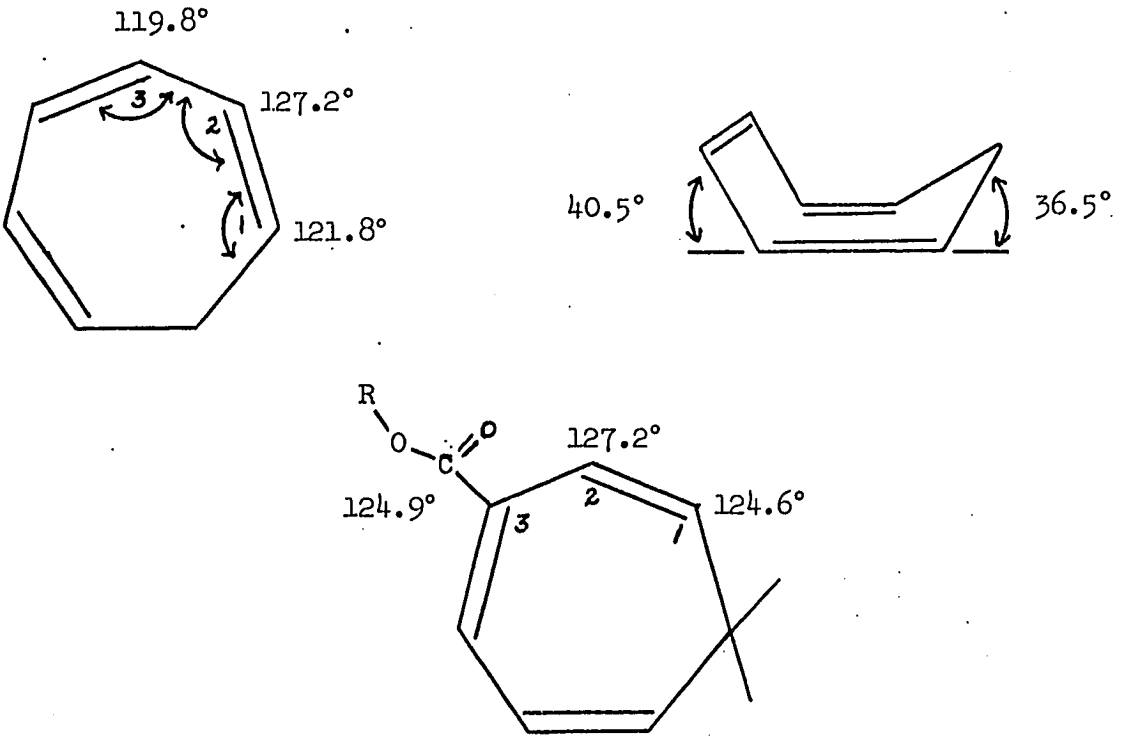

Figure 1

respectively.

As can be seen from these structures, the angle at C_3 is less than the angle at C_2. Decreasing this internal bond angle shifts s-character from the σ bonds of the ring into the external bond, thereby strengthening the external bond.[40] Since the binding energy of C-C single bonds varies more with hybridization than that of C-H bonds, an alkyl substituent at C_3 is stabilized relative to an alkyl substituent at C_2. Therefore, hybridization effects could account for the small enthalpy difference noted between the 2- and 3-isomers.

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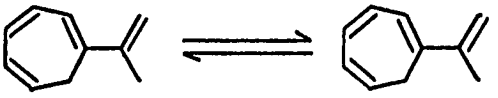
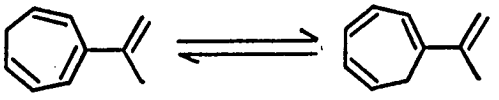
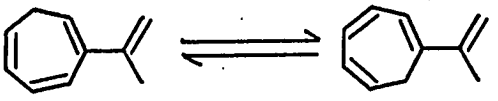
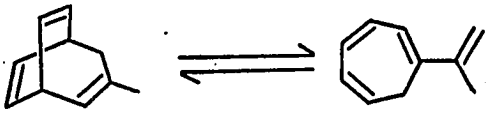
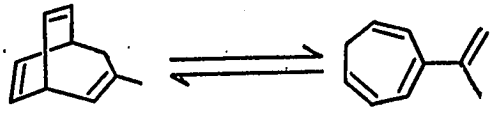
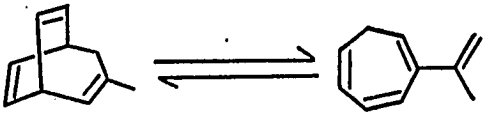
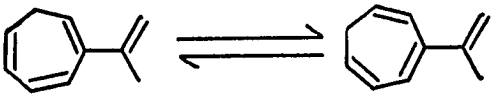
Table XIII. Entropies and Enthalpies of Isomerization for the Isopropenylcycloheptatriene System

Isomers	ΔS(e.u)	ΔH(kcal/mole)
	0.0	0.0
	0.72 ± 0.71	-0.82 ± 0.35
	0.52 ± 0.28	-1.17 ± 0.14
	14.0 ± 2.5 12.6 ± 2.5[a]	3.72 ± 1.22
	13.3 ± 1.9 11.9 ± 1.9[a]	4.54 ± 0.93
	13.5 ± 2.4 12.1 ± 2.4[a]	4.88 ± 1.15
	-0.27 ± 0.37	-0.38 ± 0.18

[a] Corrected by Rln2 for the entropy of mixing for the isopropenyl isomer's dl forms.

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An interesting aspect of the isopropenylcyclohepta-triene system is the appearance at equilibrium of 3-methyl-bicyclo[3.2.2]nona-2,6,8-triene, 2. The free energies for this isomer *vs.* the monocyclic isomers are shown in Tables II, III and IV. At all temperatures shown, 2 is less stable than the monocyclic isomers. However, it is informative to consider the various contributions to ΔG as expressed in

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

equation 1. The equilibria were run at three different temperatures, and ΔH and ΔS were calculated by a computerized least squares plot of ΔG *vs.* temperature (^{o}K) where the slope equals $-\Delta S$ and intercept equals ΔH.

Table XIII gives the experimentally determined values of ΔH calculated by various bond energy schemes. In all cases the calculated values are much higher than the experimental values and at first glance these schemes seem of little value in predicting ΔH for bicyclic systems. However if the difference (3.7-15.4 kcal for $2 \rightleftharpoons 5$ as calculated from Tables VI and XIII) can be explained on the basis of ring strain, the methods may be of some value. The strain energy of several bicyclic systems can be estimated from data now available in the literature. Bedford *et al.*[41] have determined the heat of formation of bicyclo[2.2.1]heptane (-18.0 kcal/mole) and have calculated a strain for this molecule of 18.4

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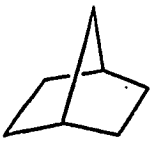
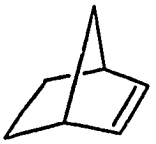
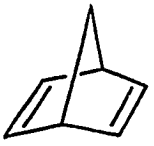
kcal/mole. Turner et al.[42] have used this information to calculate the heats of formation and strain energies (S.E.) in other bicyclo[2.2.1]systems (Table XIV).

Table XIV. Estimated Heats of Formation and Strain Energies[42]

Compound	ΔH_f (kcal/mole)	S.E. (kcal/mole)
	-8.4	18.4
	24.7	22.8
	59.7	29.0

Recently, Westrum and Wong[43] have obtained the heats of formation and strain energies for several other bicyclic systems (Table XV).

The following scheme has been used by Turner et al.[42] to calculate the heats of formation and strain energies of related systems. First, calculate the heat of formation in the gas phase ($\Delta H_f(g)$) of the compound by the Franklin method,[31] then add the strain energy of the totally saturated molecule of the system with which you are concerned. This gives an estimate of the gas-phase heat of formation

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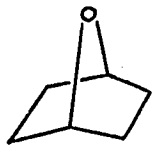
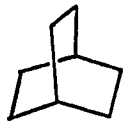
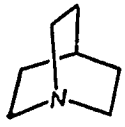
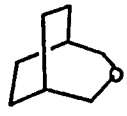
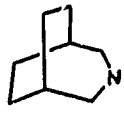
Table XV. Heats of Formation and Strain Energies in Selected Bicyclic Systems[43]

Compound	ΔH_f (kcal/mole)	S.E. (kcal/mole)
		6.5
	-35.2	9.2
	-5.6	9.7
	-13.2	9.5
	-65.9	5
	-24.3	7

(ΔH_f(g-real)) of the real molecule. As a check on the method, this value subtracted from the experimental heat of formation gives the heat of vaporization of the system. If one does this for bicyclo[2.2.2]octane, the following numbers are obtained.

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Example 1: Bicyclo[2.2.2]octane

ΔH_f(liq) = -35.2 kcal/mole Westrum & Wong[43]

ΔH_f(g) = -31.8 kcal/mole Franklin[31]

Strain Energy = 9.2 kcal/mole Westrum & Wong[43]

ΔH_f(g)real = ΔH_f(g) + S.E. = -31.8 + 9.2 = -22.6 kcal/mole

$\Delta H_v = \Delta H_f$(g-real) - ΔH_f(liq) = -22.6 - (-35.2) = 12.6 kcal/mole

The value for the heat of vaporization (12.6 kcal/mole) seems high by ca. 2 kcal/mole, since by Trouton's rule bicyclo[2.2.2]octane would have to have a boiling point > 300°, which seems unlikely although it is not known.*

Once the real heat of formation, ΔH(g-real), of the saturated compound has been estimated, other compounds in the system are ready for analysis. For example, what is the strain energy in bicyclo[2.2.2]octene? The heat of hydrogenation of bicyclo[2.2.2]octene to bicyclo[2.2.2]octane is 28.3 kcal/mole[44] and the Franklin method gives ΔH_f = -3.0 kcal/mole. By using the scheme of Turner et al.,[42] one subtracts the heat of hydrogenation (ΔH_H) from the heat of formation (gas phase) and then subtracts from this ΔH_f, as calculated by the Franklin method (see Example 2).

---

* The melting point of bicyclo[2.2.2]octane is 169-70°.[45]

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Example 2: Bicyclo[2.2.2]octene

ΔH_f(g) = -3.0 kcal/mole Franklin[31]

ΔH_H = -28.3 kcal/mole Turner[44]

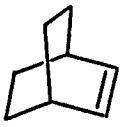
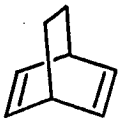
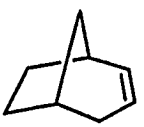
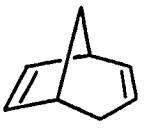
ΔH_f(g-real) of bicyclo[2.2.2]octane = -22.6 kcal/mole

S.E. = ΔH_f(g-real) - ΔH_H - (ΔH_f(g)) = 8.7 kcal/mole

This compares well with the 9.7 kcal/mole obtained by Westrum and Wong[43] (Table XV).

By using this scheme, one can calculate the strain energy in bicyclo[2.2.2]octa-2,5-diene and bicyclo[2.2.2]octa-2,5,7-triene (barrelene). It is also possible to calculate the strain energies in the bicyclo[3.2.1] system since Schleyer et al.[45] have shown that the enthalpy ($\Delta\Delta H$) difference between

Table XVI. Strain Energies (kcal) of Several Bicyclic Systems

Compound	ΔH_f(Franklin)[31]	ΔH(hydrogenation)	S.E.(Calcd)
	-3.0	-28.3[44]	8.7(9.7)[43]
	+25.7	-56.2[44]	7.9
	-3.0	-26.8[47]	7.2
	+25.7	-57.9[47]	9.6
	+54.5	-93.8[48]	16.7

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bicyclo[2.2.2]octane and bicyclo[3.2.1]octane is negligible. Therefore the ΔH_f(g-real) for the compounds are identical. Table XVI gives estimated strain energies for several bicyclic systems.

For the bicyclo[3.2.2]nonane system, an estimate, however crude it may be, can be made of the strain energy. With oxygen and nitrogen in the three bridge of the bicyclo[3.2.2]-nonane system, the strain energies are 5 and 7 kcal/mole, respectively.[43] The difference in strain energy between bicyclo[2.2.2]octane and quinuclidine has been estimated at 0.3 kcal/mole[43] (Table XV). From an interpretation of data obtained from lithium-ammonia reduction studies of 3-methylbicyclo[3.2.2]nona-2,6,8-triene and 3-methylbicyclo[3.2.1]-octa-2,6-diene, it appears that the "strain" energy of the bicyclo[3.2.2]triene is less than that of bicyclo[3.2.1]diene. (See Section III). In Table XVI the strain energy of bicyclo-[3.2.1]octa-2,6-diene has been estimated as 9.6 kcal/mole. This is probably a good estimate for 3-methylbicyclo[3.2.1]-octa-2,6-diene. Thus the "strain" energy of 3-methylbicyclo-[3.2.2]nona-2,6,8-triene is less than 9.6 kcal/mole.

Thus it seems possible that much of the observed difference between the calculated (Table VI) and observed ΔH's (in Table XIII) can be attributed to ring strain. However, the discrepancies warrant further investigation.

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From Equation 1 and Table XIII, it can be seen that the entropy term (i.e. ΔS) is the overwhelming factor in ΔG for the equilibrium of 3-methylbicyclo[3.2.2]nona-2,6,8-triene with the positional isomers. If one considers ΔS to be a measure of the degree of randomness in a system, this seems very logical. 3-Methylbicyclo[3.2.2]nona-2,6,8-triene is constrained into a bicyclic system and, thus, does not have the freedom of movement (i.e. degree of randomness) of the isopropenylcycloheptatrienes. This should be so and is reflected in the entropy of isomerization. Benson[49] has shown that when one constrains a C_7 open chained hydrocarbon into a C_7 cyclic compound, ΔS is raised ca. 4.4 e.u. The transformation of the isopropenylcycloheptatrienes into the bicyclo[3.2.2]system causes the exocyclic sp^2-sp^2 C-C single bond to be constrained and therefore raises ΔS by 4.4 e.u. The bicyclic system also prevents the flipping of the four single bonds in the cycloheptatriene ring. Now if flipping causes a rise in ΔS of only one-half, or 2.2 e.u., for each single bond, the total change in ΔS would equal 13.2 e.u. (4 x 2.2) + 4.4 , which accounts very well for the ΔS which is observed (Table XIII).

Therefore, in conclusion, it can be seen that 1-isopropenylcycloheptatriene predominates at equilibrium and the factors which control this reaction can, to some extent, be

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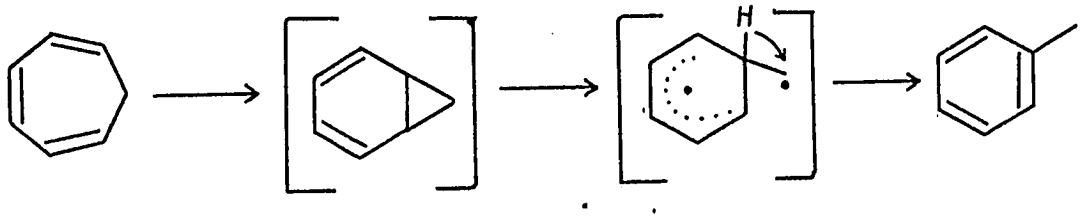
ascertained. Hybridization effects, it has been shown, can account for several observed effects, and resonance has been discounted as being important. In the bicyclic-monocyclic equilibrium, ΔS was found to be the decisive term for determining ΔG; the deviation of ΔH from that calculated could be a measure of the ring strain in the bicyclic system but the deviation seems too large compared with the calculated strain energies.

Thermal Rearrangements of the Isopropenylcycloheptatriene System

Introduction

Ring Contractions. Woods[50] has shown that cycloheptatriene undergoes a rearrangement at 478° to afford toluene. Others[51] have observed the same reaction under similar conditions. It was proposed that this reaction proceeded *via* norcaradiene which was then cleaved to a diradical which went on to product. Klump and Chesick[51] have studied the kinetics



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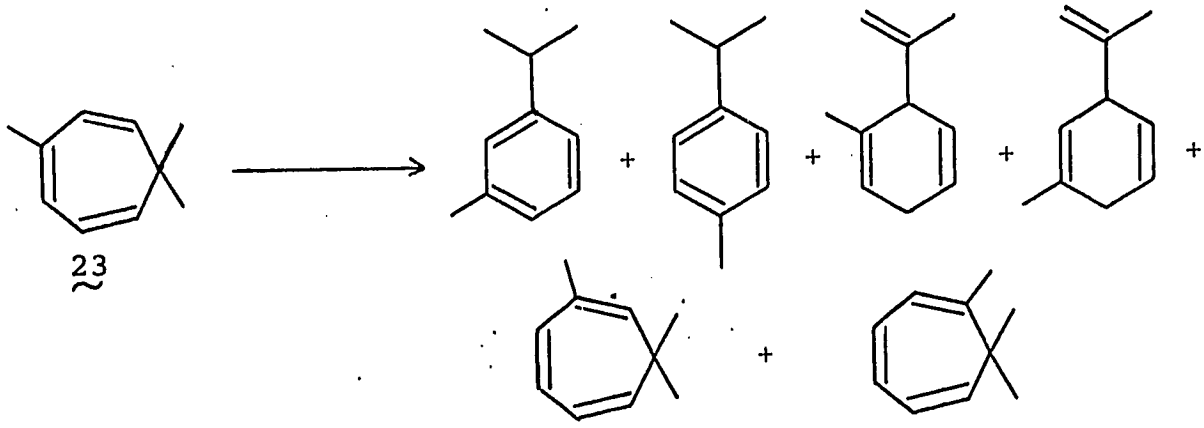
of this reaction, and their results lend support to the above mechanism. Dauben et al.[11] reported that 7-methylcycloheptatriene at 650° rearranges to ethylbenzene; they proposed a similar mechanism. 7-Methylcycloheptatriene has also been shown by Eggers[23] to give not only ethylbenzene, but all of the xylenes and some styrene. He has shown by a kinetic treatment of the data that equilibrium is established faster than ring contraction and, therefore, the products arise from the methylnorcaradiene isomers of the methylcycloheptatrienes in the equilibrated mixture. Buchi and Burgess[20] have reported that cycloheptatriene-1-carboxaldehyde rearranges to phenylacetaldehyde at 400°. These results seem to be in conflict with Conrow's[10] claim that at 400°, 7-ethylcycloheptatriene gives little, if any, propylbenzene.

More recently, Berson and Wilcox[52] have studied the thermal behavior of 3,7,7-trimethylcycloheptatriene and have observed ring contraction and skeletal rearrangements. Thus, when 3,7,7-trimethylcycloheptatriene, 23, was heated, several



23

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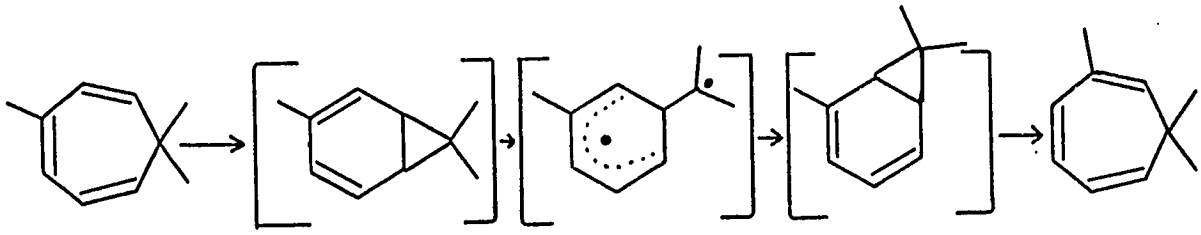
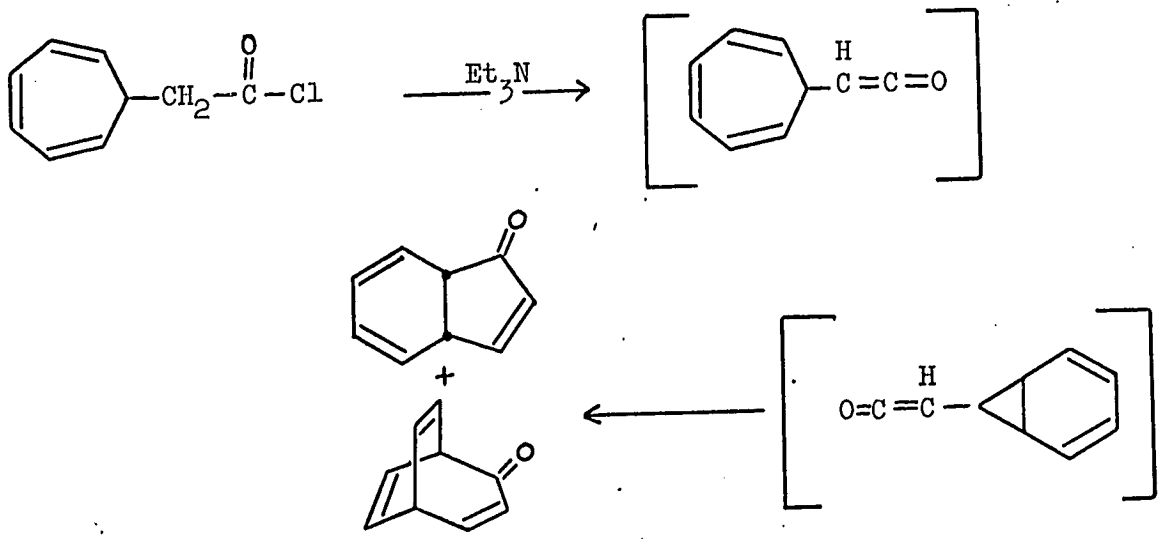
benzene and 1,4-cyclohexadiene derivatives were isolated, along with 1,7,7- and 2,7,7-trimethylcycloheptatriene. They propose that the ring contraction products occur by cleavage



of substituted norcaradienes and that the skeletal rearrangement products arise as indicated in the above scheme.

Molecular Rearrangements. Goldstein and Odell[53] reported that when cyclohepta-2,4,6-trienylacetyl chloride was treated with triethylamine, bicyclo [3.2.2] nona-2,6,8-triene-3-one was isolated along with 8,9-dihydroindenone. The follow-



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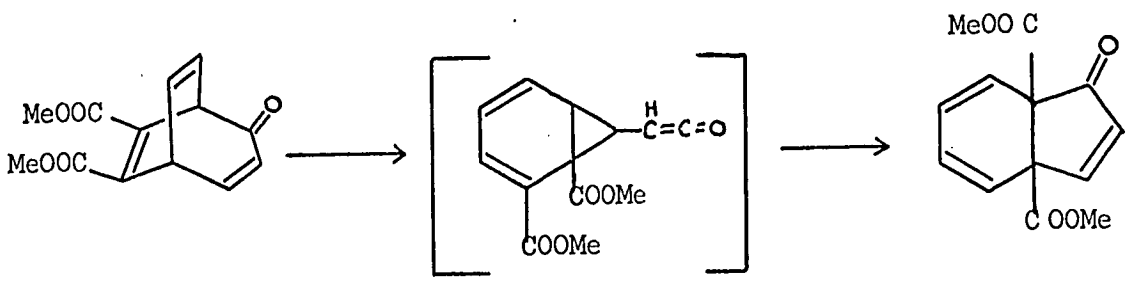
ing reaction sequence was proposed by these authors.

In a similar reaction, Schleyer and Daub[27] have shown that 7-vinylcycloheptatriene at 150° rearranges to give bicyclo[3.2.2]nona-2,6,8-triene as one of the products; they propose a vinylnorcaradiene as an intermediate.

Kinstle and Carpenter[54] have thermalized 6,7-dicarbomethoxybicyclo[3.2.2]nona-3,6,8-trien-2-one, 24, to the substituted cis-dihydroindenone, 26. They propose that the starting ketone rearranges to a norcaradiene ketene intermediate, 25, which undergoes a concerted ring closure to the cis-dihydroindenone. Alternatively, the ketene, 25, might undergo a vinylcyclopropane diradical ring opening with reclosure to the final product. The intermediacy of the ketene was supported by trapping experiments using methanol and cyclohexylamine in xylene to afford the methyl ester and the amide, respectively.



24 25 26

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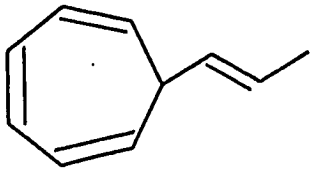
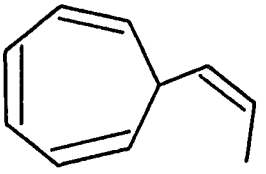
Results and Discussion

As a preliminary study in the high temperature thermolysis of 7-alkylsubstituted cycloheptatrienes, a mixture of cis- and trans-7-propenylcycloheptatrienes,* 27, was thermalized in a micropyrolysis apparatus. An nmr spectrum

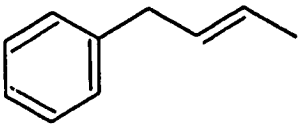


27a



27b

of the reaction products at 350-360° (uncor) showed a triplet superimposed on a doublet in the δ 2.0-2.5 region, indicating isomerization of the 7-isomer to the 3- and 1-isomers respectively. Also observed was some aromatic hydrogen absorption at δ 6.9-7.2. The products from this run were



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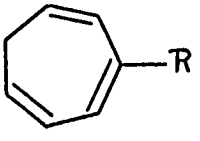

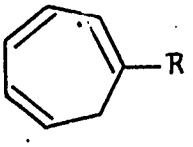

29

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* This was first prepared by T. Henry of this laboratory by the reaction of tropylium fluoborate with a mixture of cis- and trans-propenylmagnesium bromide in tetrahydrofuran.

