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HARTLESS, RAY LAWSON. Protonation of the Isopropenylcyclopentadienyl Anion: Trapping of the Isomer Mixture with Tetracyanoethylene. (1971) Directed by: Dr. David B. Knight pp. 71

The isomers obtained by protonation of the isopropenylcyclopentadienyl anion undergo reactions on standing which change the relative percentages of each isomer in the mixture. The suitability of tetracyanoethylene as a trapping agent is confirmed by the internal consistency of the relative percentages of the Diels-Alder adducts and isomers.

Trapping of the isomer mixture with tetracyanoethylene yields three stable Diels-Alder adducts. The adducts were isolated by fractional crystallization and identified by their characteristic nuclear magnetic resonance, infrared spectra, and elemental analyses. The adducts and their relative percentages were: 7-isopropylidene-5,5,6,6-tetracyanonorbornene ( $11.4 \pm 2.0\%$ ), 2-isopropenyl-5,5,6,6-tetracyanonorbornene ( $28.9 \pm 1.3\%$ ), and 3a,6,6-trihydro-4,4,5,5-tetracyanoindene ( $58.5 \pm 3.2\%$ ). Protonation of the anion yielded  $17 \pm 3\%$  dimethylfulvene,  $25 \pm 2\%$  2-isopropenyl-1,3-cyclopentadiene, and  $57 \pm 2\%$  1-isopropenyl-1,3-cyclopentadiene.

b

PROTONATION OF THE ISOPROPENYLCYCLOPENTADIENYL  
ANION: TRAPPING OF THE ISOMER MIXTURE  
WITH TETRACYANOETHYLENE

by

Ray Lawson Hartless

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Approved by

David B. Knight  
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APPROVAL SHEET

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R.L.H.

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## INTRODUCTION

Mesomeric intermediates can undergo reactions which yield a mixture of products. The nature of the mixture is governed by the orientation of the attacking species on the mesomer. Several explanations of the orientation in these types of reactions have been presented, but they are not mutually exclusive in all cases. The explanations include charge density, Ingold's postulate, ion-pair formation, leaving group effects, product stability, and extent of geometric change. The reliability of the proposed orientation factors can vary depending on the particular system to which they are applied.

Hammond (1) explained the carbanion protonation reaction in terms of the transition state and charge density. The geometric center of charge density is the attacked site when the transition state appears early; whereas the site of highest charge is attacked if the transition state appears late. This implies that the product distribution is not a function of stability for a highly reactive mesomer, since the products should be structurally different from the transition state.

Ingold (2) postulated that when addition of a proton to a mesomeric anion leads to products of unequal stability, the product formed most rapidly is the thermodynamically

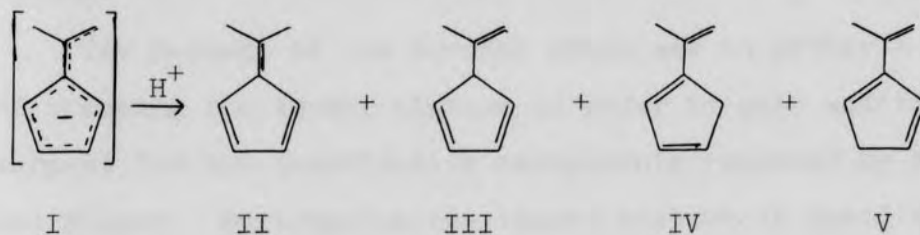
least stable. There are examples of benzyl type carbanion reactions in which attack is more rapid at the benzyl carbon atom than in the aromatic ring (3).

Steric effects have been reported to have an effect on the orientation of an attacking species (4). These effects include ion-pair formation (5), leaving group interference (6), and hindrance to attack by bulky substituents. Solvent effects have been reported to affect the reactivity of mesomeric species (7).

Hine (8,9) has shown that the extent of geometric change in going from mesomer to products is useful in predicting product distributions. This Principle of Least Motion (PLM) predicts that the reaction will proceed via the path which involves the least atomic displacement.