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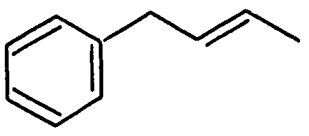
collected on column C0880-1 and were shown to be 1-phenyl-2-butene, 28, by comparison of nmr with an authentic sample and a mixture of cis- and trans- 3- and 1-propenylcycloheptatriene, 29.

The 7-isomer (250 µl) was then thermalized at 450-460° (uncor) and the products were separated by glpc. The products were shown to be 1-phenyl-2-butene, 28, and 2-methylindene, 30, by comparison of nmr's with authentic samples (ref. 105 for 2-methylindene) and, tentatively, the positional isomers of propenylcycloheptatriene. Two other unidentified products were also present.



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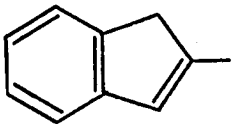

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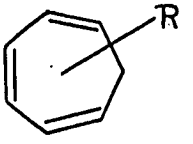

A large-scale preparation at 450-460° (uncor) made possible the isolation of one of the unidentified compounds which was tentatively assigned the structure of cis-1-methyl-8,9-dihydroindene, 6, on the basis of its nmr spectrum which exhibited signals at δ = 1.10 ppm (d, 3 H, methyl), 2.00-3.00 ppm (m, 2 H, allylic), 3.20-3.80 ppm (m, 1 H, doubly allylic), and 5.15-5.80 ppm (m, 6 H, vinyl).

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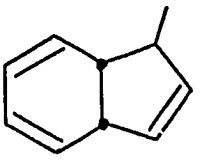
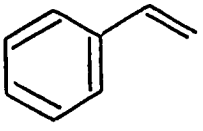
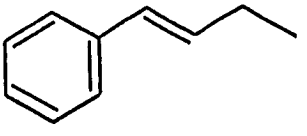


6

At 450-460° (uncor) 1-phenyl-2-butene was formed in the greatest percentage. To test whether this compound could be rearranging further, it was thermalized at 550° (uncor) and the products collected. They were shown to be styrene, 1-phenyl-1-butene, 31, and 3-methylindene, 32, by nmr compar-





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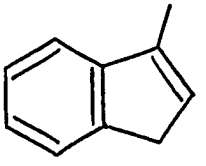

32

ison with authentic samples (ref.105 for 3-methyl indene). The 3-methylindene had a retention time identical to that of the second unidentified product of the 450-460° thermolysis. Also isolated from the rearrangement of 1-phenyl-2-butene was a compound assigned the structure of 1,2-dihydronaphthalene, 33, by comparison of its nmr spectrum with that of an authentic sample.

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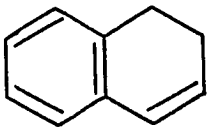
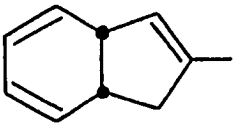


33

This preliminary study led us to investigate the thermolysis of 7-isopropenylcycloheptatriene in the range of 250-500°. The products of this thermal reorganization could easily be separated by chromatography on silica gel impregnated with silver nitrate and elution with mixtures of Skelly "F",ether, and methanol followed by glpc (see Experimental Section for further details). At 250° and 300° the 7-, 1-, and 3-isopropenylcycloheptatrienes were the only products isolated (see Table XVII). It is interesting to note in this regard, however, that in the equilibration at 259°, cis- 2-methyl-8,9-dihydroindene, 7, is formed in increasing amounts



7

with time. Thus 4.9%, 8.3%, and 17.6% were detectable after 15, 30, and 120 minutes respectively in solutions that ex-

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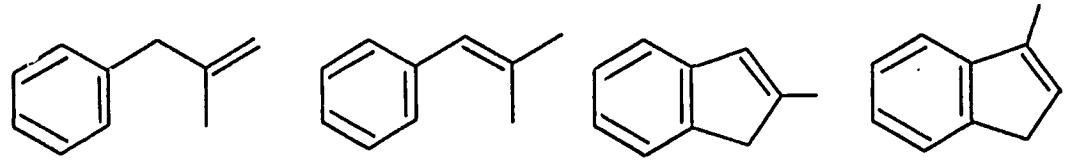
hibited <10% material loss. Therefore it seems possible that upon continued heating, cis-2-methyl-8,9-dihydroindene might be almost the only product detectable. However, equilibration is much faster than rearrangement and the reaction was, therefore, investigated at no times longer than 120 minutes at 259°.

In the range 350-450°, the 2-, 3-, and 1-isopropenyl isomers were still present; in addition several new products also appeared (see Table XVII). They were identified as methallylbenzene, 34, β,β-dimethylstyrene, 35, and the 2- and 3-methylindenes by the comparison of nmr and infrared



34 35 30 32

spectra with those of authentic samples. Also obtained was cis-2-methyl-8,9-dihydroindene on which a complete structure proof was performed. cis-2-Methyl-8,9-dihydroindene was hydrogenated over Pd-C catalyst and the product was compared by infrared analysis with the product obtained from the hydrogenation of 2-methylindene over Raney nickel W-2 cata-

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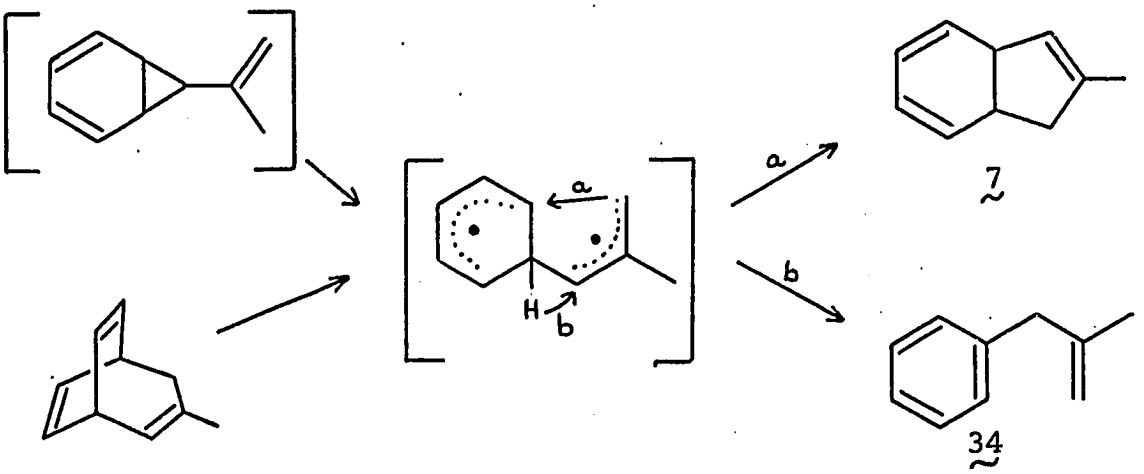
lyst.* The two products were shown to be identical (see Experimental Section for further details).

The formation of the methallylbenzene and cis-2-methyl-8,9-dihydroindene can easily be rationalized. The norcaradiene form of the 7-isomer may cleave to form a diradical



which can then recombine to form the dihydroindene (pathway a), or undergo a 1,2-hydrogen shift (pathway b) to form methallylbenzene.

The methylindenes could be formed from the dihydroindene, 7, by dehydrogenation.[55] Thermolysis of cis-2-methyl-8,9-dihydroindene does indeed give both 2- and 3-methylindenes, in a ratio of 2:1 as compared with a 1:2 ratio in thermolysis of 7-isopropenylcycloheptatriene. This behavior may be

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* This catalyst was graciously provided by I. Haddad of this department.

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Table XVII. Thermal Reorganization of 7-Isopropenylcycloheptatriene at Various Temperatures

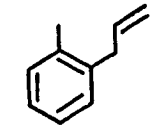
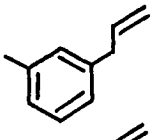
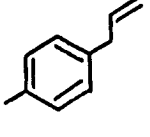
Compound	250°	300°	350°	400°	450°
34			1	4	12
7			11	34	42
1	17	4			
2	16	8			
3		16	18	15	trace
4	60	30	22	14	trace
5	7	42	48	29	trace
35				trace	6
30				2	6
32				3	12
					4
					
					
Others (includes indene)					17

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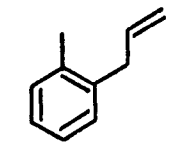
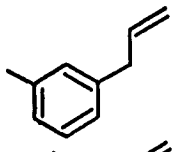
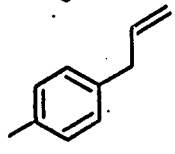
Table XVIII. Thermal Reorganization of cis-2-Methyldihydroindene at 450°

Compound	% Composition
34	3
7	60
35	3
30	4
32	2
	9
	
	
Others	19

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explained by the following reasoning. The 7-isomer in the norcaradiene form may cleave to a diradical as already shown or it may undergo a 1,5-hydrogen shift to form the 3-isomer which also may undergo isomerization. This process could continue until all of the positional isomers are formed. It has already been shown in this and other work[23] that equilibration is a faster process than rearrangement. Each positional isomer would have a norcaradiene form which could cleave to a diradical with closure or rearrangement to products. This scheme is outlined in Figure 2 and shows that the 1- and 2-isopropenylcycloheptatrienes could give rise to 3-methylindene. It must also be pointed out that cis-2-methyl-8,9-dihydroindene is fairly stable under the reaction conditions (see Table XIII). and that it has an alternative pathway for rearrangement (vide infra), whereas the proposed methyldihydroindene intermediate in Figure 2 should be unstable under the reaction conditions due to the double bond at the bridgehead position. The substituted toluenes were not observed, but may be present as some of the unidentified products.

The formation of β,β-dimethylstyrene is an interesting problem. Whereas the thermolysis of trans-1-phenyl-2-butene at 450° yields trans-1-phenyl-1-butene, the thermolysis of methallylbenzene up to 500° yields only unchanged starting

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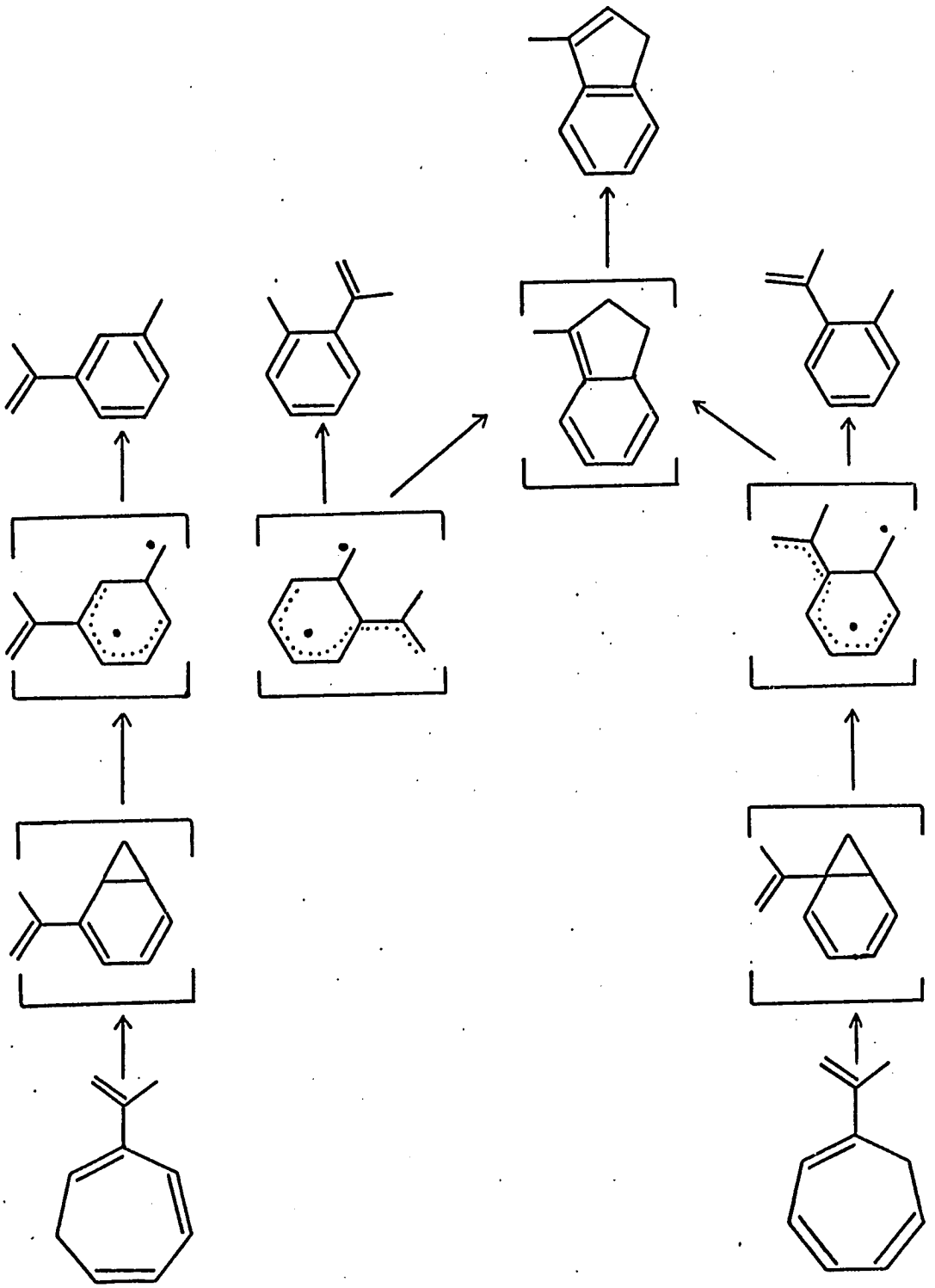

Figure 2

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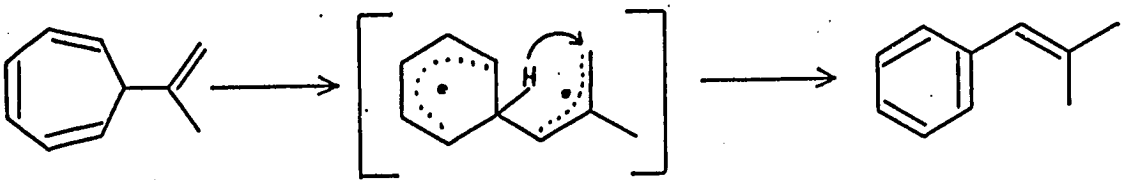
material. The pathway to β,β-dimethylstyrene may be as follows. Such a process would be of high energy and, ac-



cordingly, this isomer is first observed at 450°. This process is not possible with methallylbenzene since it would require temporary loss of aromaticity and may account for its stability under identical conditions. The intermediate radical in the isomerization of 1-phenyl-2-butene to 1-phenyl-1-butene is stabilized by the methyl substituent at C_1. This may account for the easier isomerization of 1-phenyl-2-butene since in the methallylbenzene case, the methyl group is at C_2 and provides no stabilization of the radical.

At 450° and above, several new products appear in amounts sufficient enough to permit identification. They were collected and identified by comparison of physical data and retention times with authentic samples. The products were shown to be the o-, m-, and p-allyltoluenes. Their formation can be seen with the aid of some other work in similar systems.

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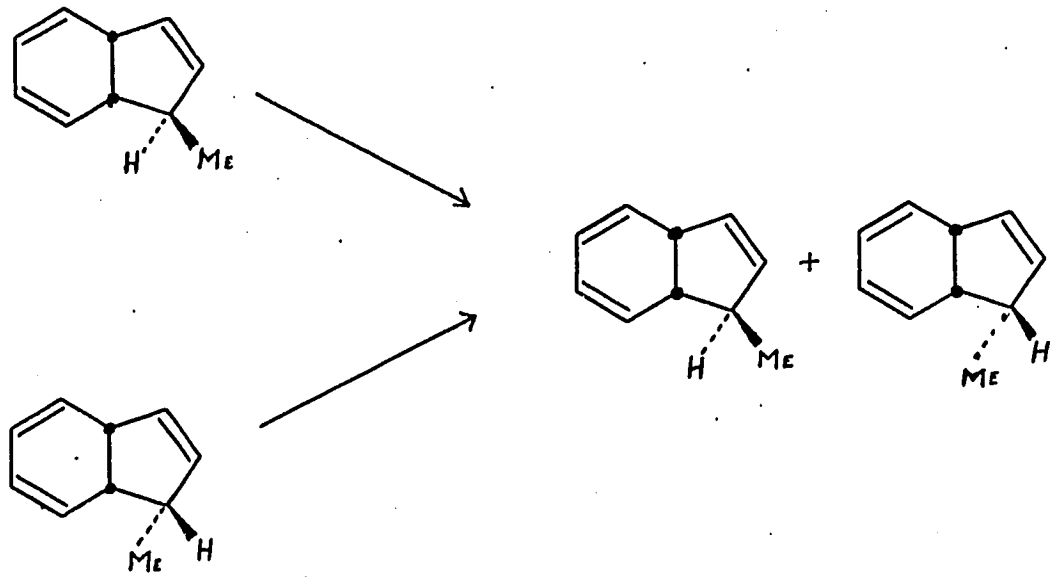
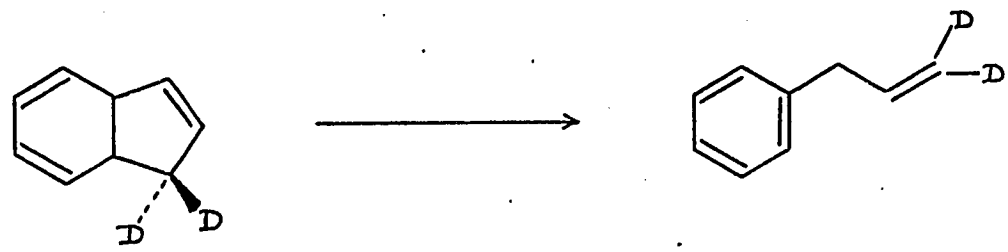
Grimme[56] has shown that when either pure exo or endo-1-methyl-8,9-dihydroindene is heated, a mixture of exo and endo products is formed. Grimme has also shown that cis-1,1-dideutero-



8,9-dihydroindene thermally rearranges to dideuteroallylbenzene (among many other products), as shown by nmr analysis, with deuterium only in the terminal vinyl position.



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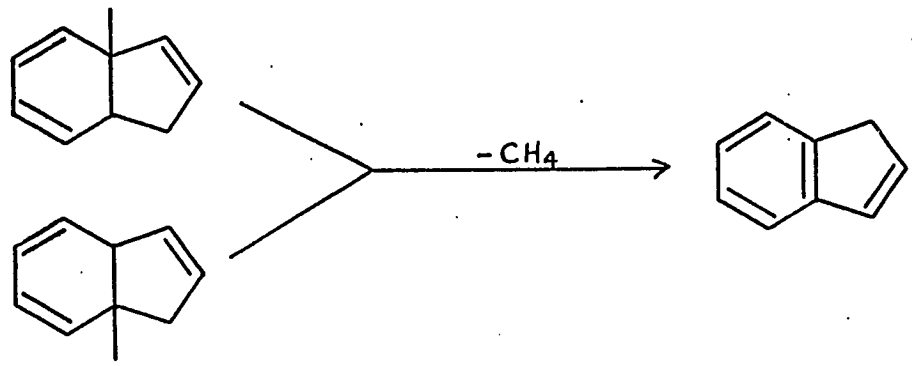
The first data suggest that the dihydroindene opens to a cis, cis, cis, cis-1,3,5,7-cyclononatetraene intermediate which then undergoes ring flipping that causes interconversion to the observed mixture of products upon closure. The other data show that perhaps cleavage of a dihydroindene occurs between C_1 and C_8 since no deuterium scrambling was observed in the final product by nmr analysis.

The scheme used to rationalize the formation of the allyltoluenes employs interconverting cyclononatetraene intermediates with closure to various dihydroindenes whose cleavage yields the final products (Figure 3).

The indene formed at the higher temperatures could also be accounted for by this scheme. The dihydroindenes formed with methyl groups at the bridgehead positions could lose



CH_4 to form indene. Pines and Kozlowski[57] have previously

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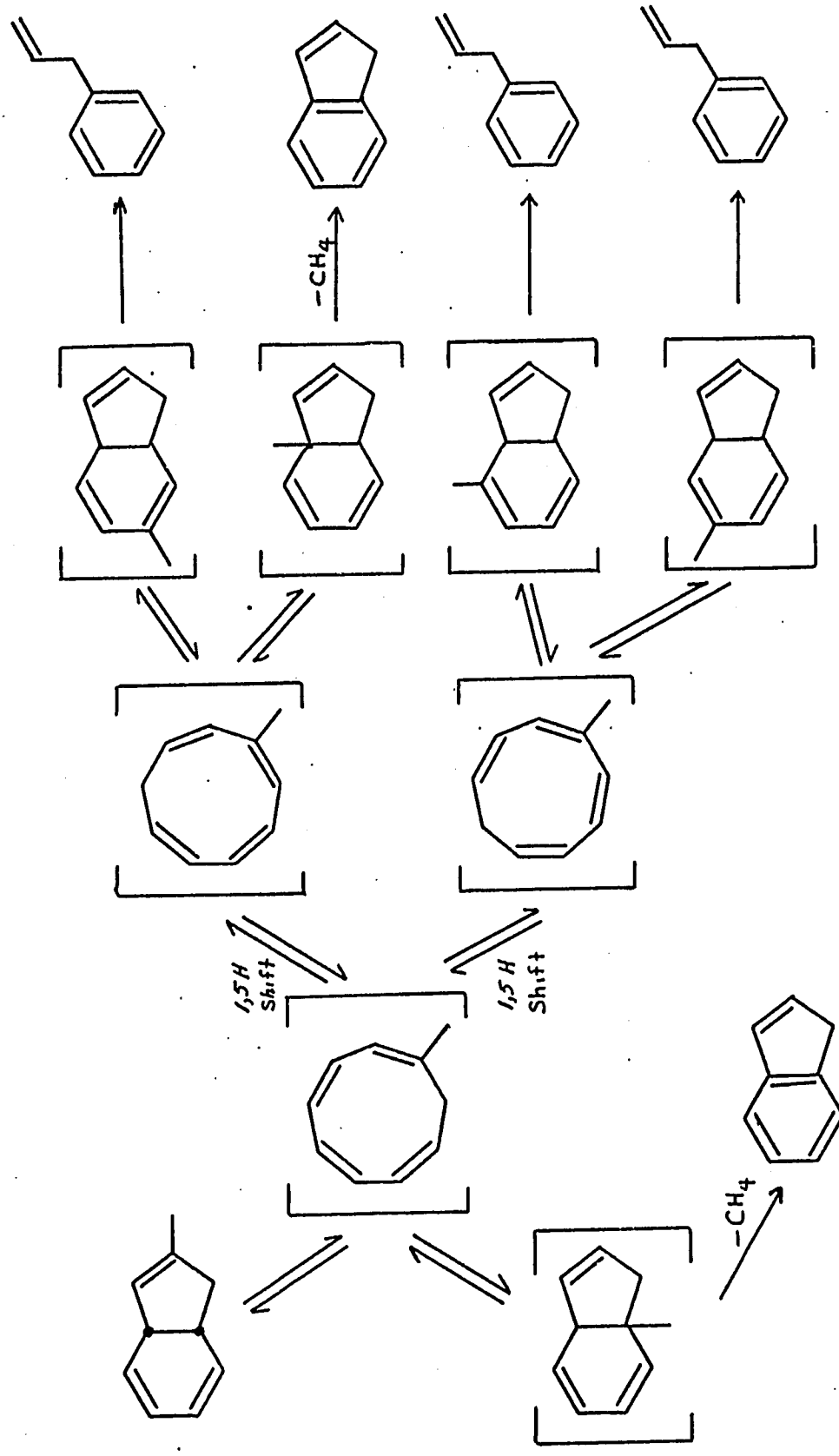

Figure 3

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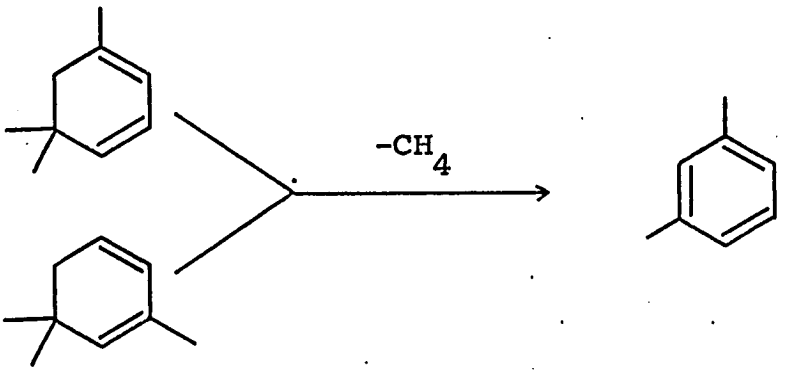
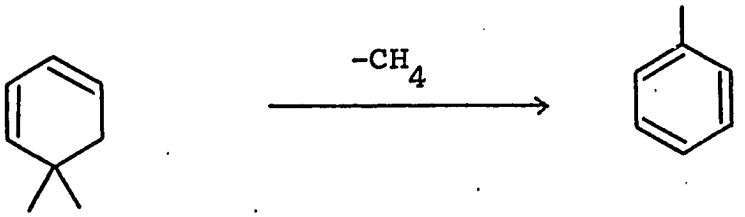
observed the loss of CH_4 in cyclohexadiene systems to form benzene derivatives.

Thus it can be seen that the thermolysis of 7-isopropenylcycloheptatriene at elevated temperatures leads to several interesting products. Their modes of formation can be correlated with data in the literature and explained on mechanistic grounds.





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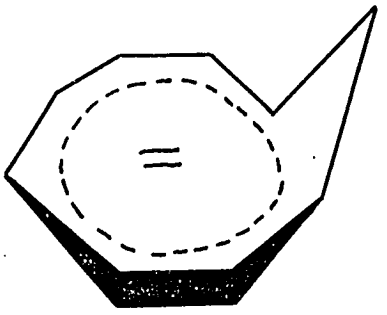
SECTION II

STABILIZATION OF ANIONS BY HOMOCONJUGATION

Introduction

Anions stabilized by homoconjugation have generated considerable interest in the recent literature. Winstein *et al.*[58] have reported that treatment of bicyclo[6.1.0]-nonatriene with excess potassium in tetrahydrofuran or 1,2-dimethoxyethane at -80° gives the monohomocyclooctatetraene dianion. They were able to obtain nmr data on this anion which could only be accounted for by structure 8.



8

The nmr spectrum of the bicyclo[3.2.1]octadienyl anion, 9, has also been observed[59] and shows extensive delocalization.

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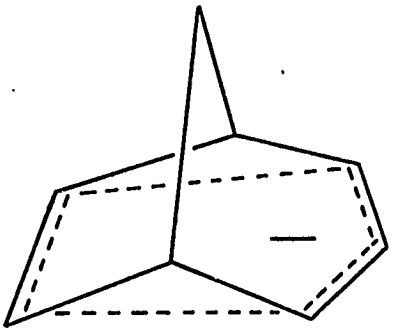

9

Figure 4 shows the chemical shifts (τ-scale) of the protons in the parent diene and the anion.[59a] HMO calculations[59a] predict that C_2 and C_4 will have the greatest charge

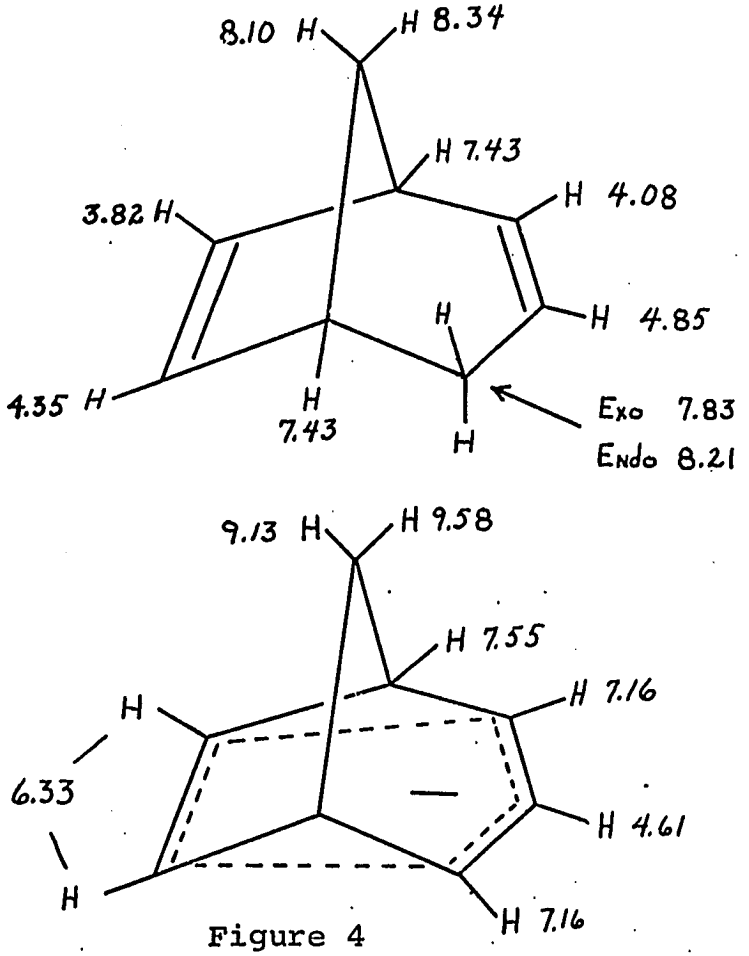

Figure 4

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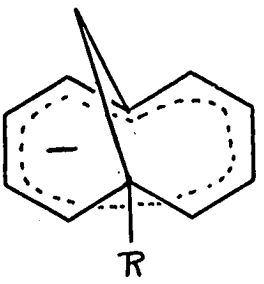
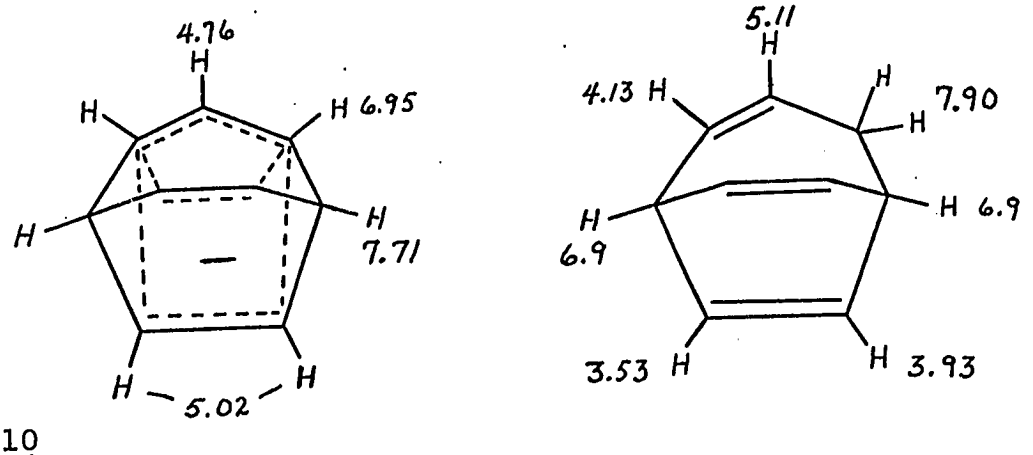
densities (0.43 of a negative charge each), C_6 and C_7 considerably smaller charge densities (0.06 each) and C_3 the least at 0.02 of a negative charge. The nmr results correspond very well with this prediction.

Böll[60] has observed a homoaromatic anion and Winstein



and Grutzner[61] have reported data on the bicyclo[3.2.2]nonatrienyl anion, 10. The nmr chemical shifts (τ -scale) of 10 are shown in Figure 5 along with those of the parent triene.



10

Figure 5

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It is completely consistent with a delocalized, homoaromatic structure with substantial negative charge of C_6, C_7, C_8 and C_9.

This anion is of interest with regard to Goldstein's designation[3] of it as a bicycloaromatic ion based on molecular orbital symmetry arguments. This term describes a bicyclic ion with three π-bridges (two even and one odd) which contains 4 n π electrons and which as a consequence possesses enhanced thermodynamic stability. Thus the interaction of the nonbonding molecular orbital (NBMO) of the odd-membered bridge with the highest occupied molecular orbital or lowest unoccupied molecular orbital, depending on which possesses the same symmetry as the NBMO, lowers the lower energy molecular orbital of the interacting pair while raising that of the higher one. When this is done for three bridges, significant contributions to stabilization are achieved. Goldstein[3] has stated that in order to be bicycloaromatic, the ions must be isoelectronic with a bishomoconjugatively destabilized reference. However, of more importance is the effect of the additional π-bridge which converts a bishomoaromatic ion to a bicycloaromatic ion.

By molecular orbital symmetry arguments the basis set of p orbitals in the bicyclo[3.2.2]nonatrienyl anion is "Mobius"[4] or "anti-Hückel"[62] (i.e. it has one inversion of

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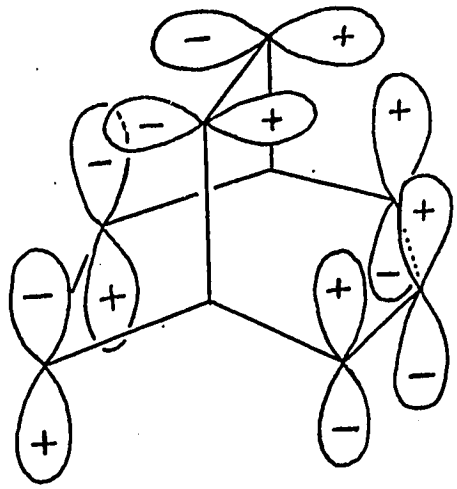
phase*) and, therefore, is aromatic when it contains 4n π electrons.



Homoconjugative interactions have been demonstrated by techniques other than nmr spectroscopy. Brown and Occolowitz[63] have performed the base-catalyzed deuterium exchange of bicyclo[3.2.1]octa-2,6-diene, 11, and bicyclo[3.2.1]oct-2-ene, 12, and have demonstrated a large stabilizing effect in 11 due to homoconjugative interactions. Their results showed that 11 exchanged 3×10^{-4} times faster than the monoene. Since they found that cyclohexene exchanges at

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* This is more easily visualized if one considers just the orbitals in one half of the molecule.

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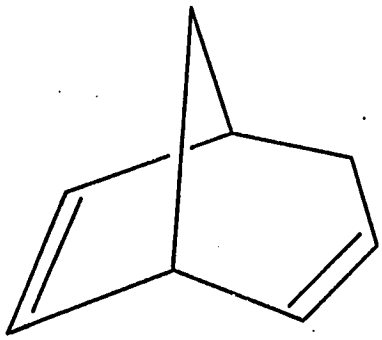

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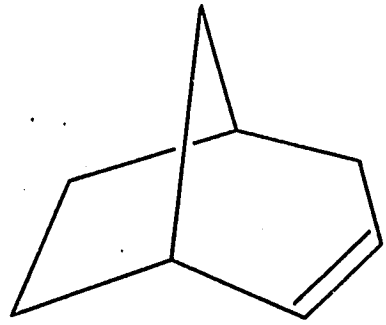

12

about the same rate as the monoene, it seems that the diene is extremely reactive, with the remote double bond aiding formation of a carbanionic center.

Results and Discussion

The energetics of delocalization in the 3-methylbicyclo-[3.2.2]nona-2,6,8-triene were studied since compounds of this structure are of theoretical interest with regard to homoconjugation or bicycloaromaticity[3] in the anion. This material could be obtained as one of the products from the thermolysis at ca. 160° of 7-isopropenylcycloheptatriene.

Due to previous successes in generating the anions of homoconjugated systems and observing them by nmr,[58-61] 3-methylbicyclo [3.2.2] nona-2,6,8-triene was treated with potassium or cesium amide in liquid ammonia and was observed by nmr spectroscopy at 37°. The only spectrum obtained, however, was that of the starting material. An anion is probably

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formed under these conditions, though, since a 1:9 mixture of starting triene and 3-methyl-4-propylbicyclo [3.2.2] nona-2,6,8-triene was obtained when the methylbicyclononatriene was treated with potassium amide and 1-chloropropane in liquid ammonia at ca. -33°. The major product was identified primarily on the basis of a molecular ion at m/e 174.133 and its nmr spectrum which is similar to the starting triene below τ 8.0 and, in addition, exhibits a multiplet at τ 8.0-8.4 (1 H, C_4 proton), a sharp multiplet centered at 8.58 (7 H, methylene and allylic methyl), and a distorted triplet at 9.04 (3 H, methyl).

When a solution of 3-methylbicyclo [3.2.2] nona-2,6,8,-triene and potassium amide in liquid ammonia was warmed to 50° in an attempt to generate a larger concentration of anion, the nmr spectrum changed completely. After 3 hours at 50°, no starting material could be observed, but the nmr spectrum suggested that some rearrangement had occurred. A large-scale reaction yielded a single isomer (molecular ion at m/e 132.093). This isomer was identified as the fluctional compound, 3-methyl-tricyclo [3.3.1.$0^{2,8}$]nona-3,6-diene, 13, primarily on the basis of its ambient temperature nmr spectrum which is quite similar to that reported[64] for barbaralane. The exceptions were that the downfield triplet (τ 5.52, vinyl) has a relative area of one and there is an additional peak (singlet, 3 H, methyl)

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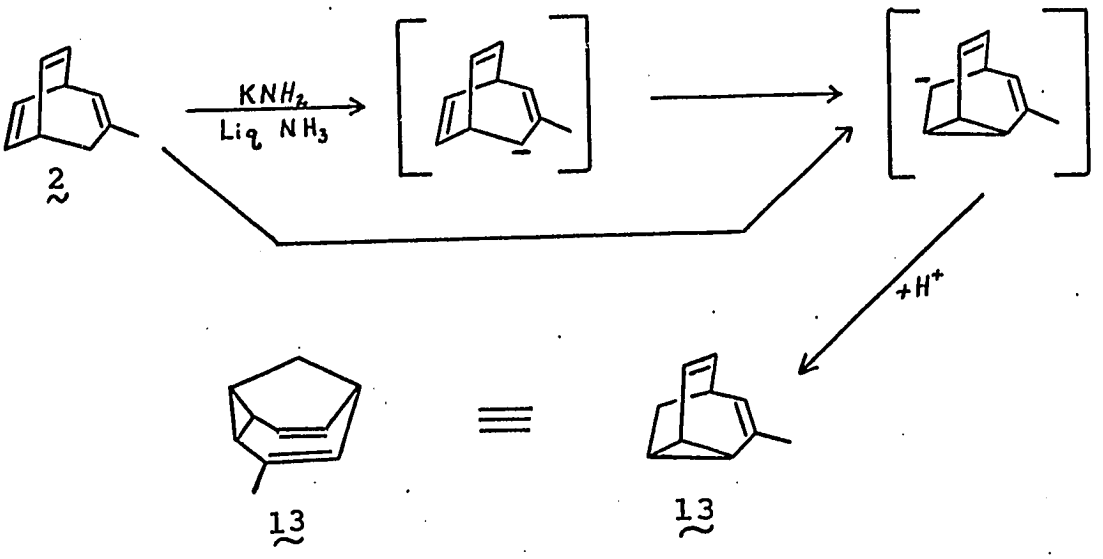

Figure 6

at δ 2.28. The formation of the tricyclic isomer can easily be rationalized as shown in Figure 6.

Although the anion could not be observed spectroscopically, the evidence for its existence is very convincing. Therefore, to obtain information concerning the question of stability of the anion relative to an appropriate bishomoaromatic model, base-catalyzed deuterium-exchange experiments were performed. The bishomoaromatic model selected for comparison was 3-methylbicyclo[3.2.2]nona-2,6-diene, which was conveniently synthesized by the method of Hoffman *et al.*[65] The synthesis involves the Diels-Alder reaction of 1,3-cyclohexadiene with the methallyl carbonium ion generated

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in liquid sulfur dioxide with silver trichloroacetate and methallyl iodide.

Solutions of 0.1 M triene and diene were allowed to exchange in 1.00-1.03 N potassium t-butoxide in dimethyl sulfoxide-d_6 at 25°. Aliquots were taken at varying time intervals and the diene or triene recovered by glpc. The deuterium content was analyzed by low-voltage mass spectrometry and appropriate corrections were made for the natural abundance of isotopes and for an M-1 peak in the mass spectrum of the triene.[66] Duplicate runs were made on each compound and several molecular ion regions (usually five to ten) were traced for each aliquot analyzed. Also the undeuterated diene or triene was analyzed at the same time as a reference for the calculation of the deuterium content. This was necessary to provide relative uniformity of the electron voltage used in each analysis.

The rate of exchange of 3-methylbicyclo[3.2.1]octa-2,6-diene, 17, was also obtained for comparison purposes. This compound was synthesized via two different methods. Hoffmann et al.[65] have reported a 40% yield when cyclopentadiene is treated with the methallyl carbonium ion as described previously. However, in this laboratory these results could not be reproduced. Rather, the yield was ca.2-3% and two interesting side products were encountered. 3-Methyltricyclo[3.2.1.$0^{2,7}$]-

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oct-2-ene, 14, was identified on the basis of its nmr spectrum, which is quite similar to those reported[67] for tricyclo[3.2.1.$0^{2,7}$]oct-2-ene, with the exceptions that there is a signal for only one vinyl proton at τ 4.50 (broad doublet, J = 7 Hz) instead of a triplet at 4.26 and there is an extra signal at 8.22 (d, 3 H, methyl, J = 2 Hz). The other product was identified on the basis of its nmr and ir spectra as 3-methyl-4-trichloroacetoxybicyclo[3.2.1]oct-2-ene, 15. Elemental analysis for C, H, and Cl was also satisfactory for this structure. In addition, the trichloroacetate can be converted to 3-methyltricyclo[3.2.1.$0^{2,7}$]oct-2-ene by heating with quinoline at 195°; however, this conversion does not occur in concentrated ammonium hydroxide, which is used in the workup of the reaction, even at 25° for 24 hours. The origin of these products is unclear. Whether the acetoxy group is exo or endo in 15 could not be readily determined, but Jeffords[68] has shown that the treatment of 1-methyl-exo-3,4-dibromobicyclo[3.2.1]oct-2-ene and exo-3,4-dibromobicyclo-[3.2.1]oct-2-ene with aqueous silver nitrate yield only exo bromoalcohols. The addition of trichloroacetate ion 16 is therefore expected to occur from the exo direction. Although great care was taken to keep the reaction mixture dry, it is possible that a small amount of moisture may have initiated

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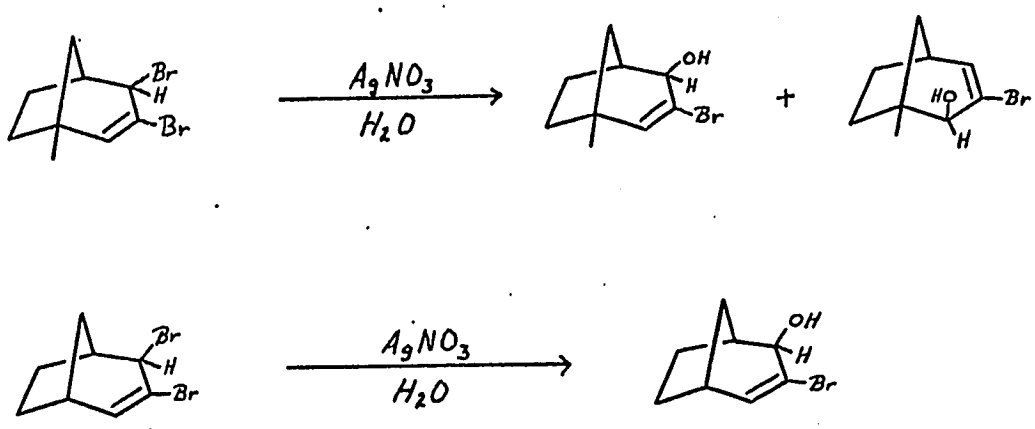
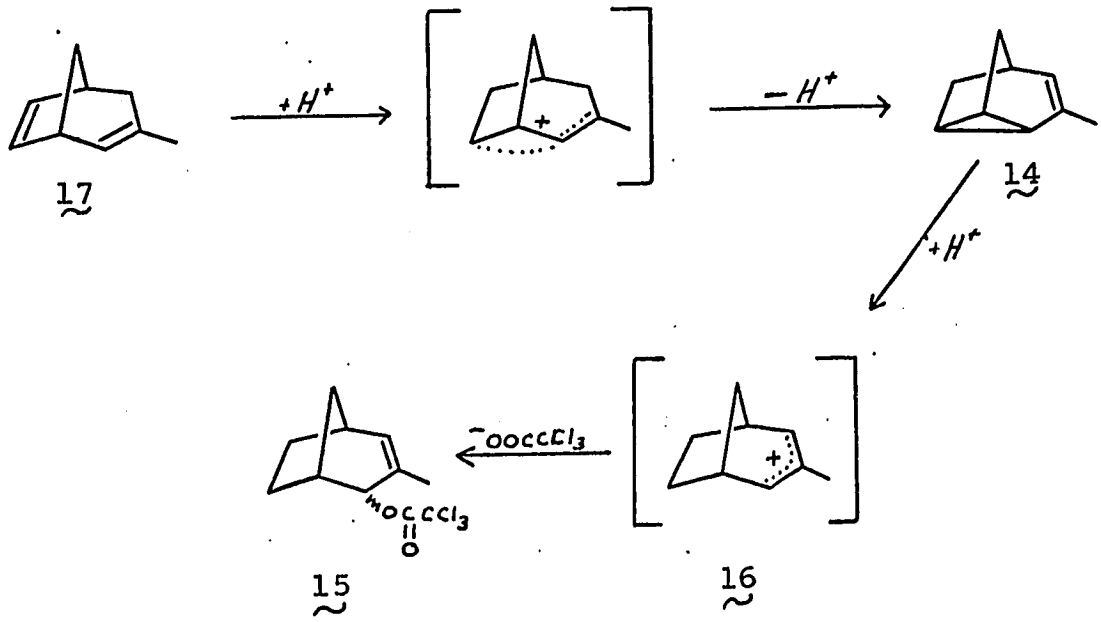


acid-catalyzed rearrangements, as indicated in the following scheme.



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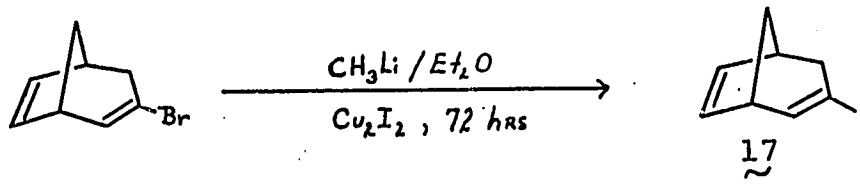
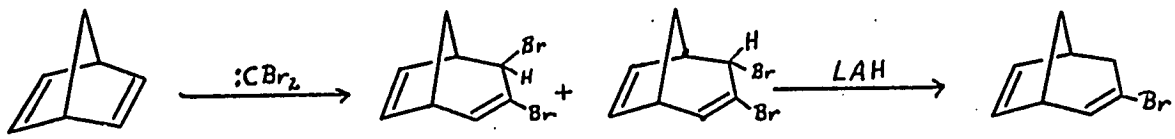
The diene can be synthesized conveniently by the Corey procedure[69] starting with the readily available 3-bromobicyclo[3.2.1]octa-2,6-diene.[70] This bromide is synthesized



17

by the addition of dibromocarbene to norbornadiene followed by treatment of the resulting mixture of dibromides with lithium aluminum hydride.



The rates of deuterium exchange of 2, 17, and 18 are listed in Table XIX, along with another rate available in the literature. The correlation coefficients for the kinetic runs of 2, 18, and 17 were 0.995, 0.9996, and 0.9996 respectively as calculated by a computerized least squares fit of

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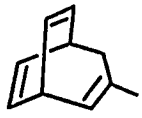
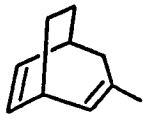
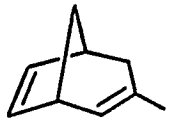
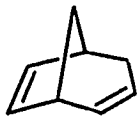
the raw data.

Table XIX. Rates of Deuterium Exchange in Selected Hydrocarbons

Compound		Rate (1 $mole^{-1} sec^{-1}$)	Temperature °C
	2	$(1.05 \pm 0.2) \times 10^{-3}$	25
	18	$(1.40 \pm 0.1) \times 10^{-6}$	25
	17	$(1.98 \pm 0.06) \times 10^{-5}$	25
	11	$(5.0 \pm 0.2) \times 10^{-4}$ [a]	25

[a] Calculated from raw data available in ref. 63.

Long-term exchanges were performed on 2, 17, and 18 and the position of deuteration was determined by nmr spectroscopy. Each deuterated sample was integrated at least eleven times and the relative peak areas with standard deviations were determined with reference to several peaks whose intensity are not expected to change under the conditions of deuterium exchange. These areas were then compared to those of undeuterated samples and the number of deuteriums calculated

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as the difference. The number of deuteriums from nmr analysis was then compared with the amount of deuterium determined by mass spectrometry. In all cases studied, the results agreed to within 0.2 deuterium atom per molecule. Nmr analysis showed that exchange occurred only at C_2 and C_4 with no exchange at the methyl group. By this method of analysis not more than 0.05 of a deuterium atom per hydrogen atom could have been incorporated at other positions. Also no rearrangement products (i.e. tricyclic isomers) were observed so rearrangements occurred to less than 3%, if at all, in the compounds studied. This analysis, it should be pointed out, is less rigid in the case of 18 since after one week 18 had exchanged only to the extent of 0.6 of a deuterium; however, nmr and mass spectrometry analysis agreed to well within the limits of error of the analytical method.