Assessment of the relative importance of the explanations of orientation in reactions of mesomeric species was the basis of a study by Hine and Knight (10), specifically the reactions of the anion (I) derived from dimethylfulvene. They reported the results of the kinetically controlled protonation of the anion (I) derived from dimethylfulvene under conditions that hopefully would ensure kinetic control, and they discussed the relative importance of factors which orient the attack of the proton on the mesomeric species. They noted that simple protonation of the anion can give dimethylfulvene (II), 5-isopropenyl-1,3-cyclopentadiene (III), the linearly conjugated product

1-isopropenyl-1,3-cyclopentadiene (IV), or the cross conjugated product 2-isopropenyl-1,3-cyclopentadiene (V).



The focus of the study was the quantitative assessment of the ratio of the four isomeric products. The quantities of each isomer were obtained by planimetric integration of the nmr spectrum of the isomer mixture. This technique was used since the components were not amenable to simple physical separation. The reported values for isomers II, IV, and V were 21%, 57% and 21% respectively. No conclusive evidence for the presence of III was obtained. However, Hine and Knight reported that it is possible III was formed in significant amounts but rearranged prior to analysis.

It was noted that discussion of orientation factors governing the proton attack was pertinent only if the protonated isomer products represented the kinetically controlled mixture and not a mixture derived from subsequent rearrangements. The possible ways by which the results could be equivocated include Diels-Alder addition of the

isomers with themselves and with each other, and uncatalyzed sigmatropic migration of hydrogen around the ring system.

The purpose of the present study was to devise a means of trapping the isomer mixture in order to gain additional support for the quantitative assignments reported by Hine and Knight. By trapping the isomer mixture as rapidly as possible, it was expected that the extent of Diels-Alder addition and sigmatropic rearrangement would be reduced, thereby providing a more precise estimate of the kinetically controlled protonation mixture.

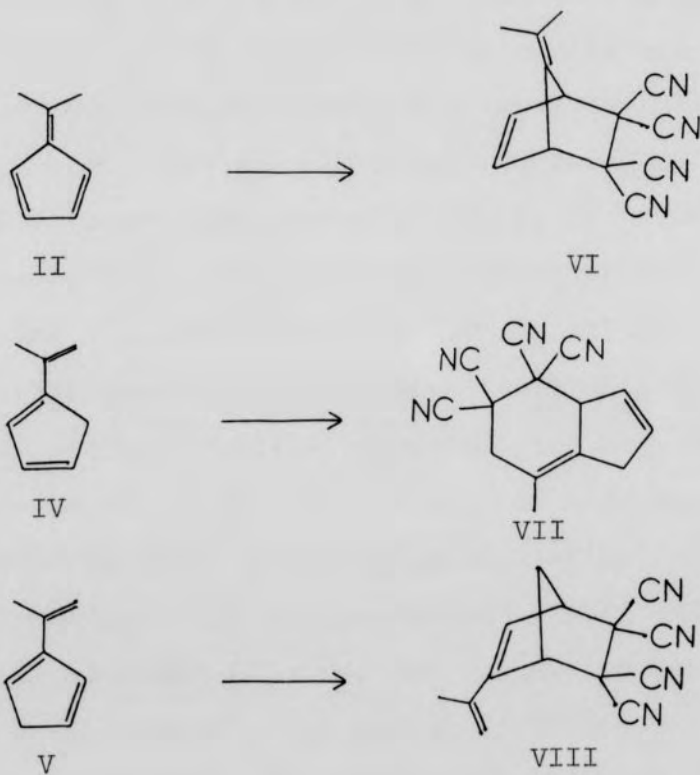
The trapping agent selected was tetracyanoethylene (TCNE), since it is known to be highly reactive toward conjugated dienes and the reaction proceeds via a Diels-Alder addition to yield stable solid adducts. The unusually high reactivity of TCNE toward conjugated double bonds to yield stable adducts is attested by the comparative reaction rates of maleic anhydride and TCNE with conjugated dienes (11). The reactions of TCNE and maleic anhydride with 2,3-dimethylbutadiene at 25° had rate constants of 240 and 2.0  $\text{l}\cdot\text{mole}^{-1}\cdot\text{hour}^{-1}$  respectively. Trans-pentadiene reacted with TCNE and maleic anhydride at 25° with rate constants of 27 and 0.92  $\text{l}\cdot\text{mole}^{-1}\cdot\text{hour}^{-1}$  respectively. It has been noted by Middleton *et al.* (12), that an exothermic reaction occurs when TCNE is mixed with most conjugated