The rate of deuterium exchange of 3-methylbicyclo [3.2.2] -nona-2,6,8-triene is 750 times greater than that of the corresponding diene. This rate increase may be attributed to several factors, including the slight differences in the geometries of the two compounds and differences in the field and orbital electronegativity inductive effects for an ethano vs. an etheno bridge.

The differences in geometries of the two systems have little, if any, effect on the rates. The rate of exchange

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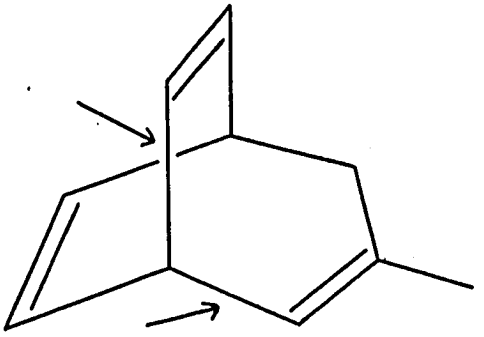
of 3-methylbicyclo [3.2.1] octa-2,6-diene is only 14 times greater than that of bicyclo [3.2.2] nonadiene. Here the methylene group forces the double bonds into closer proximity and, therefore, overlap is better for delocalizing an anion. Yet the increase in rate is small so that the effect of geometry is probably much smaller between 2 and 18.

Orbital electronegativity inductive effects (i.e. those effects initiated by the polarity of the bond(s) linking the substituent to the reaction site) also contribute very little to the enhanced rate of exchange. Inductive effects tend to fall off quite rapidly over each intervening σ bond.



In this case there are two intervening bonds and if one uses the fall-off factor of 2.7,[71] the inductive effect is $1/(2.7)^2$ or 14% of the original.[72] However, several authors[72,73] consider that 2.7 may be too small, and Dewar and Grisdale[73a] state that the σ inductive effect of a substituent is unimportant at atoms separated from it by more than one bond.

The field effect might be significant but not the major factor. This effect is due to the electric dipole field of

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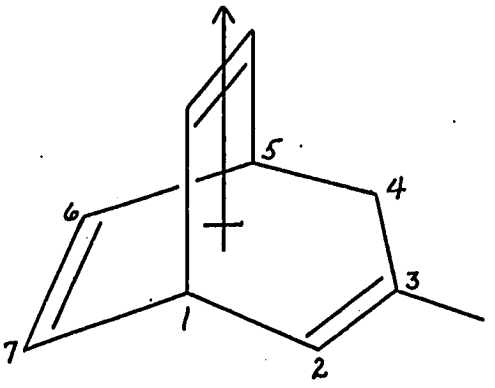
the substituent influencing the reaction center. The extra double bond in the triene has a group dipole moment perpendicular to a plane through C_2, C_3, C_4, C_6 and C_7 with a prob-



able magnitude of .2-.3 Debye. This is estimated from the values of dipole moments of cyclic monoenes that have been

Table XX. Dipole Moments of Selected Cyclic Monoenes

Compound	Dipole Moment (Debye)
	0.445[74]
	0.132[75]
	0.22[76]
	0.331[77]

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reported. (Table XX).

Just how much stabilization the components of this dipole will have on the anion is very hard to ascertain at this time. However, since the reaction was carried out in solution, the dipole and the incipient anion will be solvated and their electric charge partially dispersed by a shell of solvent molecules. This polarization of surrounding solvent molecules will reduce the field produced by the substituent at the reaction center.[78]

The total contribution of inductive and field effects can be estimated from the data in the literature. Thus Schröder and Kumps[79] have reported that norbornadiene undergoes marked hydrogen exchange at 100° compared with only a small amount of exchange for norbornene at 139°. Streitwieser and Caldwell[80] have shown that norbornadiene exchanges vinyl hydrogens ca. 20 times faster than norbornene. Breslow et al.[81] in a study of 7-norbornenyl anion, have shown that 3-cyanocyclopentene exchanges ca. 10 times faster than cyanocyclopentane in 1 M potassium methoxide in methanol-OD at 90°. Thus it seems that field/inductive effects probably have some role (ca. 10-20 fold increase in rate) but are not the major factor contributing to the enhanced rate of exchange (ca. 750 times) of 3-methylbicyclo [3.2.2] nona-2,6,8-triene relative to 3-methylbicyclo [3.2.2] nona-2,6,diene. Since the

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effect of geometry is also small, it seems reasonable to attribute an important role to bicycloaromatic delocalization -- in other words, there seems to be significant delocalization of the negative charge by the third π-bridge in the anion, thus contributing to its thermodynamic stability as manifested in its enhanced rate of exchange.

The "inductive effect" of a methyl group could also be studied by the rates of exchange of 3-methylbicyclo[3.2.1]-octa-2,6-diene and bicyclo[3.2.1]octa-2,6-diene. Thus it has been shown that the latter compound exchanges ca. 10-20 times faster than the compound with a methyl group in the 3-position. This difference would normally be ascribed to the destabilizing or positive inductive effect of the methyl group.[5]

This inductive effect could have both σ and π components. It is interesting, therefore, to note that both nmr evidence[59] and molecular orbital calculations[59a] indicate that the amount of negative charge on C_3 in the anion is very small (vide infra). Thus destabilization due to any σ inductive effect should be very small, and since there is a nodal plane bisecting C_3 in the highest occupied and lowest unoccupied molecular orbitals of the anion, there will be little interaction with the methyl group orbitals. Thus it is not clear that an inductive effect is actually responsible for the

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decrease in the rate of exchange that is observed.

There are both theoretical calculations[82] and experimental results[83] which suggest that alkyl groups actually serve to delocalize negative charge in an electron-rich molecule. Thus in the gas phase for the following reaction Brauman and Blair[83] found that the orders of relative acid-

$$R - OH + R' - O^- \rightleftharpoons R - O^- + R'OH$$

ities were 1) neopentyl > t-butyl > isopropyl > ethyl > methyl > water and 2) t-butyl ≈ n-pentyl ≈ n-butyl > n-propyl > ethyl. These orders are consistent with a model in which the alkyl groups, being polarized, stabilize the charge by an induced dipole.

If this is so, then how can one explain the slower rate of exchange of 3-methylbicyclo[3.2.1]octa-2,6-diene relative to bicyclo[3.2.1]octa-2,6-diene? It has been suggested that the destabilizing effect of alkyl groups is due to steric hindrance to solvation.[84]

If the partial negative charges are distributed in the anion as below,[59a] a methyl group should have a greater destabilizing effect when located at C_6 or C_7 if destabilization results from σ and/or π electron polarization. However, since > 85% of the charge is calculated[59a] to be on the $C_2C_3C_4$ bridge, solvation of the anion, especially in a solvent

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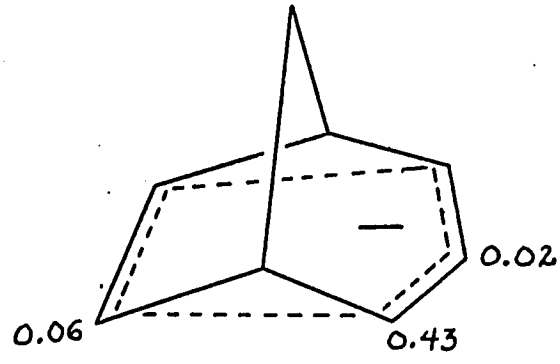
such as dimethyl sulfoxide, should be of greatest importance in this region; thus a C_3 methyl group should show the greater



effect if steric hindrance to solvation is involved.

It can be seen that these two explanations predict different relative rates of exchange for bicyclo[3.2.1]octa-2,6-diene substituted at C_3 and C_6. As yet no data are available on the rate of exchange of the latter compound.

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SECTION III

REDUCTION OF HOMOCONJUGATED SYSTEMS UNDER BIRCH REDUCTION CONDITIONS

Introduction

Whereas the reduction of aromatic systems by alkali metals and alcohol in liquid ammonia has been extensively investigated, that of nonconjugated double bonds has not. However, research in this area has resulted in several reactivity relationships. Krapcho and Nadel[85] interpreted the relative rates of reduction of a series of cycloalkenes which decreased in the order norbornene > cyclopentene > cycloheptene > cyclohexene as reflecting the decreasing amount of strain in the corresponding double bonds. Also, in a series of acyclic olefins, the reduction order parallels, to some extent, the decreasing order of the heats of hydrogenation (i.e. monosubstituted > disubstituted > trisubstituted > tetrasubstituted).

Gardner and co-workers[86] have reported that certain nonconjugated double bonds are reduced by lithium or sodium in liquid ammonia without added alcohol. They suggested that this reactivity could be correlated with the energy of the lowest unoccupied molecular orbital (LUMO), as qualita-

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tively shown by the longer wavelength ultraviolet light absorption. Under these conditions norbornadiene is readily reduced but norbornene is not and the authors report that this difference in ease of reduction is not due to a difference in strain energies since a substituted cyclobutene (i.e. bicyclo [4.2.0] oct-7-ene) is inert under the reaction conditions.

The mechanism for the reduction of double bonds is probably analogous to that proposed for the reduction of benzene and its derivatives. This involves protonation of an initially formed solvated radical anion in the rate-determining step.[84a,87] If this is the rate-determining step, then the rate of reduction can be seen to be dependent on a number of factors including a) delocalization of the π-electrons and b) release of strain (probably angle strain) in the activated complex (both relative to the ground state), and c) steric hindrance to solvation of the activated complex.[85] The first factor can in certain cases by correlated with the energy of the LUMO whereas the second will often parallel the heats of hydrogenation.

These two factors will sometimes operate in different directions and either may dominate in any given reaction. For example, the LUMO of benzene is much lower than that of cycloheptatriene, but the latter is reduced instantaneously

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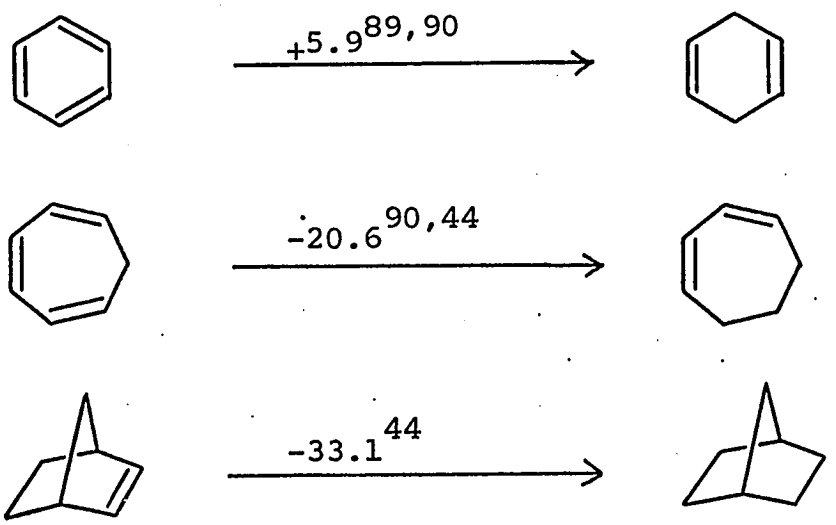
at -33° by lithium in liquid ammonia, whereas benzene is only reduced slowly at elevated temperatures (≥ 60°) under these conditions.[88] This is, of course, primarily due to the loss of the resonance energy of benzene in the activated complex as is reflected in the relative heats of hydrogenation.



However, norbornene, which is even more strained, is apparently not reduced as readily as benzene; this is due to the small degree of π-electron delocalization in its activated complex and, in this case, a correlation can be made with the LUMO energies.

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Results and Discussion

To further investigate the relative importance of strain and electron delocalization on the alkali metal-ammonia-alcohol reduction of nonconjugated double bonds, several bicyclic dienes and trienes have been chosen for study. These are intermediate between fully conjugated and nonconjugated systems and promise to provide additional information on the relative role of delocalization *vs.* strain in alkali metal-ammonia-alcohol reductions.

The compounds studied have been previously described (*vide infra*) and are listed in Table XXI. These compounds were all completely resistant to reduction by 0.5 M lithium in liquid ammonia at *ca.* -33° for 75 minutes. The reaction mixtures were quenched by the addition of excess acetone.[91] However, in the presence of 0.3 M absolute ethanol, both 2 and 17 are almost completely reduced in the same period, whereas 18 is largely unchanged. These data are given in Table XXI.

The single products of the reduction of 2 and 17 were identified as 18 and 3-methylbicyclo[3.2.1]oct-2-ene (20), respectively, on the basis of comparison of their infrared spectra[92,93] (and, in the case of 20, the nmr spectrum[93]) with those of authentic samples.

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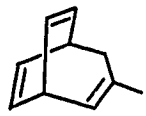
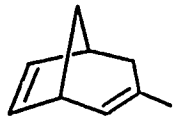
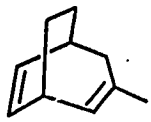
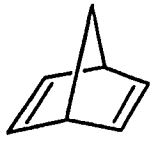
Table XXI. Reduction of Selected Bicyclic Systems

Compound		% Reduction (75 min/NoEtOH)	% Reduction (5 min/EtOH)
	2	0.0	68%[c]
	17	0.0	54%
	18	0.0	0.0[b]
	19	98[a]	

[a] This is identical to the results of Gardner et al.[86]

[b] Reduction to the extent of 7.5% was found after 75 minutes.

[c] In 15 minutes 2 and 17 were reduced to the extent of 100 and 95% respectively.

Since the ease of reduction of nonconjugated double bonds has been correlated with the energy of the lowest unoccupied molecular orbital (LUMO) as estimated by the longer wavelength ultraviolet absorption,[86] these data for 2, 17, 18 and norbornadiene (19) were obtained and are given in Table XXII.

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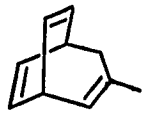
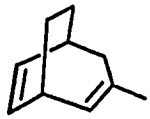
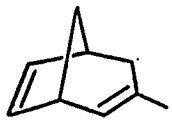
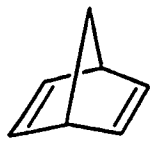
Table XXII. Ultraviolet Absorption of Bicyclic Systems

Compound		ε(235 nm)	ε(250 nm)	ε(265 nm)
	2	829	98	58
	18	144	5	0
	17	733	24	5-7.7
	19	157[a]	63	9
	11	134[67a]	<10	

[a] Similar to spectrum reported by Winstein et al.[94]

It is evident from Table XXII that the degree of interaction of p orbitals on adjacent bridges in these three compounds and the perturbation of the corresponding energy levels from those of noninteracting double bonds is reflected in the magnitude (ε) and wavelength of the end absorption. Such behavior is well supported by theory and has been discussed in detail by Murrell.[95] Models clearly indicate that replacement of an ethano bridge (in 18) with a methano bridge (in 17), forces the double bonds closer together. Also,

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replacement with an etheno bridge (in 2) allows simultaneous interaction of all three double bonds. This latter effect is similar to, but less than that observed in barrelene.

At first glance the reactivity order for these compounds appears to correlate with the energy of absorption of ultraviolet light. However, if one takes into account the statistical factor of two which favors protonation (assumed to be the rate-determining step) of 2 relative to 17, it can be seen that the "intrinsic" reactivity of 17 is actually slightly greater. This is contrary to what one would expect since the activated complex for the protonation of 2 should be stabilized relative to that of 17 not only by π-delocalization but also by the field effect of the extra double bond. However, any inductive effect of the double bond is probably very small (see Section II).

Another method of observing the energy of the LUMO is by looking at the charge transfer values of the tetracyanoethylene complexes of these bicyclic systems as given in Table XXIII.

Dewar and Lepley[96] have shown that a linear relationship exists for the energy of the charge transfer bond vs. the energy of the highest occupied molecular orbital (HOMO). Bhattacharya and Basu[97] have obtained such a linear relationship with the complexes of iodine and aromatic hydrocarbons.

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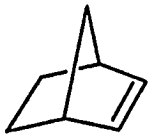
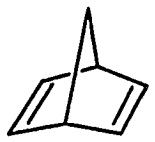
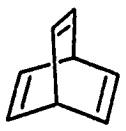
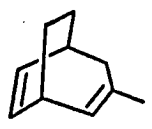
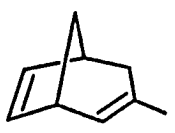
Table XXIII. Absorption of Charge Transfer Complexes of Tetracyanoethylene with Selected Bicyclic Systems

Compound	$\lambda_{max}(CH_2Cl_2)$
	424 nm[98]
	472 nm[98]
	549 nm[98]
	490 nm
	460 nm
	484 nm

Grunewald[98] has also found this linear relationship to hold for tetracyanoethylene complexes of norbornene, norbornadiene, and barrelene. If this linear relationship holds, barrelene is predicted to have an ionization potential of 8.2 ev. This ionization potential has recently been determined by Dewar et al.[99] to be 8.24 ev. Thus the linear

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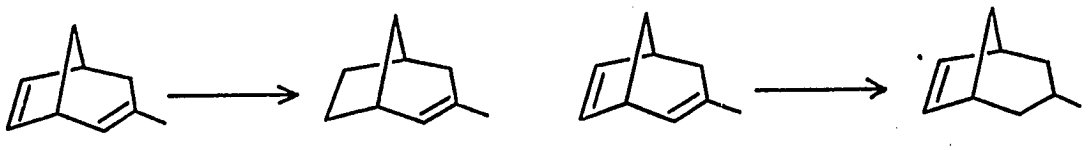
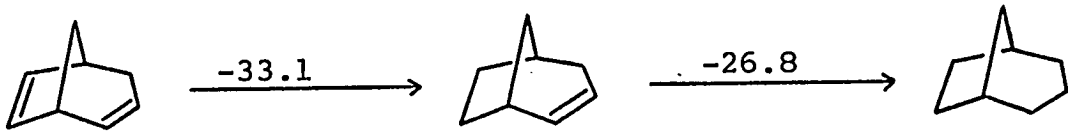
relationship, at least for this case, seems valid.

Thus, if the LUMO is assumed to be the mirror image of the HOMO, then the LUMO's of 2 and 17 are lower than that of norbornadiene. This is consistent with the ultraviolet spectra of these compounds as shown in Table XXII.

However, although the LUMO's of 2 and 17 are lower than that of norbornadiene, the latter is reduced with lithium in liquid ammonia with no added proton source, whereas 2 and 17 show no reduction under these conditions. Thus the greater reactivity of 17 vs. 2 must lie with another factor, and consideration of the "strain" energies of the double bonds being reduced as approximated by the corresponding heats of hydrogenation seems to lead to a plausible explanation. The double bond which is reduced in 17 is undoubtedly



17 20 17 21



11 12 22

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the one with the larger heat of hydrogenation (i.e. the one in the five-membered ring), as shown by the data of Turner and Mallon.[48] The values of ΔH_h 17→20 should be essentially equal to ΔH_h 11→12 while ΔH_h 17→21 is probably less than ΔH_h 12→22 since 17→21 involves hydrogenation of a trisubstituted double bond as compared with the reduction of a disubstituted one in the latter case.

The heats of hydrogenation of the double bonds in 2 and 18 which are reduced under the reaction conditions are not as easily estimated from the published data. However, the fact that the double bonds are part of six-membered rings rather than five-membered rings, as in 17, suggests that they are somewhat less strained. The following series in which successive 3,5-bridging of a cyclopentene and 3,6-bridging of cyclohexene and cyclohexadiene rings by C_2H_2, C_2H_4 and C_3H_4 bridges leads to a decrease in ΔH_h[44,47,48] of the cyclopentene or cyclohexene double bond also indicates less strain in the compounds relative to 17.

Since the charge transfer bands of 2 and 17 are a reasonably accurate measure of the relative energy of the HOMO's,[96-98] and if the LUMO is the mirror image of the HOMO, then the LUMO in 2 is lower than in 17. Yet 17 is reduced faster if the statistical factor is applied, so Gardner's[86]

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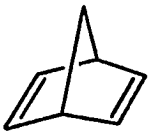


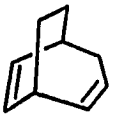
-35.0

-33.1

-31.1

-27.9

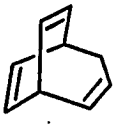
-28.3



Unk.

-37.6

-27.9



Unk.

argument does not seem valid in this case. Thus it appears that strain energies are determining the relative rates of reduction of the double bonds in these two compounds, and if this is true, then a crude approximation of the strain energy in 2 can be obtained (See Section I).

In the case of 18, the strain energy is less than that of 2 and 17, and the LUMO is also higher than those of 2 and 17. Thus both arguments predict that 18 should be reduced more slowly than 2 and 17. If one compares 18 to norborna-diene, both strain energy and LUMO arguments again predict

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that norbornadiene should be reduced faster; this is the observed result. The LUMO of 17 has been shown to be lower than that of norbornadiene, 19, but 19 is reduced faster. The strain energy of 19 is, however, larger than that of 17; thus, strain energy again seems to be the controlling factor in the rate of reduction.

Whether a methyl group on norbornadiene would slow the rate of reduction enough by steric hindrance to solvation of the activated complex or by perturbation of the energy of the LUMO to offset the strain argument remains to be determined. However, the evidence seems to indicate that "strain" energy, not steric hindrance to solvation or the energy of the LUMO, is the dominant factor in determining the rate of reduction of nonconjugated double bonds.

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SECTION IV

EXPERIMENTAL

Microanalyses were performed by Dr. Franz Kasler of the University of Maryland Department of Chemistry. The nmr spectra were obtained in carbon tetrachloride solutions with tetramethylsilane (TMS) as an internal reference on a Varian A-60D nmr spectrometer. All ir spectra were obtained neat in 0.025-mm cells on a Perkin-Elmer 337 grating infrared spectrometer unless otherwise noted. Ultraviolet spectra were obtained on spectrograde n-hexane solutions on a Cary 14 or 15 spectrophotometer with 1.000-cm quartz cells. All preparative glpc work was done on a Varian Aerograph A90-P3 with a thermal conductivity detector. Analytical glpc work was performed on a Varian Aerograph 1200 flame ionization detector instrument with a recorder equipped with Disc integrator. (See Appendix 1 for glpc columns used.) Mass spectra were obtained on a Varian M-66 mass spectrometer or a LKB 9000 gas chromatograph-mass spectrometer at the National Institutes of Health, Bethesda, Maryland.

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Preparation of Tropylium Fluoborate

This compound was synthesized by employing the Organic Synthesis preparation of Conrow.[28] Cycloheptatriene, 24.2 g (J. T. Baker Chemical Co.) and 100 g phosphorous pentachloride in 800 ml of carbon tetrachloride (CCl_4) were stirred for 3 hours, filtered and the solid double salt was added to 400 ml of ice-cold absolute ethanol; then 50 ml aqueous fluoboric acid (48%, J. T. Baker) was added. The product was collected by filtration, washed with anhydrous ether (Et_2O) and dried in a vacuum desiccator. Yield: 31 g (70%) (lit.[28] 34-38 g).

Preparation of 7-Methoxy-1,3,5-cycloheptatriene

The procedure of Dauben et al.[11] was used. Tropylium fluoborate, 44.2 g (0.25 mole), was added to 16.2 g (0.30 mole) sodium methoxide dissolved in 300 ml of absolute methanol. The reaction was stirred for 40 minutes, 300 ml pentane was added, the pentane layer was extracted with 4 x 250 ml water, and the water layer extracted with 8 x 200 ml pentane. The organic layer was dried over anhydrous magnesium sulfate, filtered, and the pentane distilled off at atmospheric pressure. The residue was distilled in vacuo to give a main fraction of 25.5 g (84%) bp 46-46.5°/9 mm (lit.[11] 81%, bp 54-55°/13 mm).

This fraction was the expected product as shown by nmr

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signals at δ = 3.05-3.30 ppm, multiplet (1 H, allylic), 3.37 ppm, singlet (3 H, methoxide methyl), 5.37 ppm, doublet of doublets (2 H, vinyl, J_{17} = 4.0 Hz, J_{12} = 10 Hz), 5.88-6.25 ppm, multiplet (2 H, vinyl), 6.48-6.70 ppm, multiplet (2 H, vinyl).

Preparation of 2-Bromopropene[100]

To a 3000-ml, three-necked, round-bottomed flask equipped with a Tru-bore stirrer and a reflux condenser were added 600 ml of carbon tetrachloride, 215 g (2.5 moles) of methacrylic acid and 2-3 ml of pyridine. Bromine (ca. 400 g) was added dropwise and the reaction mixture was stirred until the bromine color persisted. The carbon tetrachloride solution was then washed with aqueous sodium thiosulfate solution and dried over anhydrous magnesium sulfate. After the mixture was filtered, the carbon tetrachloride was removed in vacuo. (Note: All carbon tetrachloride must be removed in this step as it is impossible to separate it from the final product.) After the carbon tetrachloride was removed, 1000 ml of DMF was added to the flask and the solution was heated to 90-100°. Then solid potassium carbonate was slowly added and the product was collected with the aid of a condenser and an attached Dry Ice trap (carbon dioxide given off carries the product through a regular spiral con-

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denser). After no further reaction was observed on addition of potassium carbonate, the flask was heated until no additional liquid distilled at a head temperature less than 110°. The product was washed three times with water, dried over calcium chloride, filtered and distilled. The yield was 130 g (47.5%), bp 47.5-48.0°.

Preparation of 7-Isopropenyl-1,3,5-cycloheptatriene

To a 500-ml, three-necked, round-bottomed flask equipped with Tru-bore stirrer, addition funnel, reflux condenser and drying tube, and flame-dried under nitrogen, were added a crystal of iodine and 3.6 g (0.15 g.atom) of magnesium. The iodine was sublimed onto the magnesium and 25 ml freshly distilled dry tetrahydrofuran (THF) was added. Ten ml of a solution containing 20.3 g (0.17 mole) 2-bromopropene (90% pure) in 60 ml THF was then added with stirring and the reaction started immediately. The remainder of the solution was added dropwise with stirring over 90 minutes. The reaction was then refluxed for 105 minutes, cooled, and 12.5 g (0.10 mole) of 7-methoxycycloheptatriene in 60 ml dry THF was added dropwise with cooling over 75 minutes, during which time a light brown precipitate formed. The cooling bath was removed after the addition was complete; the reaction was allowed to warm to room temperature. The brown precipitate

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then dissolved and the reaction mixture warmed to 30-35° and maintained itself at that temperature for 60 minutes. It was then heated at reflux for 18 hours, cooled, and 8 ml of saturated aqueous ammonium chloride solution was added. Then 50 ml of ether was added and the organic layer decanted. The residue was dissolved in water and extracted several times with ether and the organic layers were combined and dried over anhydrous magnesium sulfate. The solution was then filtered, and the solvent distilled off at atmospheric pressure. The residue was distilled in vacuo to give a main fraction weighing 11.3 g (83%) bp 56.5-57.5°/9 mm, which was shown to be essentially (> 98%) a single compound by glpc on a 1.5 m 15% CO880 on 80/100 Chrom P.

An infrared spectrum exhibited prominent bands at 3075, 3020 (vinyl CH stretch), 2970, 2935, 2910, 2850 (aliphatic CH stretch), 1650 (C=C stretch), 1450, 1430, 1365, 1224, 895, 800, 742, 702, 643 and 590 cm^{-1}.

Nmr signals appeared at δ = 1.87 ppm (s, 3, allylic methyl), 2.12 ppm (t, H_7, $J_{17} = J_{67}$ = 6.0 Hz, allylic), 4.92 ppm (broad s, 2, terminal vinyl), 5.23 ppm (d of d, H_1 and H_6, $J_{17} = J_{67}$ = 6.0 Hz, $J_{12} = J_{56}$ = 9.0 Hz, vinyl), 5.93-6.33 ppm (m, H_2 and H_5, vinyl), 6.48-6.71 ppm (m, H_3 and H_4, vinyl.

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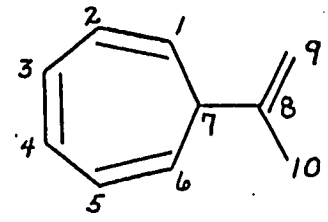

The ultraviolet spectrum exhibited λ_{max}^{hexane} = 257.5 nm (ε 3140).

Exact Mass: Calcd for $C_{10}H_{12}$: 132.094. Found: 132.091.

Thermal Reorganization of 7-Isopropenyl-1,3,5-cycloheptatriene

7-Isopropenyl-1,3,5-cycloheptatriene (10 g) in 30 ml of dimethylacetamide (DMA) was heated at reflux (167-168°) under nitrogen for 8 hours. After the solution was cooled, water was added and the solution extracted with pentane. The pentane solution was dried over anhydrous magnesium sulfate, filtered, and the pentane distilled at atmospheric pressure. The residue was distilled in vacuo (52-58°/5 mm) to remove any polymeric material; the distillate weighed 6.2 g.

Glpc analysis on column CO880-3 indicated that the distillate contained at least 5 components. All compounds were subsequently identified, and nmr, ir, uv, and mass spectra (exact masses) were obtained on all previously unidentified

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compounds (vide infra).

The first compound (1% of the mixture) had a retention time on the CO880 column identical to that of the 7-isomer; enhancement with authentic 7-isomer gave only one peak on the chromatogram. The second compound (26% of the mixture) was identified as 3-methylbicyclo [3.2.2] nona-2,6,8-triene on the basis of its spectral properties.

The third compound (4% of the mixture) had a nmr spectrum and retention time identical with 2-isopropenyl-1,3,5-cycloheptatriene. This isomer was more easily prepared by photolysis of the 7-isomer for 5 hours with a 450-watt Hanovia medium pressure mercury arc source through Vycor. All physical properties were determined on a sample obtained by photolysis.

The fourth compound (52% of the mixture) was identified as 3-isopropenyl-1,3,5-cycloheptatriene on the basis of its spectral properties, primarily nmr and uv spectra.

The fifth compound (16% of the mixture) was shown to be 1-isopropenyl-1,3,5-cycloheptatriene on the basis of its nmr and uv spectra.

3-Methylbicyclo [3.2.2] nona-2,6,8-triene

An infrared spectrum exhibited prominent bands at 3045 (vinyl CH stretch), 2990, 2955, 2925, 2870, 2805 (aliphatic

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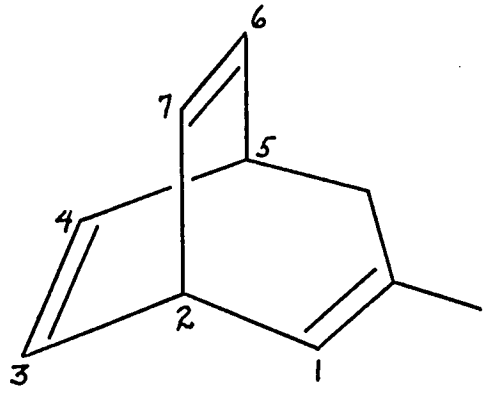
CH stretch), 1655, 1610 (C=C stretch), 1445, 1365, 1230, 1200 1018, 887, 796, 750, 680, 656 and 630 cm^{-1}.

Nmr signals appeared at δ = 1.42 ppm (s, 3, allylic methyl), 1.93 ppm (broad s, 2, allylic), 2.83-3.30 ppm (m, 2, bridgehead), 5.68 ppm (d, 1, $J_{1,2}$ = 7.0 Hz with some fine splitting, vinyl), 6.02 ppm (d of d of d, H_6 and H_4, J_{45} = J_{56} = 7.0 Hz, J_{34} = J_{67} = 7.0 Hz, J_{24} = J_{26} = 1.5 Hz), 6.40 ppm (d of d of d, H_3 and H_7, J_{23} = J_{27} = 7.0 Hz, J_{34} = J_{67} = 7.0 Hz, J_{53} = J_{57} = 1.5 Hz).



The ultraviolet spectrum exhibited an end absorption ϵ = 3400 at 220 nm with a long tail showing ϵ = 800, 100 and 60 at 235, 250 and 265 nm respectively.

Exact Mass: Calcd for $C_{10}H_{12}$: 132.094. Found: 132.091.

2-Isopropenyl-1,3,5-cycloheptatriene

An infrared spectrum exhibited prominent bands at 3085, 3020 (vinyl CH stretch), 2960, 2875, 2830 (aliphatic CH stretch), 1610, 1590 (C=C stretch), 1450, 1430, 1375, 1300, 888, 840,

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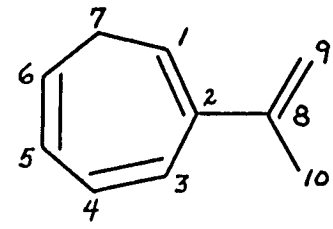
790, 738, 710, 630, and 583 cm^{-1}.

Nmr signals appeared at δ = 1.92 ppm (s, 3, allylic methyl), 2.23 ppm (t, 2, J_{67} = 7.0 Hz, allylic), 4.92 ppm (broad s, 2, terminal vinyl), 5.20-5.65 ppm (m, H_1 and H_6, vinyl), 5.38-7.16 ppm (m, H_3, H_4, and H_5, vinyl).



The ultraviolet spectrum exhibited λ_{max}^{hexane} = 229 nm (ϵ 19000).

Exact Mass: Calcd for $C_{10}H_{12}$: 132.094. Found: 132.091.

3-Isopropenyl-1,3,5-cycloheptatriene

An infrared spectrum exhibited prominent bands at 3090, 3030 (vinyl CH stretch), 2975, 2885, 2840 (aliphatic CH stretch), 1620 (C=C stretch), 1530, 1455, 1440, 1390, 1375, 1290, 891, 873, 775, 730, 705, 688, 620, and 595 cm^{-1}.

Nmr signals appeared at δ = 2.00 ppm (s, 3, allylic methyl), 2.21 ppm (t, 2, J_{17} = 6.8 Hz, allylic), 5.00 ppm (s, 1, terminal vinyl), 5.10 ppm (s, 1, terminal vinyl), 5.37 ppm (d of t, H_1, J_{17} = 6.8 Hz, J_{12} = 10.0 Hz, vinyl),

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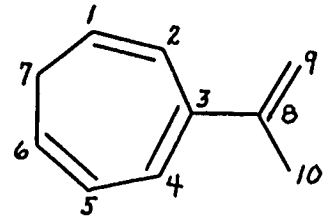
5.42 ppm (d of t, H_6, J_{16} = 6.8 Hz, J_{56} = 9.0 Hz, vinyl), 6.14 ppm (d of d, H_5, J_{45} = 6.0 Hz, J_{56} = 9.0 Hz, vinyl), 6.23 ppm (d, H_2, J_{12} = 10.0 Hz, vinyl), 6.58 ppm (d, H_4, J_{45} = 6.0 Hz, vinyl).



The ultraviolet spectrum exhibited λ_{max}^{hexane} = 225.0 nm (ϵ 10600) and λ = 276.2 nm (ϵ 9600).

Exact Mass: Calcd for $C_{10}H_{12}$: 132.094. Found: 132.087.

1-Isopropenyl-1,3,5-cycloheptatriene

An infrared spectrum exhibited prominent bands at 3090, 3025 (vinyl CH stretch), 2945, 2890, 2850 (aliphatic CH stretch), 1610, 1585 (C=C stretch), 1440, 1375, 1365, 1295, 1280, 880, 852, 789, 754, 720, 616 and 571 cm^{-1}.

Nmr signals appeared at δ = 1.94 ppm (s, 3, allylic methyl), 2.53 ppm (d, 2, J_{67} = 6.8 Hz, allylic), 4.99 ppm (broad s, 1, terminal vinyl), 5.30 ppm (broad s, 1 terminal vinyl), 5.03-5.62 ppm (m, H_6, vinyl), 5.87-6.33 ppm (m, H_2 and H_5, vinyl), 6.38-6.65 ppm (m, H_3 and H_4, vinyl).

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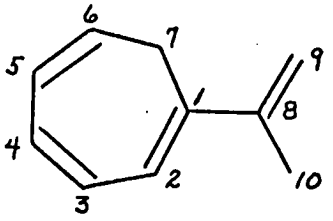

The ultraviolet spectrum exhibited λ_{max}^{hexane} = 222 nm (ϵ 21100), λ_{sh} = 227 nm (ϵ 20400), λ= 296 nm (ϵ 7300).

Exact Mass: Calcd for $C_{10}H_{12}$: 132.094. Found: 132.089.

Preparation of 3-Methyltricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene

To a tube containing 0.4 g of potassium amide in 15 ml of liquid ammonia at -78° was added 150 µl of 3-methylbicyclo[3.2.2]nona-2,6,8-triene. The tube was then sealed, removed from the cold bath, warmed to 50° and allowed to stand for 3 hours. The tube was then cooled in a Dry Ice-acetone bath, opened, and the contents quenched with 30 ml of water. The water solution was then extracted with pentane and the pentane solution was passed by glpc on column CO880-2 and the product collected. Recollection afforded pure 3-methyltricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene.

An infrared spectrum exhibited prominent peaks at 3030

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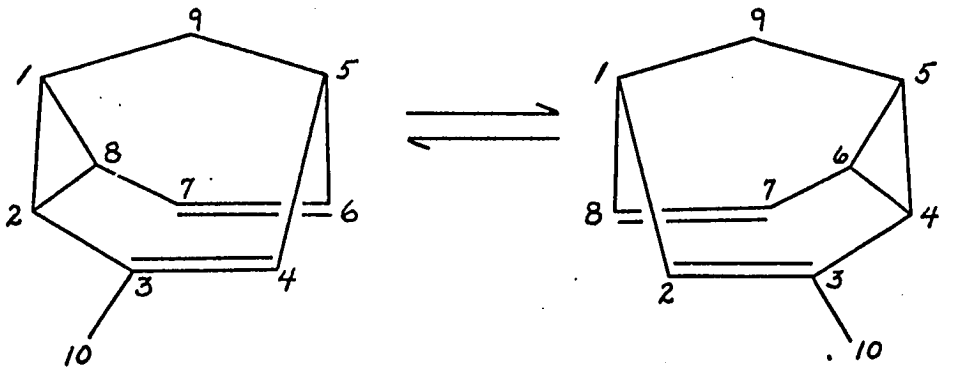
(vinyl CH stretch), 2915, 2850 (aliphatic CH stretch), 1645, 1620 (C=C stretch), 1450, 1440, 1400, 1393, 1365, 1350, 1173, 1136,1063, 1028, 1005, 936, 846, 808, 793, 736, 693, 645 and 607 cm^{-1}.

Nmr signals at room temperature appeared at δ = 1.02 ppm (t, 2, J = 2.5 Hz, methylene on C_9), 1.73 ppm (s, 3, allylic methyl), 2.00-2.47 ppm (m, H_1 and H_5, cyclopropyl bridgehead $\rightleftharpoons$ allylic bridgehead), 3.72-4.08 ppm (m, H_2, H_4, H_6 and H_8, cyclopropyl $\rightleftharpoons$ vinyl), 5.53 ppm (t, H_7, J = 7.6 Hz, vinyl).



The ultraviolet spectrum exhibited only end absorption ϵ = 3500 at 220 nm.

Exact Mass: Calcd for $C_{10}H_{12}$: 132.094. Found: 132.093.

Preparation of 3-Methyl-4-propylbicyclo[3.2.2]nona-2,6,8-triene

Into a 50-ml, three-necked, round-bottomed flask

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equipped with magnetic stirrer, gas inlet, and Dry Ice condenser, and flame-dried under nitrogen, was condensed 20-25 ml of ammonia. Potassium (0.3 g) and a little ferric chloride catalyst were added. Then 150 µl of 3-methylbicyclo-[3.2.2]nona-2,6,8-triene was added. After 30 seconds, 250 µl of 1-chloropropane was added and the reaction was stirred for 5 minutes. Then an additional 150 µl of 1-chloropropane was added and after being stirred for another 10 minutes, the reaction turned bluish-gray. The reaction was quenched with water and the water solution was extracted with pentane. The pentane solution was passed on column CO880-1 and showed two peaks: 3-methylbicyclo[3.2.2]nona-2,6,8-triene (10%) and a longer retention time peak (90%). The material corresponding to this peak was collected and identified as 3-methyl-4-propylbicyclo[3.2.2]nona-2,6,8-triene.

The infrared spectrum exhibited prominent bands at 3040, 3010 (sh, vinyl CH stretch), 2960, 2930 (sh), 2865 (aliphatic CH stretch), 1610 (C=C), 1450, 1367, 1270, 1225, 1158, 955, 942, 887, 653, and 635 cm^{-1}.

Nmr signals appeared at δ = 0.96 ppm (t, 3, methyl), 1.42 ppm (center of m, 7, methylene and allylic methyl), 1.60-2.00 ppm (m, 1, allylic), 2.70-3.25 ppm (m, 2, bridgehead), 5.70 ppm (d, 1, J = 8.5 Hz, vinyl), 5.85-6.20 ppm (m, 2, vinyl), and 6.23-6.62 ppm (m, 2, vinyl).

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Exact Mass: Calcd for $C_{13}H_{18}$: 174.137. Found: 174.133.

Preparation of Methallyl Iodide[65]

To a slight excess of sodium iodide (1.70 moles) in one l. of dry acetone was added 149.3 g (1.65 moles) of methallyl chloride; the mixture was stirred for 3 hours at room temperature. Then water was added, the hydrocarbon layer was separated , the water solution was washed with ether and the combined organic layers were washed several times with water and dried over anhydrous magnesium sulfate. The solvent was distilled off and the product distilled, bp 28°/13mm. The yield was 168.5 g (56%) (lit.[65] 28°/3-5 mm, yield 40%).

Preparation of 3-Bromocyclohexene[101]

To 1200 ml of carbon tetrachloride were added 356 g of N-bromosuccinimide, 205 g of cyclohexene, and 100 mg of benzoyl peroxide. The reaction was then cautiously heated until an exothermic reaction occurred. Some cooling (ice-water bath) was needed to control the reaction. After the reaction subsided, it was heated at reflux for an additional hour and then cooled. The succinimide was then filtered off and the CCl_4 distilled off at atmospheric pressure. Residual solvent was removed in vacuo and the product was distilled in vacuo to give 204 g (51%) bp 63.5°/15 mm (lit.[102] 76%, bp 68-70.5/

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26 mm).

Preparation of 1,3-Cyclohexadiene[102,103]

To 60 ml of quinoline heated to 180-200° was added 50 g (0.31 mole) of 3-bromocyclohexene and the distillate was collected with cooling. The distillate was washed with a dilute HCl solution, water, and then was dried over anhydrous magnesium sulfate. After filtration, the 1,3-cyclohexadiene was distilled, bp 81°; the yield was 15.2 g (61%) (lit.[102,103] yield 73%, bp 81°).

Preparation of Silver Trichloroacetate

Method A.[104] To a solution of 51 g (0.30 mole) of silver nitrate in 30 ml of water was added with high speed stirring, a solution of 49 g (0.30 mole) of trichloroacetic acid in 40 ml of water. The precipitate was removed by filtration and dried in a vacuum desiccator. The product weighed 28.6 g (0.11 mole, 37%).

Method B.[65] To a solution of 51 g (0.30 mole) of silver nitrate in 30 ml of water was added a solution of sodium trichloroacetate (0.30 mole). The gray precipitate was collected by filtration, washed with cold water and acetone, and dried in a vacuum desiccator. The product weighed 27.2 g (0.10 mole, 33%).

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Preparation of 3-Methylbicyclo[3.2.2]nona-2,6-diene[65]

Into a flame-dried 500-ml three-necked round-bottomed flask equipped with a dry ice condenser with drying tube and Tru-bore stirrer was condensed 300 ml of sulfur dioxide, which was then cooled to -50° with a dry ice-acetone bath. Then 20.4 g (0.075 mole) of silver trichloroacetate and 14.1 ml (0.12 moles) of 1,3-cyclohexadiene were added. Methallyl iodide (8.4 ml, 0.075 mole) in 15 ml of methylene chloride was added dropwise with stirring. The reaction mixture was then stirred for two hours at -50°. The SO_2 was allowed to evaporate and 80 ml of methylene chloride was added. The solution was filtered and the residue washed with methylene chloride. The filtrate was then added to cold concentrated aqueous ammonia and the organic layer was separated. The ammonia solution was extracted with pentane, the organic layers were combined, washed with water and dried over anhydrous magnesium sulfate. The solution was then filtered and the solvents distilled off at atmospheric pressure. The residue was distilled in vacuo to give a low boiling fraction (bp 37-79°/27 mm) and a fraction with bp 79-81°/27 mm. The low boiling fraction contained 1,3-cyclohexadiene, methallyl iodide, and methallyl alcohol as shown by glpc on column C0880-4. The high boiling fraction was > 95% pure. The yield was 1.6 g (16%) (lit. 20%).

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Preparation of 3-Methylbicyclo[3.2.1]octa-2,6-diene

Note: Of the two methods described below, the first gave yields of less than 3% and is not considered to be of synthetic utility.

Method A.[65] Into a flame-dried 500-ml three-necked round-bottomed flask equipped with a dry ice condenser with drying tube and a Tru-bore stirrer was condensed 300 ml of sulfur dioxide which was then cooled to -50° with a dry ice-acetone bath. Then 20.4 g (0.075 mole) of silver trichloroacetate and 10 ml (0.12 mole) of cyclopentadiene were added. Methallyl iodide (10 ml, 0.08 mole) in 15 ml of methylene chloride was added dropwise with stirring. The reaction was then stirred for 90 min. at -50°. The sulfur dioxide was allowed to evaporate and 90 ml of methylene chloride was added. The reaction was filtered and the residue was washed with methylene chloride. The filtrate was then added with stirring to cold aqueous ammonia and the organic layer was separated. The ammonia solution was extracted with pentane and the combined organic layers were dried over anhydrous magnesium sulfate. After the solution was filtered, the solvents were distilled off at atmospheric pressure and the residue was distilled in vacuo.

In no preparation (see below) was more than 200 μl (2% yield) obtained (lit. 40%). Also several side products

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were obtained (*vide infra*).

Run 1. The procedure described above was employed. Silver trichloroacetate, prepared from silver nitrate and trichloroacetic acid without rapid mixing, was used after drying overnight in a vacuum desiccator. The cyclopentadiene was freshly distilled. Work-up was done as above. Residue distilled *in vacuo* to give 3.0 g bp 45-65°/2 mm. This fraction was greater than 80% 3-methyltricyclo[3.2.1.$0^{2,7}$]-oct-3-ene.

Run 2. Silver trichloroacetate was synthesized as in Run 1. Cyclopentadiene was freshly distilled. Work-up as described was used and residue was distilled *in vacuo* to give 8.1 g (31%) bp 90-98°/0.4 mm. The product was identified as 3-methyl-4-trichloroacetoxybicyclo[3.2.1]oct-2-ene.

Run 3. Silver trichloroacetate was synthesized as in Run 1. The cyclopentadiene and methallyl iodide were redistilled. Distillation *in vacuo* of the residue from work-up yielded 6.5 g bp 90-95°/1 mm of the trichloroacetate.

Run 4. Silver trichloroacetate was prepared from sodium trichloroacetate and silver nitrate and was dried overnight in a vacuum desiccator. The cyclopentadiene was freshly distilled. After work-up, the residue was distilled *in vacuo* to give 2.1 g in the trap and 2.4 g bp 25-45°/0.7 mm. The major product was methallyl iodide but some 3-methylbi-

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cyclo[3.2.1]octa-2,6-diene was observed in the trap fraction. Collection of the products from the trap on column TCEP-1 yielded the expected product contaminated with methallyl iodide.

Run 5. Silver trichloroacetate was prepared from silver nitrate and trichloroacetic acid by rapid mixing and was dried overnight in a vacuum desiccator. The cyclopentadiene was freshly distilled. Distillation in vacuo of the residue after work-up which included a silver nitrate wash to remove methallyl iodide yielded 1.7 g in the trap, 1.4 g bp 40-90°/1 mm and 5.0 g bp 90-100°/1 mm. The latter two fractions were the trichloroacetate. The trap fraction consisted of methallyl alcohol, cyclopentadiene, and some 3-methylbicyclo[3.2.1]octa-2,6-diene.

Method B.[69] To a 1000-ml three-necked round-bottomed flask equipped with two serum-capped addition funnels, reflux condenser, magnetic stirrer, and a positive pressure balloon apparatus, and flame-dried under Argon was added 25.65 g (0.13 mole) of cuprous iodide. Anhydrous ether (50 ml) and then methyllithium in ether were added at 0° with stirring until the yellow color disappeared. 3-Bromobicyclo[3.2.1]-octa-2,6-diene (6.0 g, 0.03 mole) in 50 ml of anhydrous ether was added dropwise at 0° and the reaction was maintained at 0° for 72 hours. Then saturated aqueous ammonium chloride

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solution was added, the reaction was filtered and the residue was washed with water and ether. The ether layer was separated, the water layer was extracted with ether, and the organic layers were combined and dried over anhydrous magnesium sulfate. After the solution was filtered, the ether was distilled off at atmospheric pressure. The residue was distilled *in vacuo* to give a main fraction of 2.7 g (70%) bp 44-45.5°/13 mm. Glpc analysis on column C0880-4 showed the product to be > 95% pure.

3-Methyltricyclo[3.2.1.$0^{2,7}$]oct-3-ene

In Run 1 of the preparation of 3-methylbicyclo[3.2.1]-octa-2,6-diene by Method A, a fraction was collected bp 45-65°/2 mm. Collection of the hydrocarbon constituent of this fraction (the other constituent was chloroform) was undertaken on column C0880-2 and it was shown by its spectral properties to be 3-methyltricyclo[3.2.1.$0^{2,7}$]oct-3-ene.

This product could also be obtained by heating 3-methyl-4-trichloroacetoxybicyclo[3.2.1]oct-2-ene in quinoline at 200-210°. Extraction of the reaction with pentane which was distilled off gave *ca.* 65% yield of 3-methyltricyclo-[3.2.1.$0^{2,7}$]oct-3-ene.