dienes even at 0°. TCNE has the additional advantages of containing no protons and being symmetrically substituted. This tends to simplify identification of the adducts by nmr spectral analyses. Since isomers IV and V were inseparable by fractional distillation or preparative gas-liquid partition chromatography (glpc), the TCNE solid adducts should provide a means of separating, identifying, and quantitatively analyzing the isomer mixture.

In general, the procedure developed by Hine and Knight was followed in carrying out the kinetically controlled protonation of the dimethylfulvenide anion I. This anion was generated by treatment of dimethylfulvene with an equimolar quantity of potassium *t*-butoxide in bis(2-methoxyethyl) ether (diglyme). The anionic solution was quenched with aqueous acid. The isomer mixture so formed containing II, IV, and V was reacted as rapidly as possible with TCNE in a variety of solvents to form the Diels-Alder addition products. These adducts were isolated by fractional crystallization. The molecular structure of each of the adducts was determined by interpretation of their individual nmr spectra and supplemented by data from infrared spectroscopy and elemental analysis.

Material balance was not realized during isolation of the adducts by fractional crystallization; therefore the quantities of each were obtained by nmr spectroscopy. The

relative percentages of the Diels-Alder adducts were obtained by reacting the protonated isomers with TCNE dissolved in acetone- $d_6$ , the reaction being carried out in an nmr tube. Integration of the nmr spectrum of the resulting mixture showed  $11.4 \pm 2.2\%$  of the dimethylfulvene adduct (7-isopropylidene-5,5,6,6-tetracyanonorbornene VI),  $58.5 \pm 3.2\%$  of the adduct derived from the linearly conjugated isomer (3a,6,6-trihydro-4,4,5,5-tetracyanoindene VII), and  $28.9 \pm 1.3\%$  of the cross conjugated isomer adduct (2-isopropenyl-5,5,6,6-tetracyanonorbornene VIII).



These percentages are consistent with the results obtained by Hine and Knight, namely 21% dimethylfulvene (II), 57% lineally conjugated isomer (IV), 21% cross conjugated isomer (V), and no conclusive evidence for the presence of the deconjugated product (III).



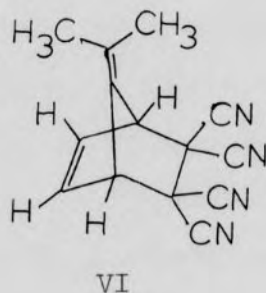
## RESULTS

The kinetically controlled protonation of the isopropenylcyclopentadienyl anion yields a mixture of three isomers, namely 21% dimethylfulvene (II), 57% 1-isopropenyl-1,3-cyclopentadiene (IV), and 21% 2-isopropenyl-1,3-cyclopentadiene (V) as previously reported (10).

In the present study, the isomerization was repeated several times following the procedure developed earlier (10). Dimethylfulvene was added to a slurry of potassium tert-butoxide in diglyme. The resulting anionic solution was added to an aqueous acid solution and rapidly extracted into an organic solvent. Analysis by analytical gas-liquid partition chromatography (glpc) revealed two peaks corresponding to 80% isomer (IV + V) and 20% dimethylfulvene. (Retention times 3.1 and 4.6 mins at 110° on Apiezon-L column). Rapidly trapping the mixture with TCNE yielded a mixture of Diels-Alder addition products. The mixture of adducts consisted of the adduct derived from addition across the conjugated endocyclic double bonds of dimethylfulvene (VI) and 2-isopropenyl-1,3-cyclopentadiene (VIII), and the adduct obtained by addition across the conjugated system containing the isopropenyl substituent of 1-isopropenyl-1,3-cyclopentadiene (VII). The isomer mixture (~ 0.04 mole)

was trapped in a variety of solvents and the solvents removed by vacuum distillation. Compound VII was isolated by fractional crystallization in toluene-petroleum ether and recrystallized in the same medium. Compound VIII was separated from VI by fractional crystallization from acetone-petroleum ether.

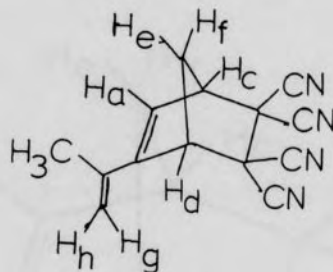
The adduct of TCNE and dimethylfulvene (VI) is a known compound (13) whose physical and spectral characteristics were consistent with the assigned structure:



The nmr spectrum in acetone- $d_6$  consisted of broadened triplets at 6.88 and 4.83  $\delta$  (olefinic and bridgehead protons respectively) and a singlet at 1.83  $\delta$  assigned to the isopropylidene methyl hydrogens. The integrated spectrum showed a proton ratio of 1:1:3 consistent with structure VI.

The infrared spectrum of VIII showed a weak absorption at 2250  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ) and strong absorptions at 1620 and 832  $\text{cm}^{-1}$  (trisubstituted olefin) and 910  $\text{cm}^{-1}$  (terminal olefinic protons) (14). The very low intensity of the

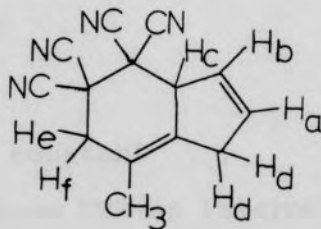
nitrile peak is consistent with the decrease expected for  $\alpha$ -substitution of an electron withdrawing group (15).



VIII

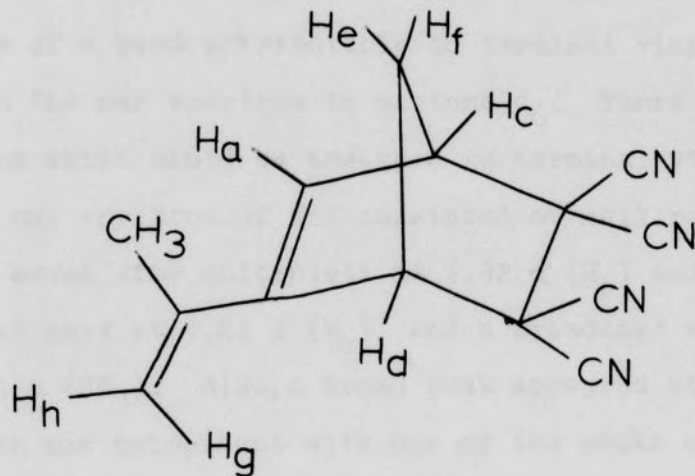
The nmr spectrum of VIII in acetone- $d_6$  contained a broadened doublet at 6.50  $\delta$  ( $H_a$ ), broadened peaks at 5.63  $\delta$  ( $H_g$ ) and 5.33  $\delta$  ( $H_h$ ), broadened five and six line multiplets at 4.69  $\delta$  ( $H_d$ ) and 4.33  $\delta$  ( $H_c$ ) respectively, an AB quartet with the doublets centered at 2.35  $\delta$  ( $H_e$ ) and 2.16  $\delta$  ( $H_f$ ), and a slightly broadened multiplet at 1.92  $\delta$  ( $CH_3$ ). The spectrum integrated for a total of ten protons which is consistent with structure VIII. The information obtained by nmr analysis is summarized in Table I. Elemental analysis, melting point, and differential thermal analysis indicated purity of sample.