An infrared spectrum exhibited prominent peaks at 3025 (vinyl CH stretch), 2910, 2845 (aliphatic CH stretch), 1640

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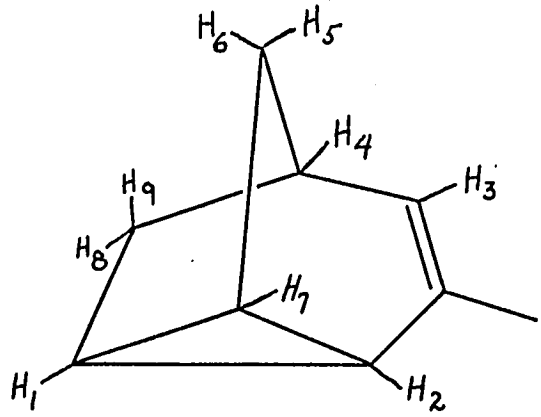
(C=C stretch), 1440, 1377, 1310, 1183, 1149, 1073, 1021, 998, 920, 908, 870, 840, 818, 794, 745, 702 and 550 cm^{-1}.

Nmr signals appeared at δ = 0.71 ppm (unsymmetrical d, H_5 and H_8, J = 11 Hz, methylene), 1.27-1.70 ppm (m, 5, methylene and cyclopropyl), 1.78 ppm (d, 3, J = 1.5 Hz, allylic methyl), 2.17-2.53 ppm (m, 1, bridgehead), 5.50 ppm (d, 1, J = 7.0 Hz, vinyl).



This nmr is very similar to that reported[67] for tricyclo[3.2.1.$0^{2,7}$]oct-3-ene with the exceptions that there is a signal for only one vinyl proton at τ 4.50 (broaden doublet, J = 7 Hz) instead of a triplet at 4.26 and there is an extra signal at 8.22 (d, 3 H, methyl, J = 2 Hz).

Anal: Calcd for C_9H_{12}: C, 89.93; H, 10.07. Found: C, 90.08; H, 9.95.

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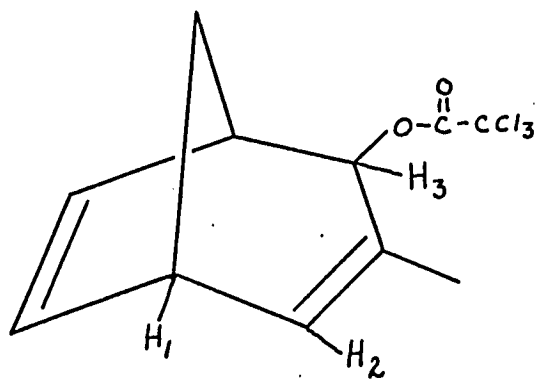
3-Methyl-4-trichloroacetoxybicyclo[3.2.1]oct-2-ene

In almost all preparations of 3-methylbicyclo[3.2.1]-octa-2,6-diene by Method A, a high boiling fraction was collected which was > 90% one compound. It was purified by distillation (bp 107-108°/1.3 mm) and was shown to be 3-methyl-4-trichloroacetoxybicyclo[3.2.1]oct-2-ene by its spectral properties. No stereochemical assignment was made for the trichloroacetoxy group. (See Section II).

An infrared spectrum exhibited prominent peaks at 2930, 2870, 2830 (aliphatic CH stretch), 1760 (C=O), 1655 (C=C stretch), 1440, 1375, 1325, 1240 (C-O-C stretch), 1180, 1058, 980, 960, 923, 898, 855, 827, and 680 cm^{-1}.

Nmr signals appeared at δ = 1.62 ppm (broad s, 3, allylic methyl), 1.42-2.33 ppm (m, 6, methylene), 2.33-2.67 ppm (m, 2, bridgehead), 5.12 ppm (broad t, H_3, J = 4.0 Hz,



allylic and α acetoxy) and 5.57 ppm (broad d, H_2, J_{12} = 6.5 Hz, vinyl).

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Anal: Calcd for $C_{11}H_{13}O_2Cl_3$: C, 46.56; H, 4.62; Cl, 37.57. Found: C, 46.84; H, 4.40; Cl, 37.34.

Preparation of exo and endo-3,4-Dibromobicyclo[3.2.1]octa-2,6-diene

The procedure of Moore et al.[70] was employed by using 63.8 g (0.69 mole) of norbornadiene, 64.8 g (0.58 mole) of potassium t-butoxide, and 177 g (0.70 mole) of bromoform. Work-up and distillation yielded 47.3 g (31%) of an 88:12 exo/endo mixture, bp 80-87°/.25 mm (lit.[70] 35%, bp 77°/0.05 mm).

Preparation of 3-Bromobicyclo[3.2.1]octa-2,6-diene

The procedure of Moore et al.[70] was employed by using 47.3 g (0.18 mole) of an 88:12 exo/endo mixture of 3,4-dibromobicyclo[3.2.1]octa-2,6-diene and 6.7 g (0.18 mole) of lithium aluminum hydride. Work-up and distillation yielded 21.3 g (64%) of the product bp 68-70°/5 mm (lit.[70] 76%, bp 63°/5 mm).

Procedure for Deuterium Exchange of 2, 17, and 18

Into a 10-ml Erlenmeyer flask, flame-dried under nitrogen and fitted with a serum cap, was weighed 0.22_x g of freshly sublimed potassium t-butoxide. To this was added by pipet 2.00 ml of dimethylsulfoxide-d_6 (DMSO-d_6) dried over molecular sieves. After the salt dissolved, the flask was placed in a 25.0° bath for 15 minutes. Then 60 µl of

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hydrocarbon was added and the flask was swirled for adequate mixing. Aliquots were removed by syringe at various times, quenched with water, and extracted with pentane. The pentane extract was then passed by glpc on column C0880-1 and the hydrocarbon was collected and analyzed by mass spectrometry.

Determination of Deuterium Content by Low-Voltage Mass Spectrometry

The parent undeuterated hydrocarbons were used as the standards. The procedure is quite simple for 3-methylbicyclo[3.2.2]nona-2,6-diene and 3-methylbicyclo[3.2.1]octa-2,6-diene which gave no $(M-1)^+$ peak. The ratio of M^+ (molecular ion) to $(M+1)^+$ for the parent hydrocarbon was obtained at a certain ionization voltage. Then all of the deuterated samples were analyzed at the same voltage. By using the M/M+1 of the standard (defined $M/M+1^*$), the following procedure was used to calculate the deuterium content.

Divide M (molecular ion of deuterated sample) by $M/M+1^*$ and subtract this number from (M+1) to give $(M+1)'$, the new value. Divide $(M+1)'$ by $M/M+1^*$ and subtract this number from (M+2) to give $(M+2)'$. Continue this for as many peaks as there are. Then total $M + (M+1)' + (M+2)' + \ldots = Z$.[66] The percent d_o remaining is found by dividing M by Z.

For 3-methylbicyclo[3.2.2]nona-2,6,8-triene, the case is somewhat more complex. The standard and deuterated com-

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pounds were all run at the same ionization voltage. However, it was impossible to eliminate the M-1 peak and, therefore, an iterative method for calculating component peak heights was used, by utilizing M/M+1* and M/M-1* from the standard.

Divide M by M/M+1* and subtract this value from (M+1) to give (M+1)'. Divide (M+1)' by M/M-1* and subtract this number from M to give M'. Repeat this procedure until the new M' and (M+1)' do not change significantly. Then repeat this procedure for each higher mass peaks (i.e. (M+1)' becomes the new M). The percent d_o is calculated as in the previous determination.

Results of Deuterium Exchange

3-Methylbicyclo[3.2.2]nona-2,6,8-triene.

Run 1 Base = 1.00 N

$k_1 = (-11.7 + 0.4) \times 10^{-4}$ sec^{-1}

$k_2 = (-11.7 + 0.4) \times 10^{-4}$ $l\ mole^{-1} sec^{-1}$

Cor. Coeff. = 0.997

%D_o	time(sec)
100	0
84.0	123
71.6	240
63.1	423
49.3	604

Run 2 Base = 1.02 N

$k_1 = (-9.24 + 0.50) \times 10^{-4}$ sec^{-1}

$k_2 = (-9.06 + 0.5) \times 10^{-4}$ $l\ mole^{-1} sec^{-1}$

Cor. Coeff. = .994

%D_o	time(sec)
100	0
89.0	70
82.2	190
74.9	310
67.2	450

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Ave. = (1.05 ± 0.2) x 10^{-3} l $mole^{-1}sec^{-1}$

3-Methylbicyclo [3.2.2] nona-2,6-diene.

Run 1 Base = 1.01 N k_1 = (-1.33 + 0.01) x 10^{-6} sec^{-1}

$\%D_o$	time(sec)
100	0
92.5	58,440
88.2	100,800
80.7	158,820
73.3	233,700

k_2 = (-1.32 + 0.01) x 10^{-6} l $mole^{-1}sec^{-1}$

Cor. Coeff. = .9997

Run 2 Base = 1.03 N k_1 = (-1.51 + .02) x 10^{-6} sec^{-1}

$\%D_o$	time(sec)
100	0
90.4	58,440
85.6	10,080
79.1	158,820
70.4	233.700

k_2 = (-1.47 + .02) x 10^{-6} l $mole^{-1}sec^{-1}$

Cor. Coeff. = .9995

Ave. = (1.40 ± 0.1) x 10^{-6} l $mole^{-1}sec^{-1}$

3-Methylbicyclo [3.2.1] octa-2,6-diene

Run 1 Base = 0.99 N k_1 = (2.00 ± 0.03) x 10^{-5} sec^{-1}

$\%D_o$	time(sec)
100	0
98.8	600
95.4	2100
89.9	5160
82.8	9600

k_2 = (2.01 ± 0.03) x 10^{-5} l $mole^{-1}sec^{-1}$

Cor. Coeff. = 0.9995

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Run 2 Base = 1.00 N $k_1 = (-1.95 \pm 0.03) \times 10^{-5}$ sec^{-1}

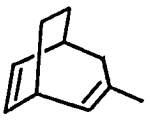
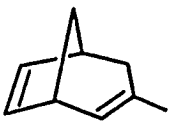
$\%D_o$	time(sec)
100	0
-----	1800
80.6	10800
71.4	16800
65.4	22200

$k_2 = (-1.95 \pm 0.03) \times 10^{-5}$ $l\ mole^{-1}sec^{-1}$

Cor. Coeff. = 0.9997

Ave. = $(-1.98 \pm 0.06) \times 10^{-5}$ $l\ mole^{-1}sec^{-1}$

Rate Constants for Deuterium Exchange at 25.0°

Compound	K ($l\ mole^{-1}sec^{-1}$)	Cor. Coeff.
	$(1.05 \pm 0.2) \times 10^{-3}$	.996
	$(-1.40 \pm 0.1) \times 10^{-6}$	.9996
	$(-1.98 \pm 0.06) \times 10^{-5}$	.9996

Attempted Isomerization of 7-Isopropenylcycloheptatriene by Hydride Exchange

Procedure. Tropylium fluoborate or trityl fluoborate (0.15 g) was dissolved in 2.0 ml of dry acetonitrile. To 6 µl of 7-isopropenylcycloheptatriene in a flame-dried equilibration tube was added 300 µl of the fluoborate/

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acetonitrile solution. After 5 min., 2 N hydrochloric acid was added as the quench and the solution was extracted with pentane. The pentane solution was analyzed on column CO880-4.

Results. In all cases after 5 minutes only one peak was observed upon analysis. This peak was collected from a large-scale reaction and shown to be β,β-dimethylstyrene by comparison of the infrared spectra with that of an authentic sample.

Treatment of 7-isopropenylcycloheptatriene with 100 μl of fluoboric acid (48%) also gave β,β-dimethylstyrene as the only product. Thus it seems that the product formation may be acid-catalyzed and this procedure was, therefore, discarded in favor of thermal isomerization.

Procedure for Thermal Equilibration of Isopropenylcycloheptatrienes

Into a heavy-walled tube (6" x 3/8") were placed 1 μl of hydrocarbon and 150 μl of distilled pentane under an Argon atmosphere. The tube was then sealed with cooling in a dry ice-acetone bath. After being warmed to room temperature, the tube was suspended in the vapors of a refluxing solvent, the constant temperature bath.

The solvents used for the equilibrations and their temperatures as determined with calibrated Anshutz thermometers were as follows.

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Phenetole (Eastman)	170.2 ± .2°
Acetophenone (Fisher Certified)	202.2 ± .2°
Diphenyl Ether (Fisher Certified)	259.0 ± .2°

After the tube was removed and cooled to room temperature, it was placed in a Dry Ice-acetone bath and cut open.

The pentane solution was then analyzed on column CO880-4 at 90° on a flame ionization detector gas chromatograph.

Procedure for the High Temperature Thermal Reorganization of 7-Isopropenylcycloheptatriene and Related Compounds

A micro pyrolysis apparatus complete with Vycor pyrolysis tube (12 mm o.d. x 7.5 in., packed with 3/16-in. i.d. glass helices treated with aqueous ammonia), serum cap, nitrogen inlet, micro combustion furnace, and receiving flask was used. The hydrocarbons were thermally reorganized at various temperatures at a rate of 4 μl/10 sec with a nitrogen flow of 10-20 ml/min. The product was collected in the receiving flask which was cooled with dry ice. Several ml of pentane was used to wash the tube and then the pentane solution was analyzed by glpc on column CO880-4. Temperatures in the range of 250-500° were used (see Tables XVII and XVIII).

Structure Proof of cis-2-methyl-8,9-dihydroindene

The products from the thermal reorganization of 6.8 g of 7-isopropenylcycloheptatriene were placed on a silica gel column impregnated with silver nitrate. The packing was

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made by treating 420 g of silica gel (28/200 mesh) with 168 g of silver nitrate in 600 ml of water. After mixing thoroughly, the water was removed *in vacuo* to dryness, and the absorbent was used with no further treatment.

The products were then eluted in 125 ml fractions as follows.

Fractions	Solvent	Compounds Eluted
1-9	90% Skelly "F" 10% ether	β,β-dimethylstyrene 2-methylindene 3-methylindene methallylbenzene
10-12	50% Skelly "F" 50% ether	2-methylindene 3-methylindene methallylbenzene
13-15	100% ether	2-methylindene 3-methylindene methallylbenzene
16-17	100% ether	1-isopropenylcycloheptatriene
18-21	100% ether	*cis*-2-methyl-8,9-dihydroindene isopropenylcycloheptatrienes
22-24	95% ether 5% methanol	*cis*-2-methyl-8,9-dihydroindene isopropenylcycloheptatrienes
25-26	90% ether 10% methanol	*cis*-2-methyl-8,9-dihydroindene
27	90% ether 10% methanol	No products eluted

The *cis*-2-methyl-8,9-dihydroindene was collected by glpc on column C0880-2 from fraction 26 of the above chromatography.

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An infrared spectrum exhibited prominent peaks at 3020 (vinyl CH stretch), 2950, 2895, 2830, 1645, 1580 (C=C stretch), 1435, 1240, 1172, 1080, 1026, 945, 830, 715, 697, 670 and 572 cm^{-1}.

Nmr signals appeared at δ = 1.75 ppm (d, 3, J = 1.5 Hz, allylic methyl), 1.90-2.60 ppm (m, 2, allylic), 2.70-3.67 ppm (m, 2, allylic bridgehead), 5.07-5.30 ppm (m, 1, vinyl), and 5.30-5.80 ppm (m, 4, vinyl).

The ultraviolet exhibited λ_{max}^{hexane} = 262.5 nm (ϵ 3700), λ = 271.5 (ϵ3350).

Anal: Calcd for $C_{10}H_{12}$: C, 90.84; H,9.16. Found: C, 90.51; H, 8.92.

To prove the cis ring fusion, 42 mg (.32 m/mole) of hydrocarbon was hydrogenated in a 10 ml round-bottomed flask equipped with magnetic stirrer over platinum oxide (10 mg) in acetic acid (1.5 ml). The temperature was 29.0° and the barometric pressure was 760.3 mm. A total of 22.7 ml (2.81 equiv) hydrogen was taken up compared to a theoretical value of 25.42 ml (3.0 equiv) (corrected for the partial pressure of acetic acid).

The hydrogenation mixture was poured into a separatory funnel and the flask was washed with 2 ml of pentane. Water (9 ml) and saturated aqueous ammonium chloride (1 ml) were added to the separatory funnel, the pentane layer was separ-

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ated and the water solution was washed with 3 x 1 ml of pentane. The pentane layers were combined, and analysis on column CO880-4 showed > 95% one compound. It was collected by glpc on column CO880-2 and shown to be cis-2-methylhydrindan by infrared comparison with an authentic sample.

Preparation of 2-Methyl-2-indanol[105]

To a 250-ml three-necked round-bottomed flask equipped with Tru-bore stirrer, reflux condenser, and addition funnel and dried under nitrogen were added a crystal of iodine and 2.4 g (0.095 g. atom) of magnesium. After the iodine was sublimed onto the magnesium by heating with a microburner, 20 ml of ether was added, followed by 10 ml of a solution containing 10.6 g (0.075 mole) of methyl iodide in 50 ml of ether. When the reaction started, the remainder of the solution was added dropwise and the reaction was then heated at reflux for one hour. 2-Indanone, 7.0 g (0.05 mole) in 60 ml of ether was added dropwise with cooling. The reaction was heated at reflux for one hour, cooled, and saturated aqueous ammonium chloride solution was added until no more solid precipitated. The organic layer was separated, the residue was washed with ether, and the organic layers were combined and dried over anhydrous magnesium sulfate. After being filtered, the ether was distilled off at atmospheric

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pressure. The residue was distilled *in vacuo* to give 4.6 g (60%) of the expected product, bp 88-91°/1.2 mm. The nmr was identical to that reported.[105]

Preparation of 2-Methylindene[106]

To a 100-ml three-necked round-bottomed flask equipped with magnetic stirrer, addition funnel, and reflux condenser was added 4.6 g (0.03 mole) of 2-methyl-2-indanol dissolved in 10 ml of pyridine. Then 7.4 g (0.05 mole) of phosphorous oxychloride in 6 ml of pyridine was added with cooling. The reaction was allowed to stir overnight. After the reaction cooled, ice water (70 ml) was slowly added. The solution was then extracted with pentane and the pentane solution was then extracted with pentane and the pentane solution was washed with 10% hydrochloric acid, sodium bicarbonate solution, and water and was dried over anhydrous magnesium sulfate. After filtration, the pentane was distilled off at atmospheric pressure. The residue was then distilled *in vacuo* to give 2.4 g (60%) of product, bp 85-87°/10 mm. The nmr was identical to that reported.[105]

Preparation of cis-2-Methylhydrindan

Into a 250-cc. hydrogenation bomb were placed 0.26 g (0.002 mole) of 2-methylindene in 30 ml of absolute ethanol and ¼ teaspoon of Raney nickel (W-2); the bomb was then

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pressurized with 1800 psi of hydrogen, heated at 150° for 5 hours and allowed to cool. The product mixture was then removed from the bomb and the bomb was washed with 95% ethanol and then with pentane. The solution was then filtered to remove catalyst, water was added and the solution was extracted with pentane. The pentane solution was washed with water and dried over anhydrous magnesium sulfate. After the solution was filtered, the pentane was distilled off at atmospheric pressure. The residue was then passed by glpc on column C0880-2 at 125° and the major peak collected. The hydrogenation gave three products on analysis: 5.6% of an unidentified product (perhaps the trans isomer), 87.5% of cis-2-methylhydrindan, and 6.9% of starting material.

An infrared spectrum exhibited prominent peaks at 2845 (off scale), 1450, 1375, 1144, 1050, 906, 888, 850, 814, and 602 cm^{-1}.

Nmr signals appeared at δ = 0.83-2.33 (broad complex m).

Anal: Calcd for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 86.80; H, 13,02.

Charge Transfer Complexes of Some Bicyclic Compounds

Procedure. Into a micro uv cell (0.4 ml capacity, 1.000 cm and matched with a regular rectangular cell) was placed 300 µl of tetracyanoethylene (TCNE) solution and

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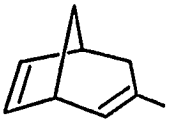
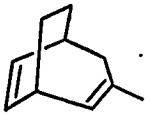
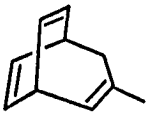
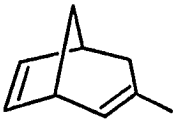
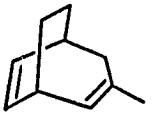
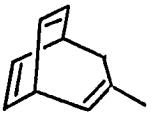
50-60 μl of hydrocarbon. The spectra were recorded in the 400-600 nm region. The tetracyanoethylene (Aldrich) used was sublimed twice. The solvents were spectral quality methylene chloride (MC and B) and analyzed reagent grade chloroform (J. T. Baker).

Results.

Compound	Solvent	TCNE conc (M)	λ_{max}(nm)
	CH_2Cl_2	5.2×10^{-3}	484 ± 2
	CH_2Cl_2	5.2×10^{-3}	460 ± 2
	CH_2Cl_2	2.1×10^{-2}	490 ± 2
	$CHCl_3$	2.1×10^{-2}	498 ± 2
	$CHCl_3$	2.1×10^{-2}	492.5 ± 2
	$CHCl_3$	2.1×10^{-2}	498 ± 2

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Birch Reductions of Bicyclic Systems

Procedure. Into a 25-ml three-necked round-bottomed flask equipped with dry ice condenser, drying tube, and magnetic stirrer and flame-dried under nitrogen was condensed ca. 10 ml of liquid ammonia. Lithium wire (10 mm, 5.0 mmole) was added and allowed to stir for 1-2 minutes. Then 30 µl of hydrocarbon (0.25 mmole) was added and the system was stirred. A proton source (absolute ethanol, 3.0 mmole) was added over the course of some runs. The reaction was quenched by acetone, ferric chloride, or excess ethanol. Then water was added slowly and the mixture was extracted with pentane. The pentane solution was then analyzed by glpc on column CO880-4.

Results.

Compound	Conditions	Time	% Reduction
Norbornadiene	Li/NH_3-Acetone	75 min.	98
Me [3.2.2] diene	Li/NH_3-($FeCl_3$ or EtOH)	15 min.	0.0
	Li/NH_3-$FeCl_3$	75 min.	0.0
	Li/NH_3/EtOH-Acetone	75 min.	7.5
Me [3.2.1] diene	Li/NH_3-Acetone	75 min.	0.0
	Li/NH_3/EtOH-Acetone	15 min.	94.6
	Li/NH_3/EtOH-Acetone*	5 min.	53.6

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Compound	Conditions	Time	% Reduction
Me [3.2.2] triene	Li/NH_3-Acetone	75 min.	0.0
	$Li/NH_3/EtOH$	15 min.	100
	$Li/NH_3/EtOH$-Acetone*	5 min.	67.8

* These are identical reactions, specifically run to measure relative rates of reduction. After 75 and 180 sec., 100 µl absolute ethanol was added in both reactions.

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APPENDIX 1

LIST OF CODE NUMBERS FOR

GAS CHROMATOGRAPHY COLUMNS

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Code	Description
CO880-1	15% IGEPAL (CO880) (nonyl phenoxypolyethoxy-ethylene ethanol) on 80/100 mexh Chromosorb P acid washed-dimethyldichlorosilane treated (AW-DMCS) in ¼ in. o.d. x 2 m copper tubing.
CO880-2	20% IGEPAL (CO880) on 80/100 mesh Chromosorb P (AW-DMCS) in ¼ in. o.d. x 1.5 m copper tubing.
CO880-3	7% IGEPAL (CO880) on 80/100 mesh Chromosorb P (AW-DMCS) in 1/8 in. o.d. x 2.5 m copper tubing.
CO880-4	5% IGEPAL (CO880) on 80/100 mesh Chromosorb P (AW-DMCS) in 1/8 in. o.d. x 7 ft. copper tubing.
TCEP-1	20% 1,2,3-tris(2-cyanoethoxy)propane on 100/120 m Chromosorb P (AW-DMCS) in ¼ in. o.d. x 2 m. copper tubing.

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APPENDIX 2

CODE NUMBERS FOR COMPOUNDS

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Code	Compound
1	7-Isopropenylcycloheptatriene
2	3-Methylbicyclo [3.2.2] nona-2,6,8-triene
3	2-Isopropenylcycloheptatriene
4	3-Isopropenylcycloheptatriene
5	1-Isopropenylcycloheptatriene
6	cis-1-Methyl-8,9-dihydroindene
7	cis-2-Methyl-8,9-dihydroindene
8	Monohomocyclooctatetraene dianion
9	Bicyclo [3.2.1] octadienyl anion
10	Bicyclo [3.2.2] nonatrienyl anion
11	Bicyclo [3.2.1] octa-2,6-diene
12	Bicyclo [3.2.1] oct-2-ene
13	3-Methyltricyclo [3.3.1.$0^{2,8}$] nona-3,6-diene
14	3-Methyltricyclo [3.2.1.$0^{2,7}$] oct-3-ene
15	3-Methyl-4-trichloroacetoxybicyclo [3.2.1] oct-2-ene
16	3-Methylbicyclo [3.2.1] octenyl carbonium ion
17	3-Methylbicyclo [3.2.1] octa-2,6-diene
18	3-Methylbicyclo [3.2.2] nona-2,6-diene
19	Bicyclo [2.2.1] hepta-2,5-diene
20	3-Methylbicyclo [3.2.1] oct-2-ene
21	3-Methylbicyclo [3.2.1] oct-6-ene
22	Bicyclo [3.2.1] octane

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23 3,7,7-Trimethylcycloheptatriene

24 6,7-Dicarbomethoxybicyclo [3.2.2] nona-3,6,8-trien-2-one

25 1,2-Dicarbomethoxybicyclo [4.1.0] hepta-2,4-diene-7-ketene

26 8,9-Dicarbomethoxydihydroinden-1-one

27 cis and trans-7-propenylcycloheptatriene

28 1-phenyl-2-butene

29 cis and trans-3- and 1-Propenylcycloheptatriene

30 2-Methylindene

31 1-Phenyl-1-butene

32 3-Methylindene

33 1,2-Dihydronaphthalene

34 Methallylbenzene

35 β,β-Dimethylstyrene

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APPENDIX 3

INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTRA

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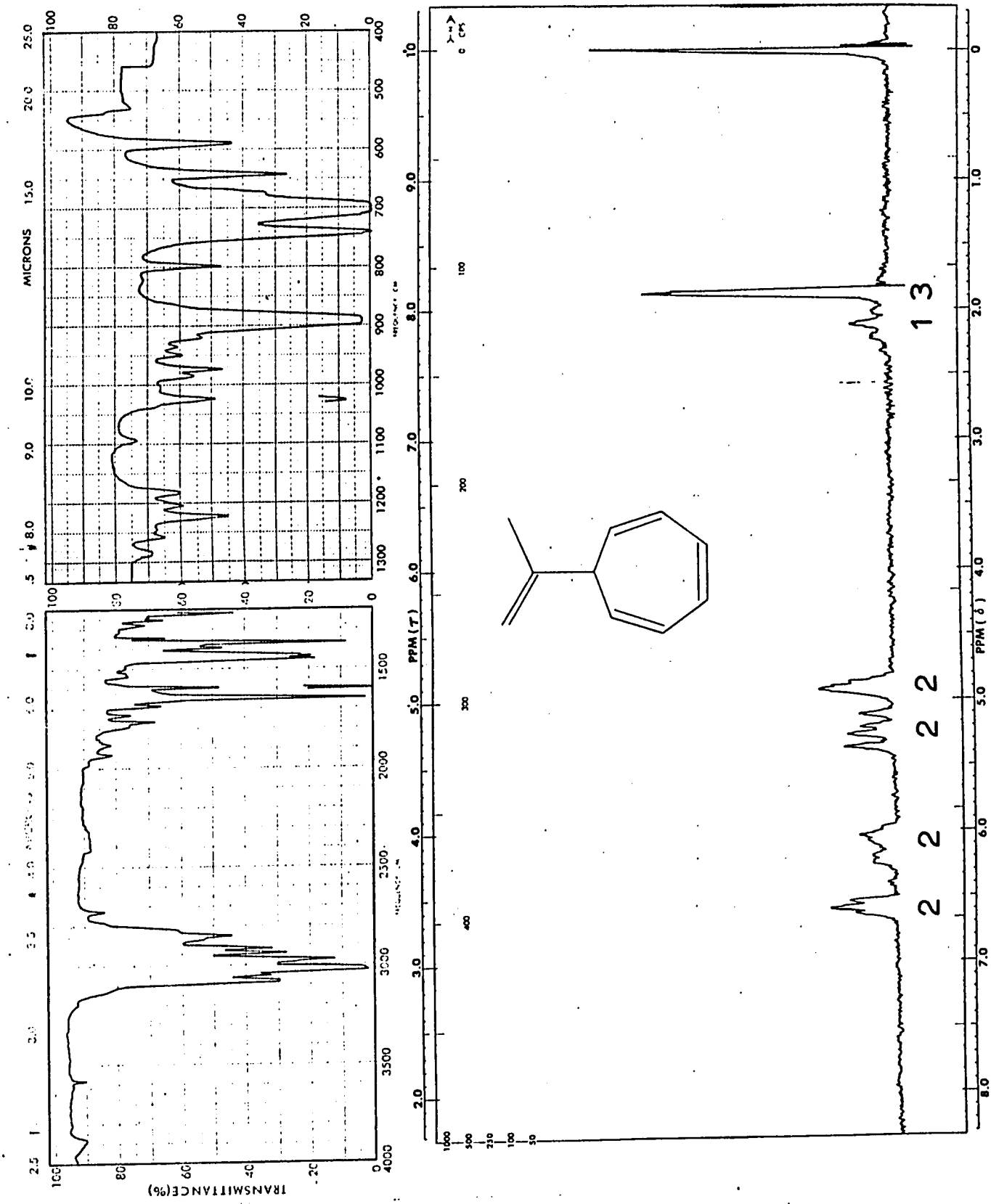

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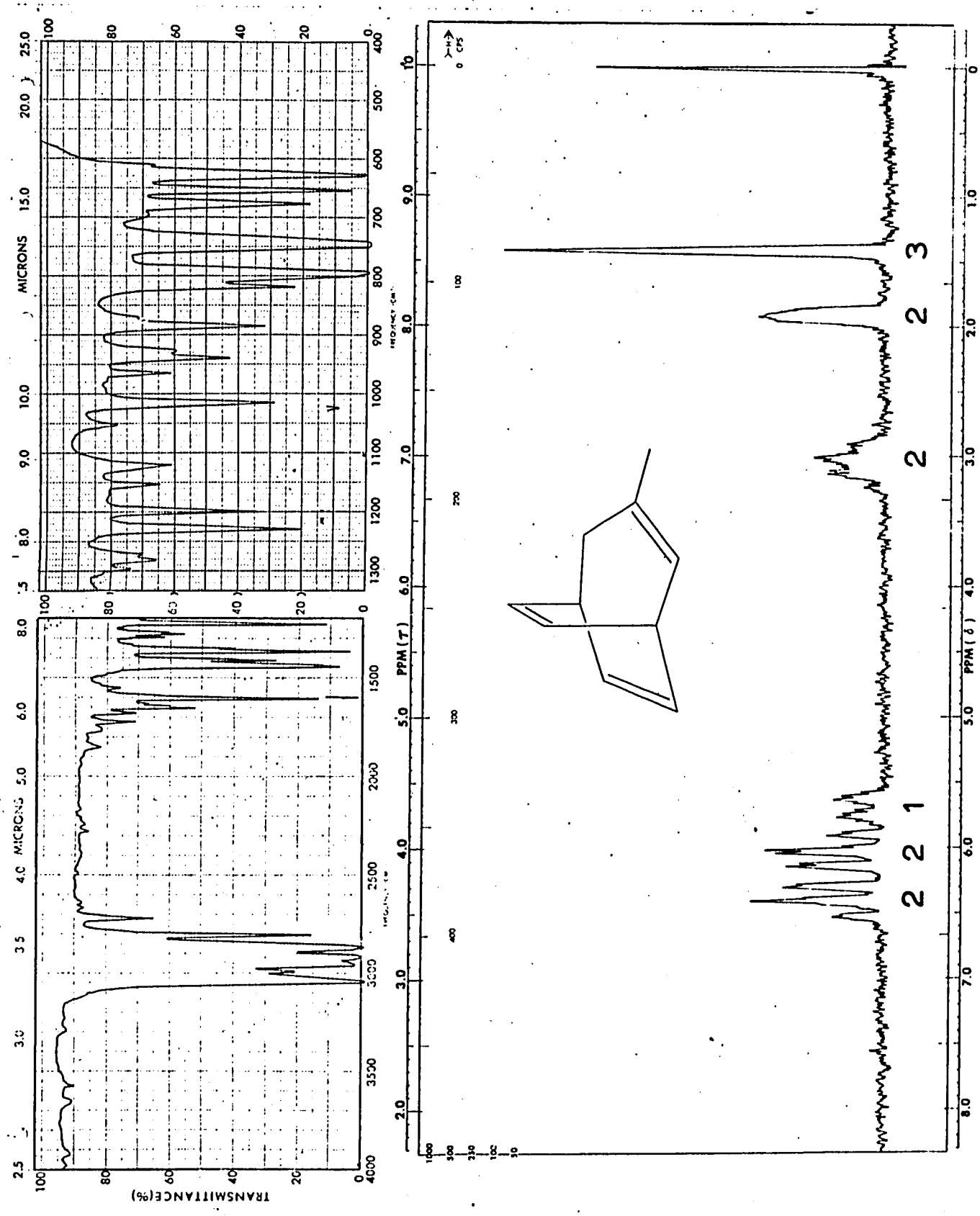

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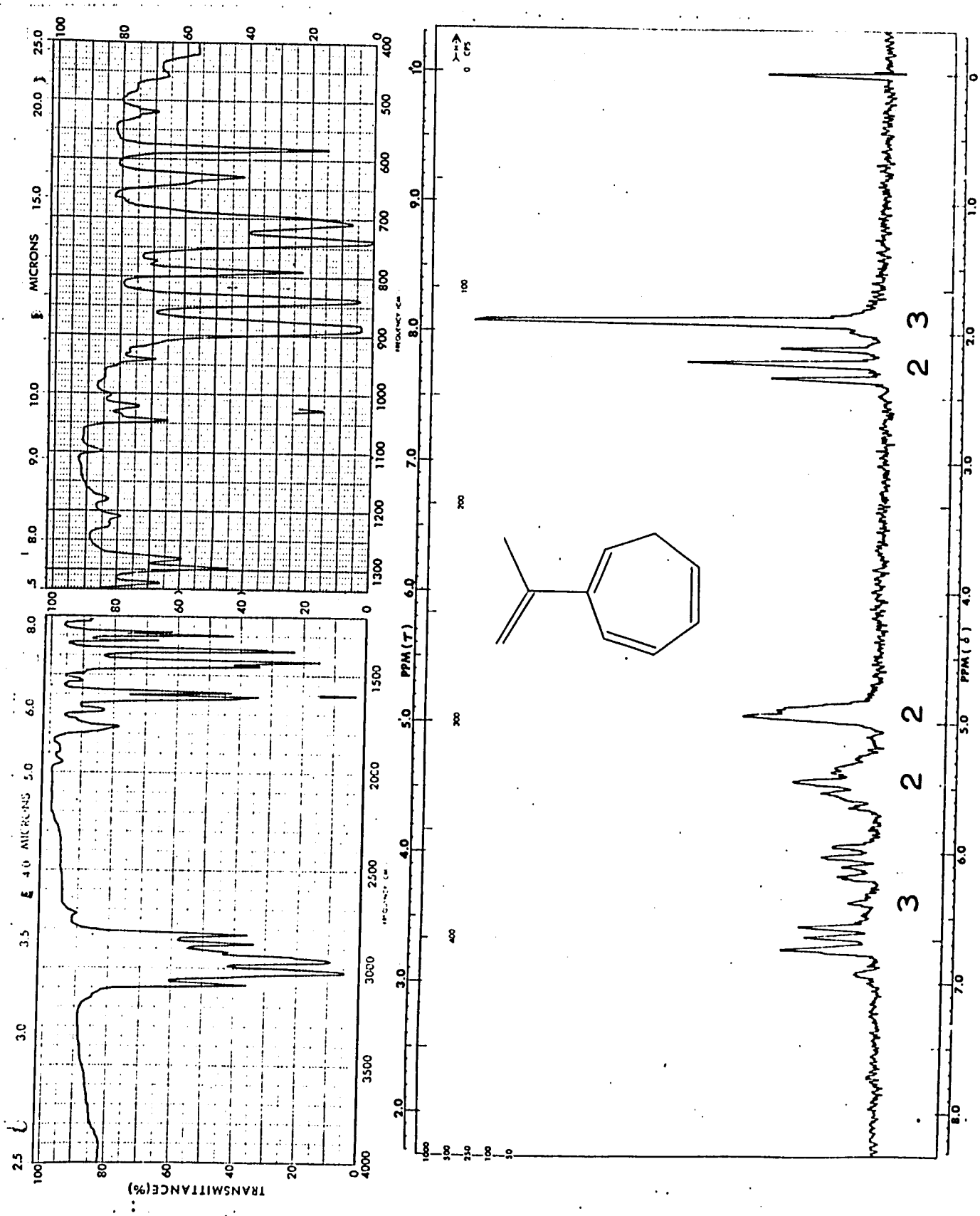

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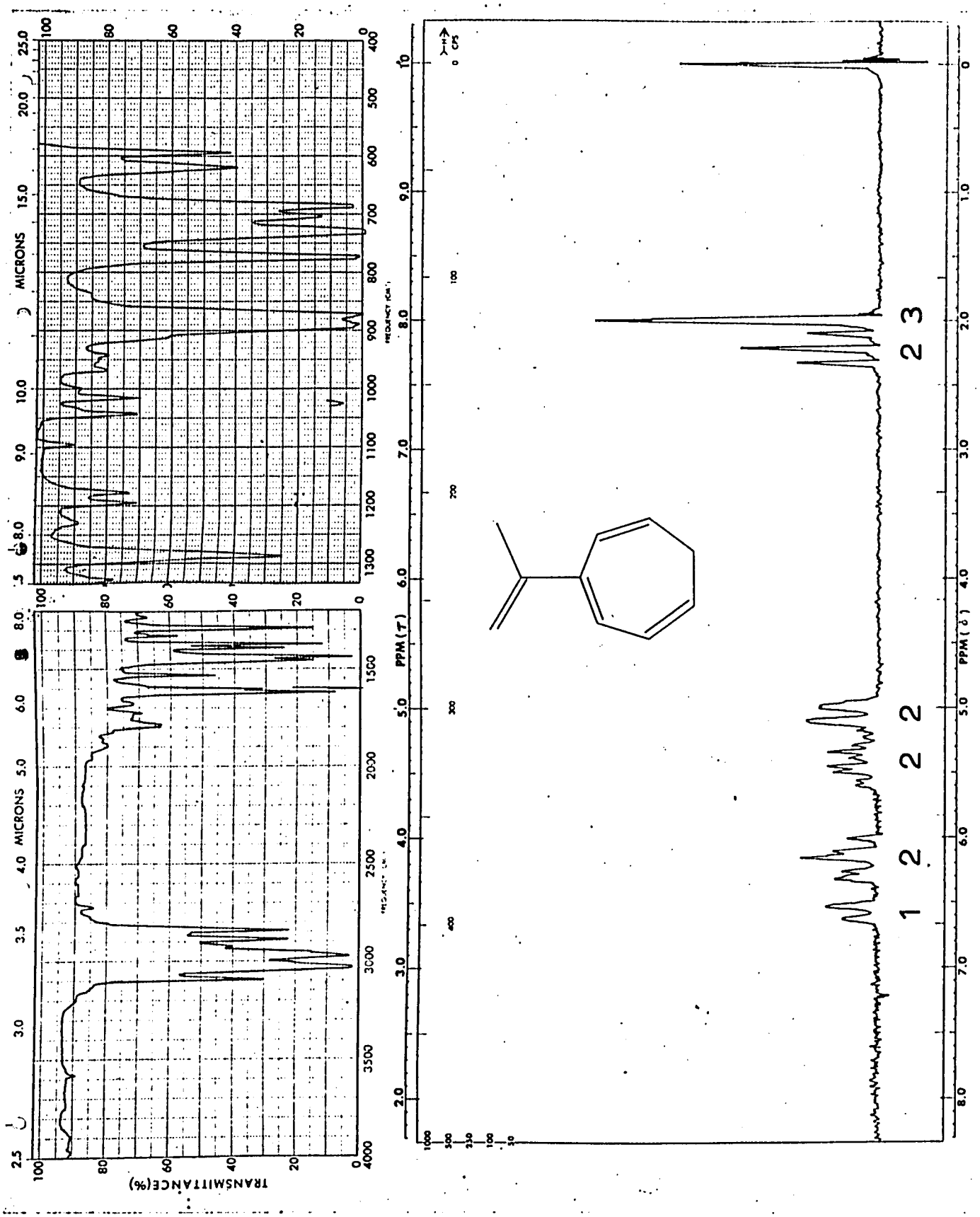

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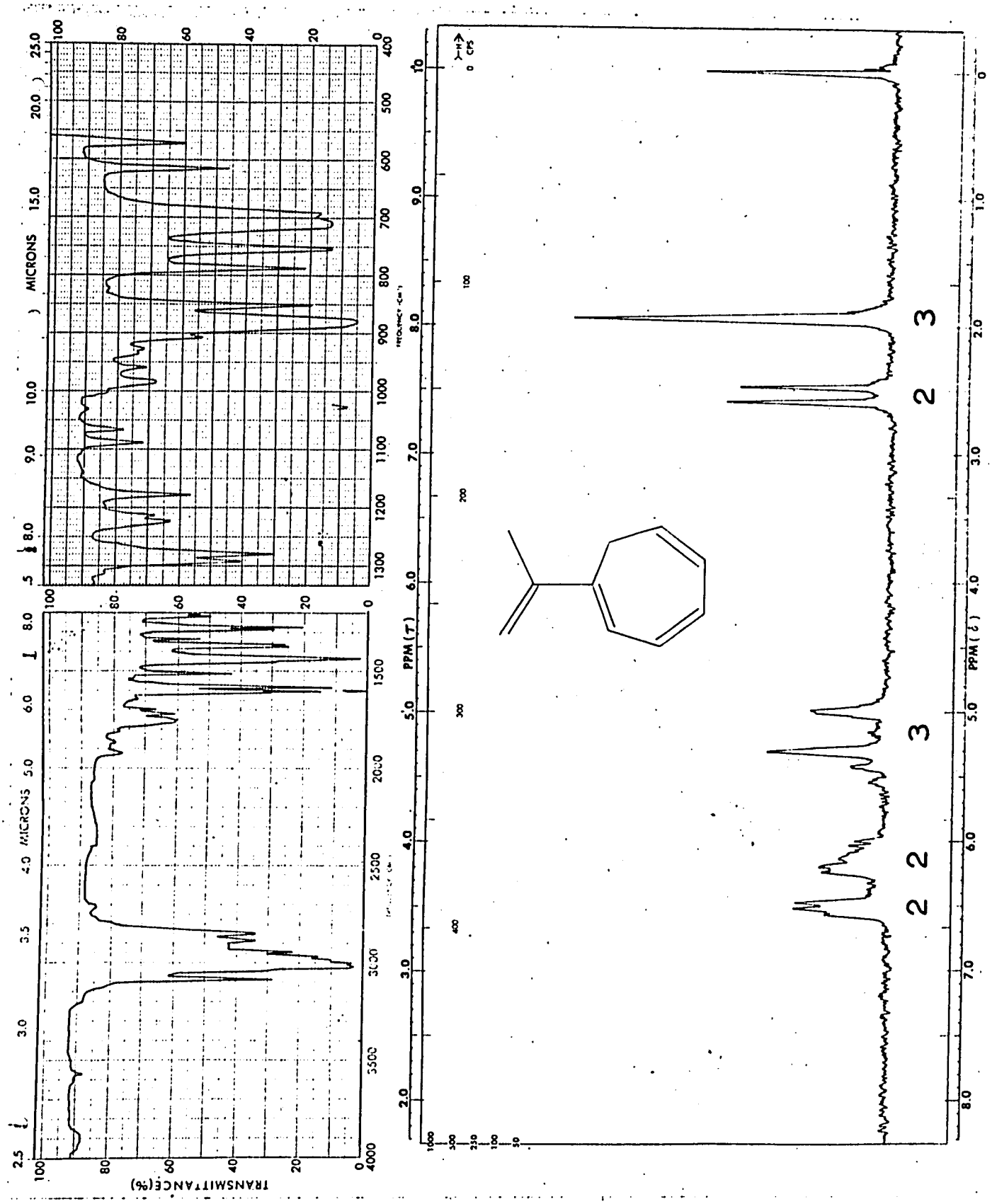

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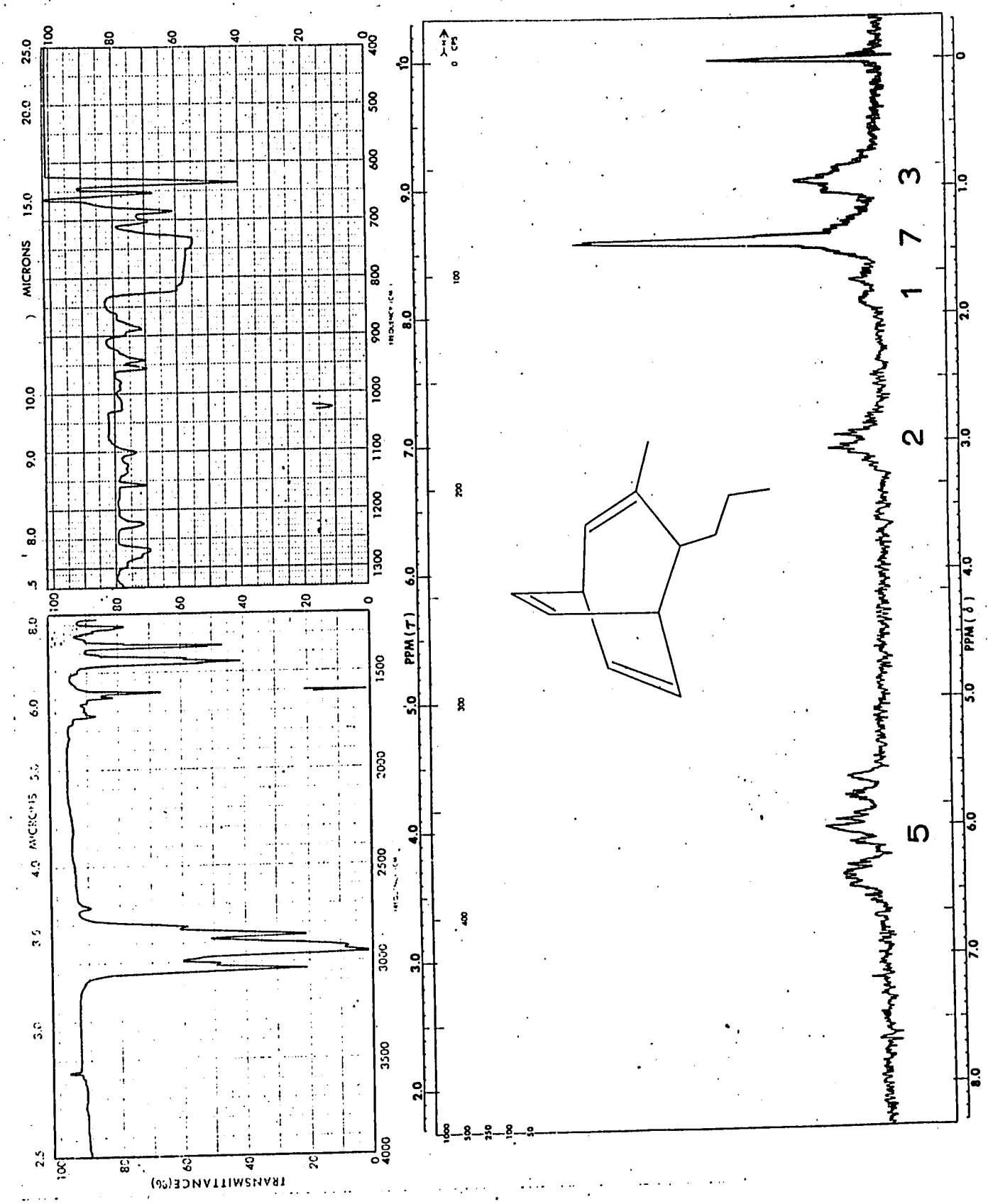