The essential feature in the infrared spectrum of VII



VII

Table I  
Chemical Shifts and Coupling Constants in Compound VIII



$\delta$  (ppm)<sup>a, b</sup>

$J$  (cps)

H <sub>a</sub>	6.50	$J_{ac} = 3.2$
H <sub>c</sub>	4.33	$J_{af} \approx 0.5^{**}$
H <sub>d</sub>	4.69	$J_{cd} = 1.5$
H <sub>e</sub>	2.35	$J_{ce} = 1.6$
H <sub>f</sub>	2.16	$J_{cf} = 1.5$
H <sub>g</sub>	5.63	$J_{de} = 1.6$
H <sub>h</sub>	5.33	$J_{df} = 1.5$
CH <sub>3</sub>	1.92	$J_{d-?} = 1.5^{**}$
		$J_{ef} = 11.5$

\*\* invoked coupling constant

<sup>a</sup> downfield shift from TMS as internal standard

<sup>b</sup> 100 MHz in acetone-d<sub>6</sub>

was the absence of a peak between  $880\text{-}910\text{ cm}^{-1}$  generally attributed to terminal vinyl protons. The infrared spectrum did contain a weak band at  $2250\text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ). The lack of a band attributable to terminal vinyl protons agreed with the nmr spectrum in acetone- $\text{d}_6$ . There were no absorptions which could be assigned to terminal vinyl protons. The nmr spectrum of VII consisted of well resolved eight and seven line multiplets at  $6.42\ \delta$  ( $\text{H}_b$ ) and  $6.09\ \delta$  ( $\text{H}_a$ ), a broad peak at  $4.21\ \delta$  ( $\text{H}_c$ ), and a broadened multiplet at  $1.83\ \delta$  ( $\text{CH}_3$ ). Also, a broad peak appeared at  $3.23\ \delta$  ( $\text{H}_d$ ) which was coincident with one of the peaks of an AB quartet with doublets centered at  $3.03\ \delta$  ( $\text{H}_f$ ) and  $2.18\ \delta$  ( $\text{H}_e$ ). The spectrum integrated for a total of ten protons which was consistent with the proposed structure. The information obtained by nmr analysis is summarized in Table II. Elemental analysis, melting point, and differential thermal analysis indicated purity of sample.

Detailed analysis of the nmr spectra of VII and VIII is discussed under Discussion and Analysis of Spectra.

Since material balance (monitored by isolated products) was not realized during bulk trapping of the isomer mixture, the trapping experiment was carried out in acetone- $\text{d}_6$  in an nmr tube. The composite nmr spectrum of the TCNE Diels-Alder adducts (Figure 1) showed peaks corresponding to each of the adducts isolated by