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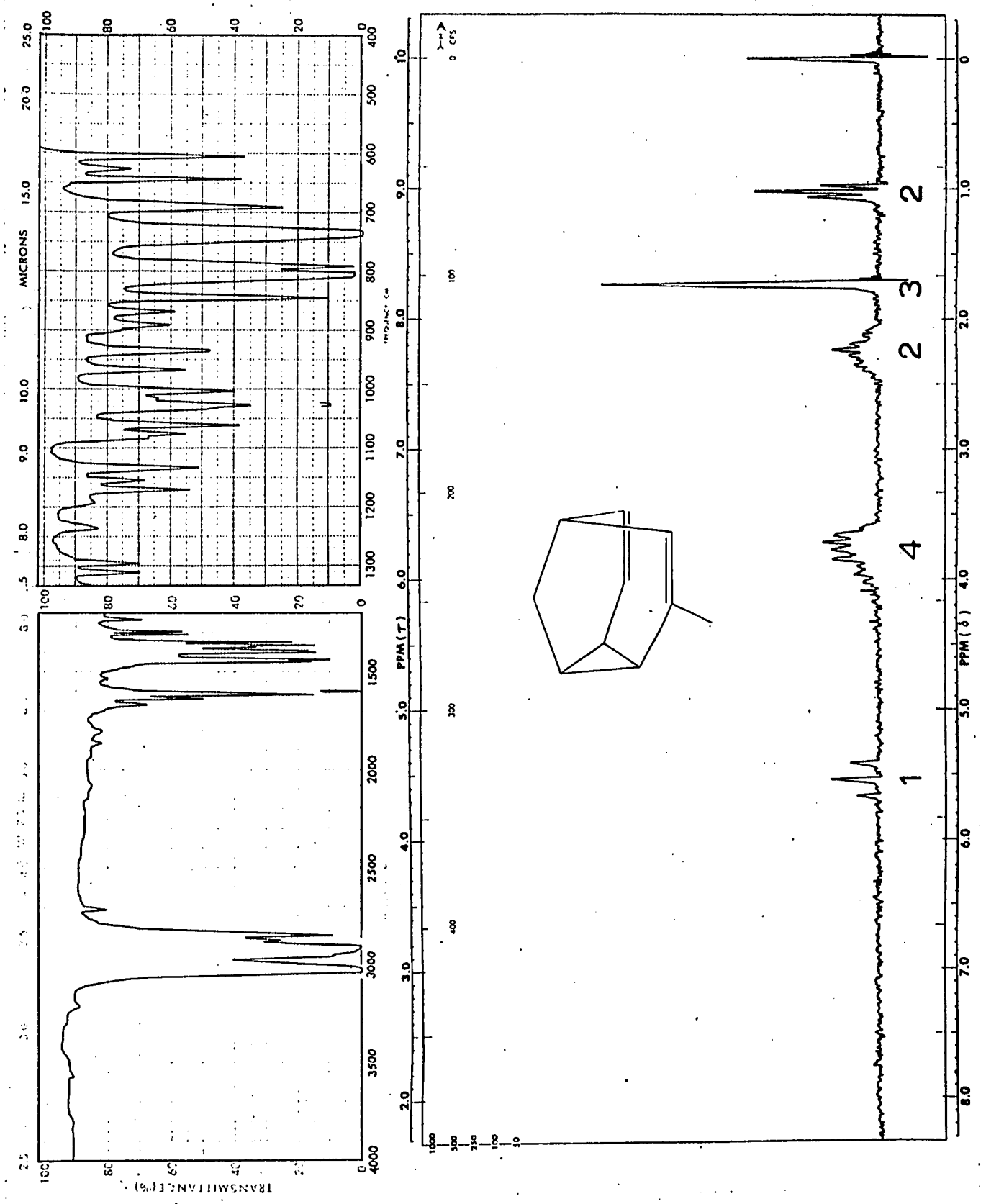

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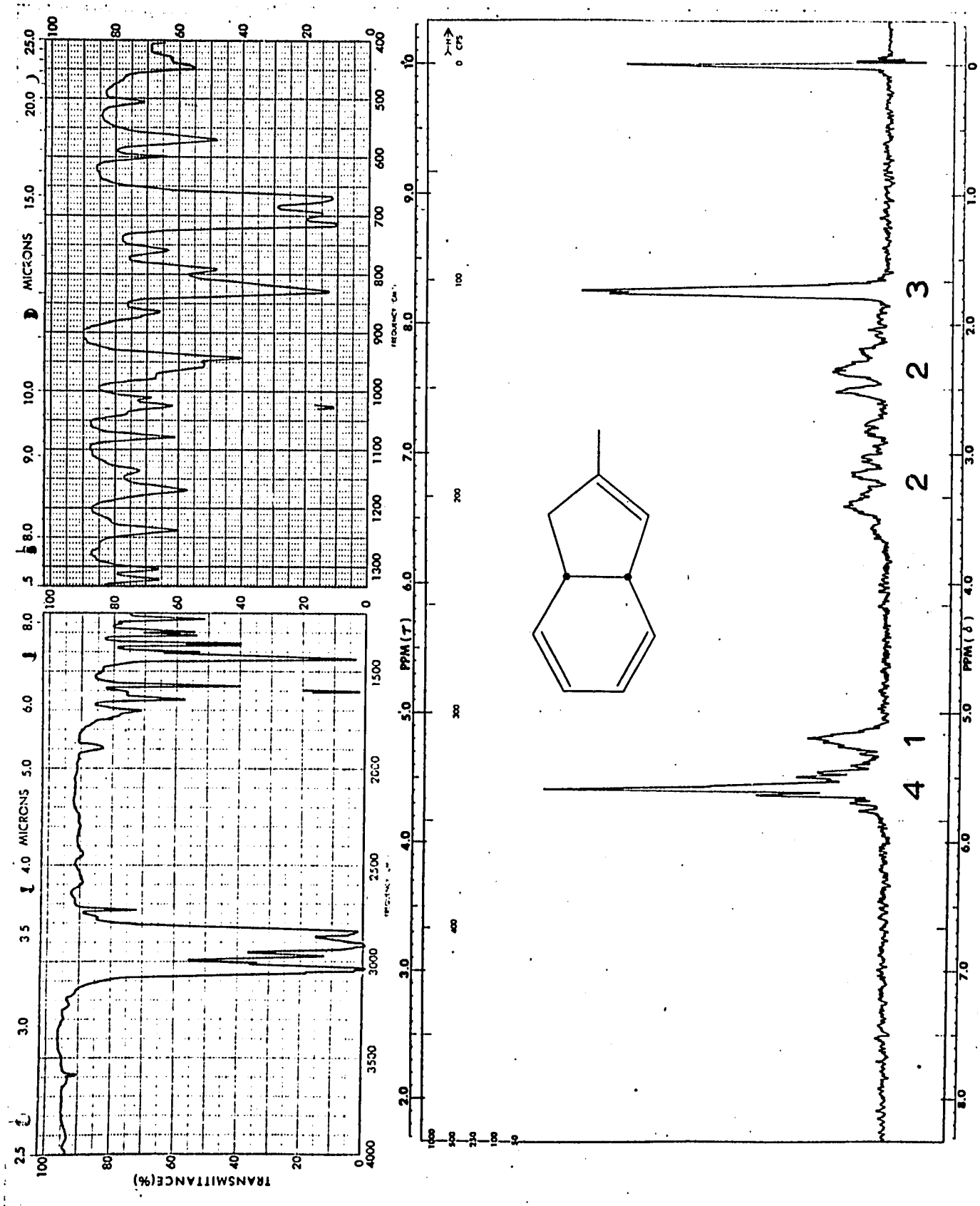

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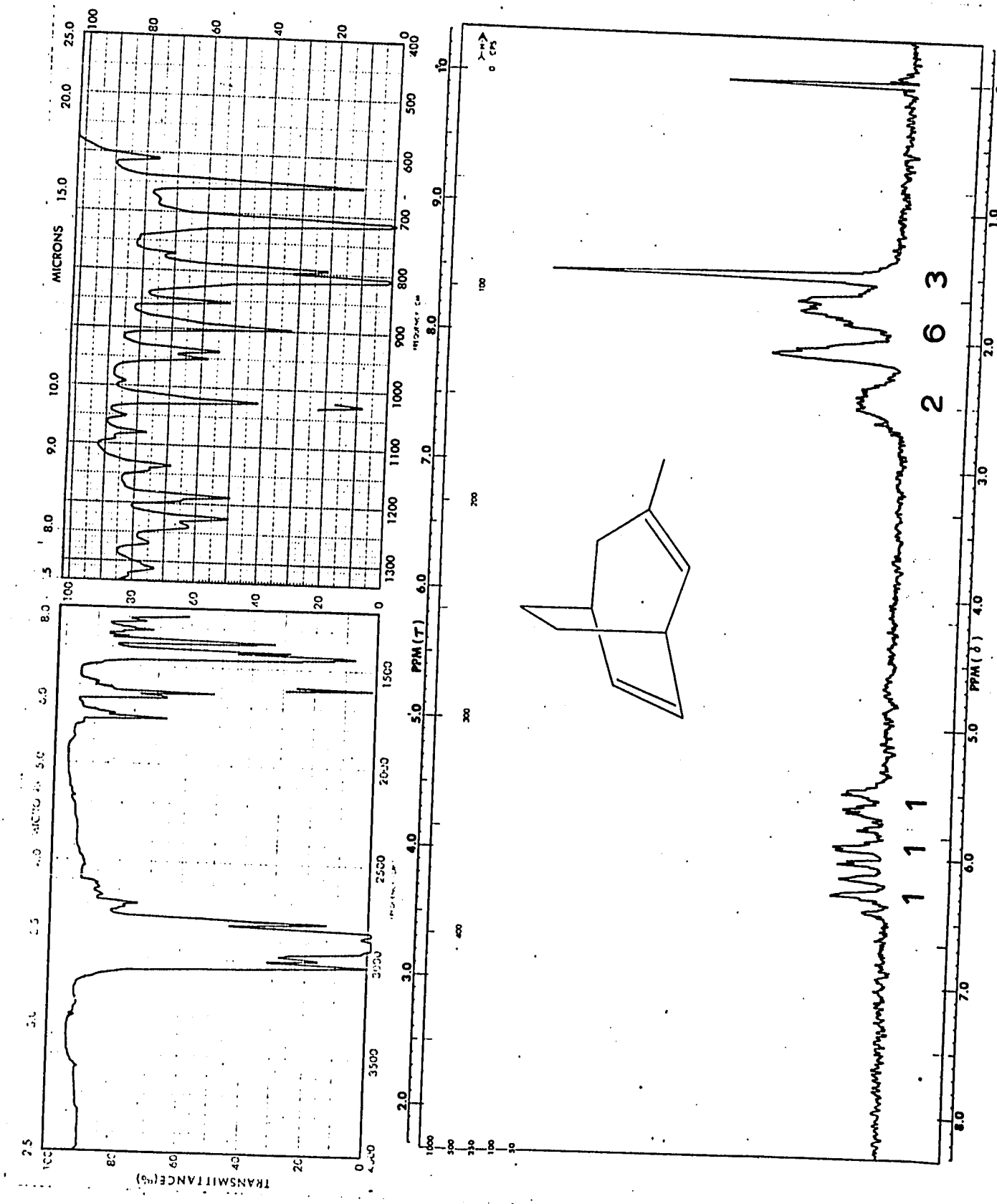

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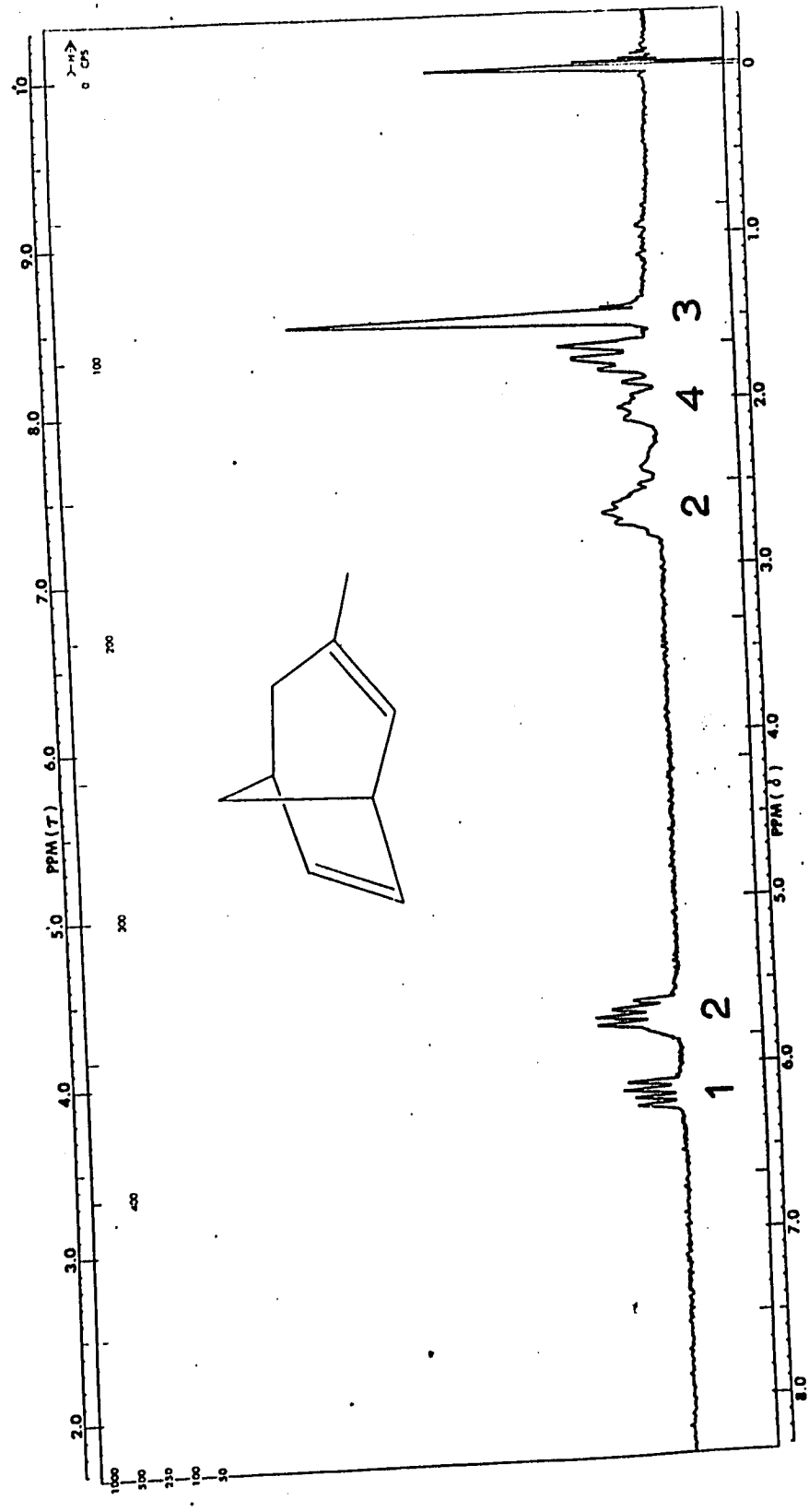

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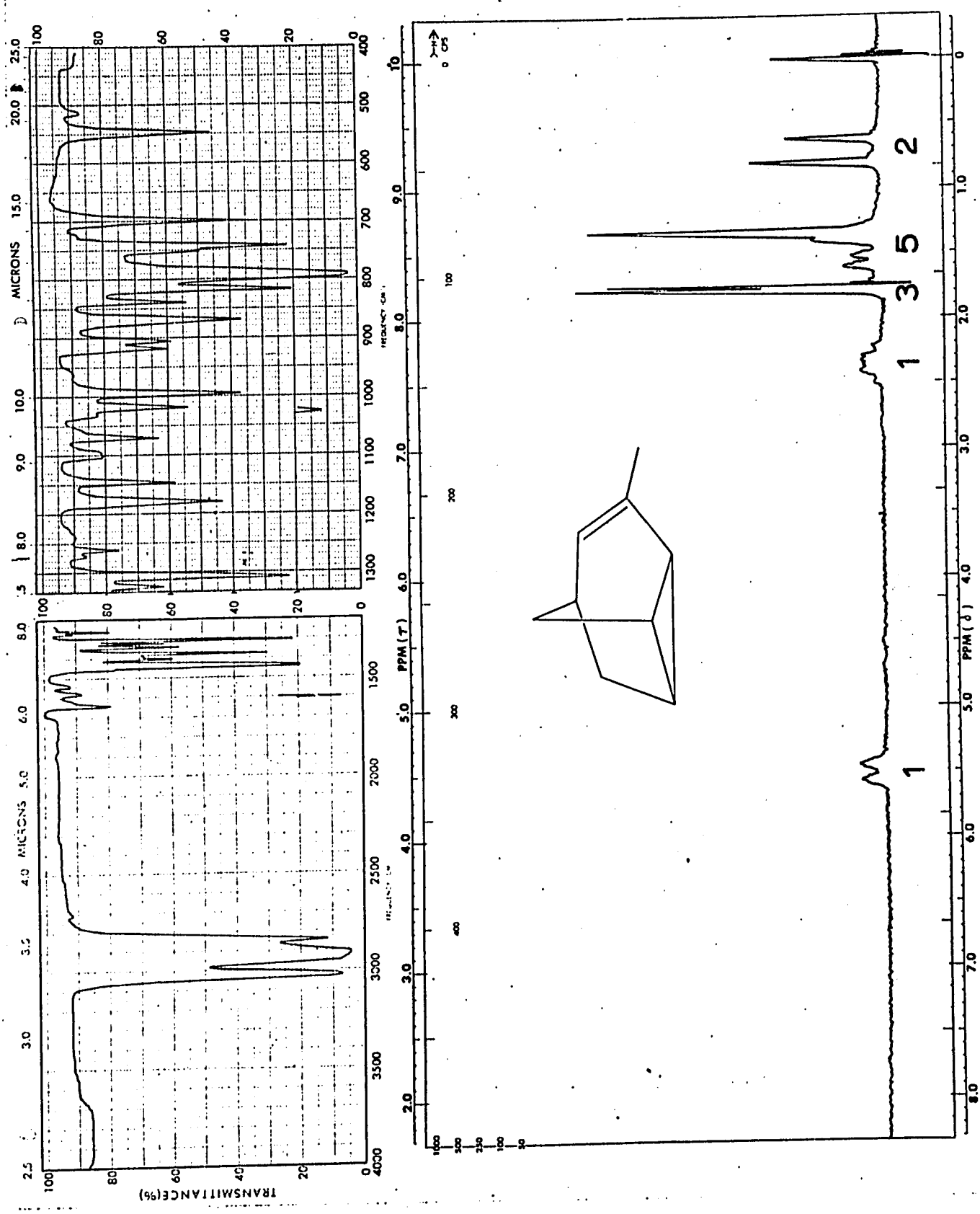

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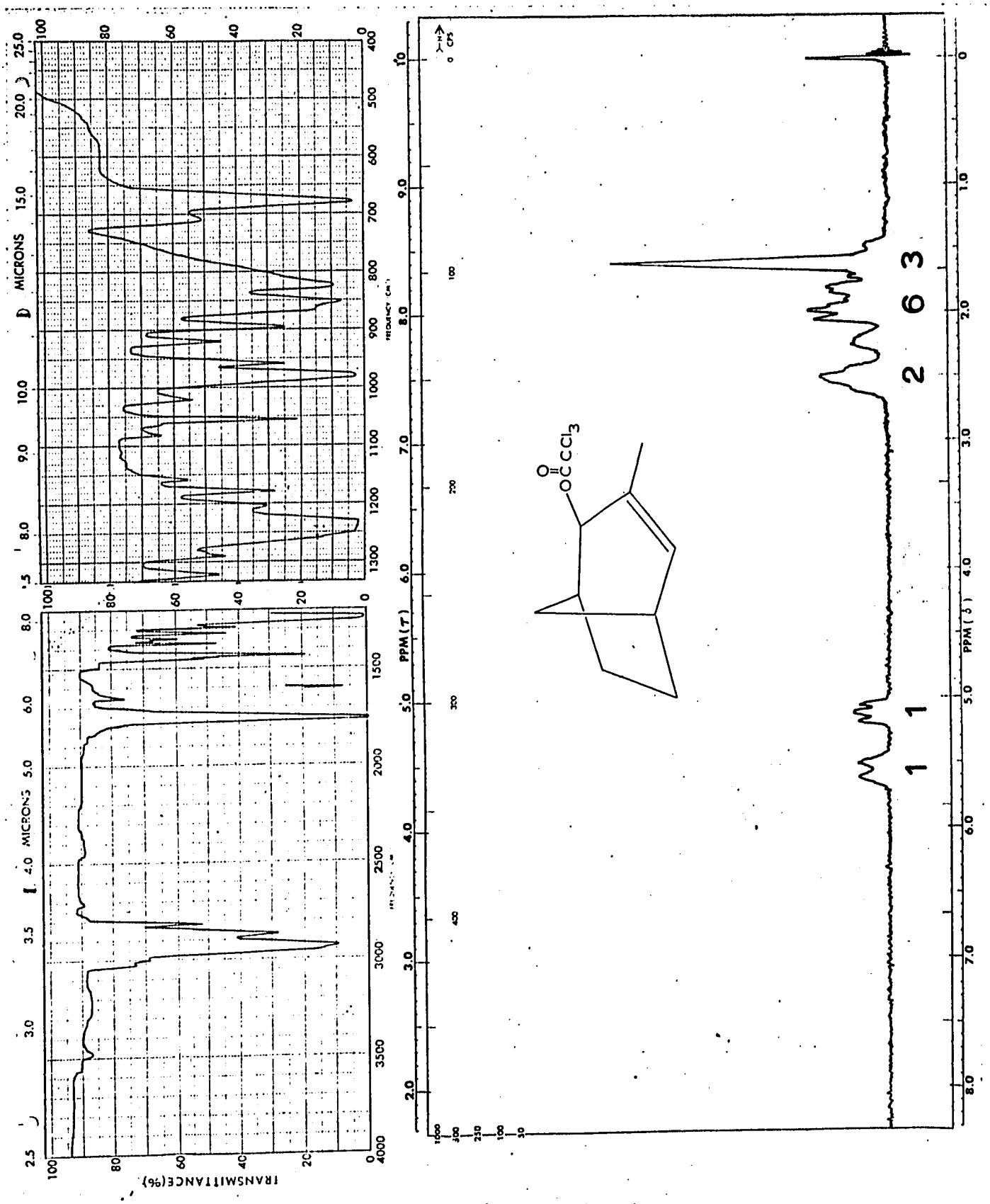

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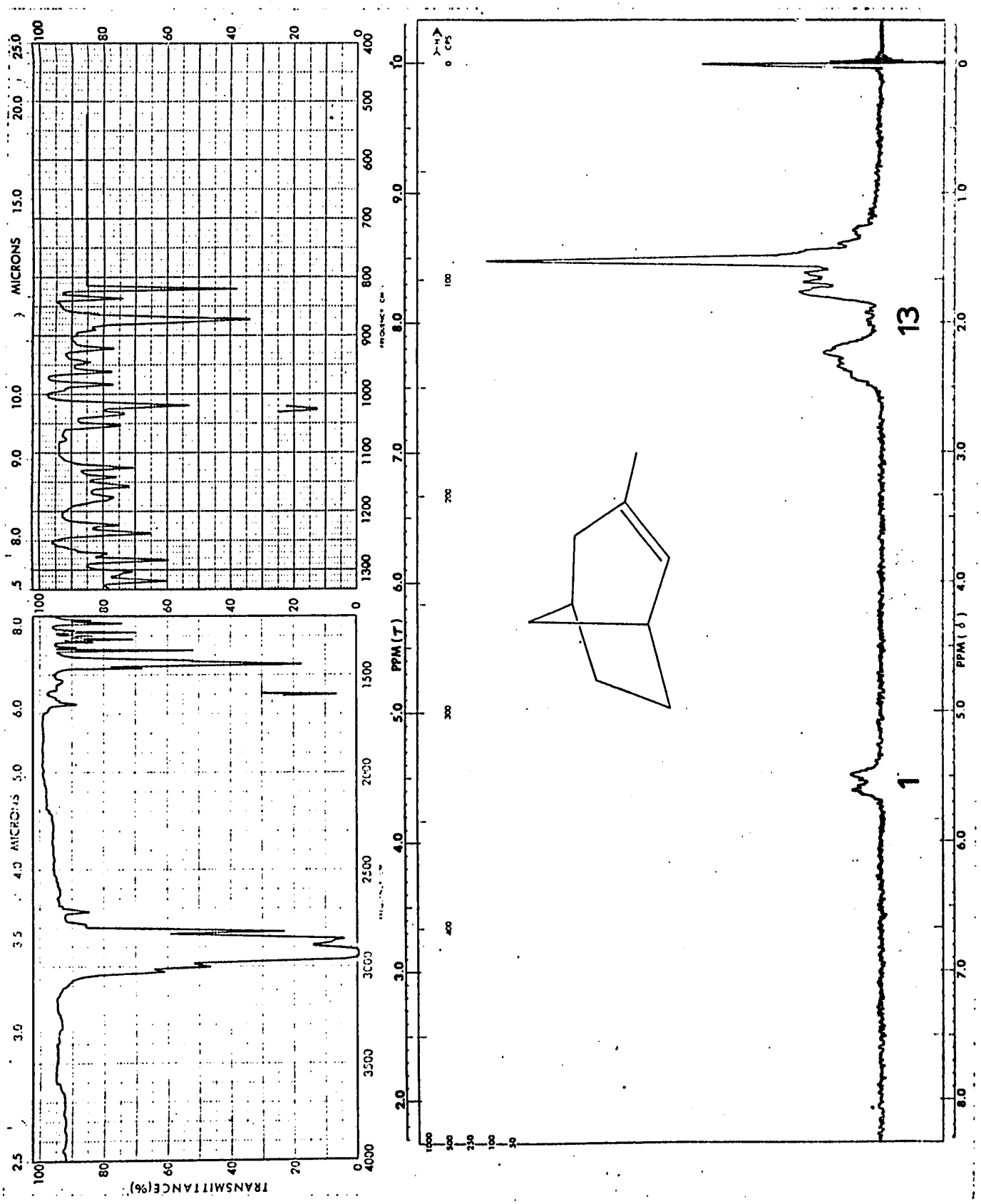

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