Figure 1 Composite NMR Spectrum of VI, VII, and VIII in Acetone-d<sub>6</sub>

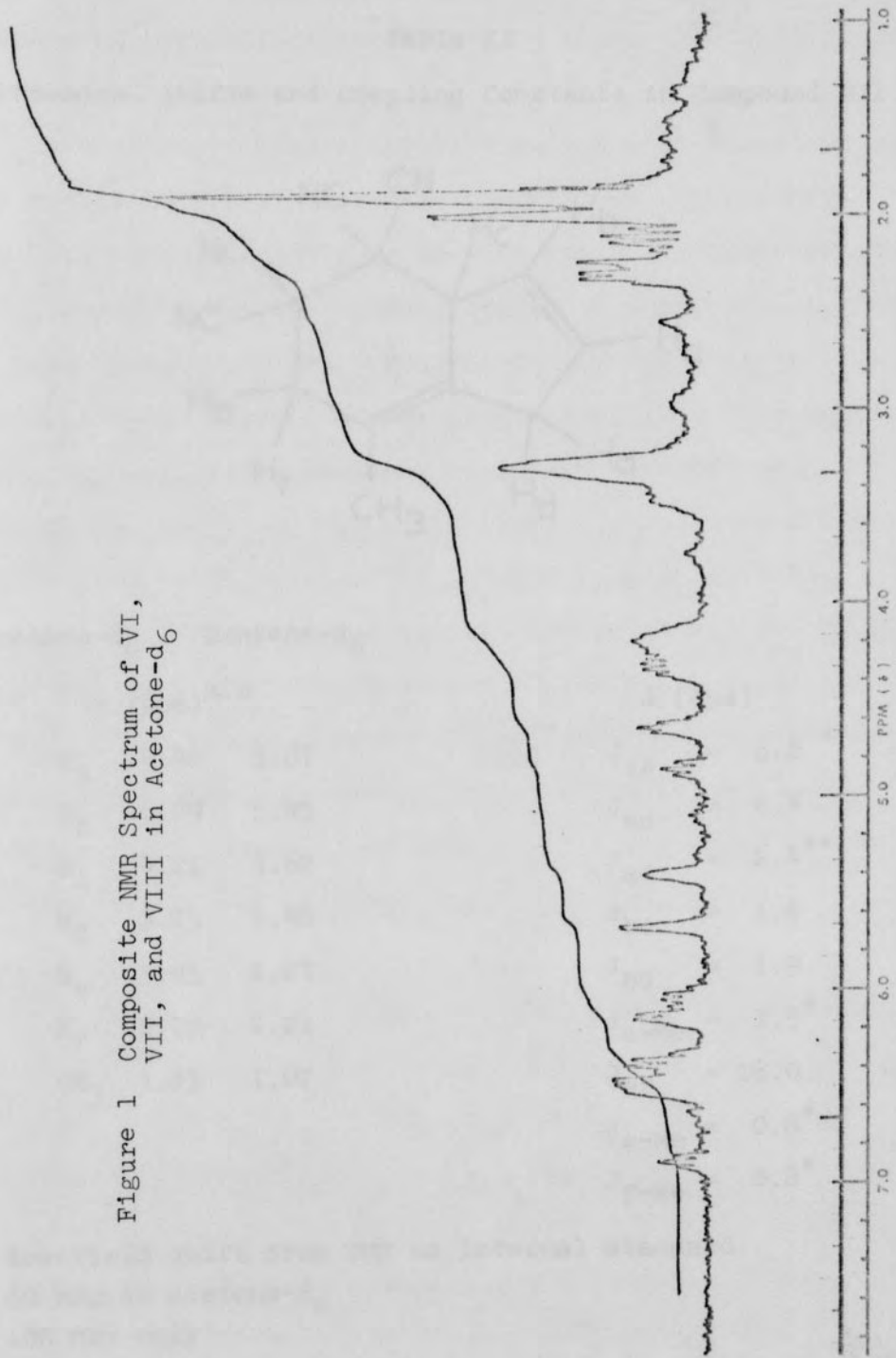
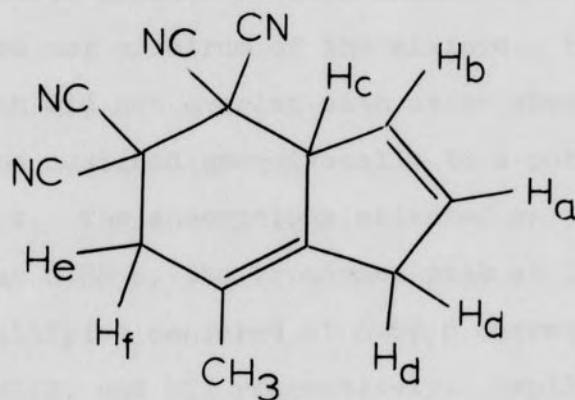


Table II

Chemical Shifts and Coupling Constants in Compound VII



	Acetone-d <sub>6</sub>	Benzene-d <sub>6</sub>	
	δ (ppm) <sup>a, b</sup>		J (cps)
H <sub>a</sub>	6.42	5.67	J <sub>ab</sub> = 6.2
H <sub>b</sub>	6.09	5.45	J <sub>ac</sub> = 2.4
H <sub>c</sub>	4.21	3.62	J <sub>ad</sub> = 2.4 <sup>**</sup>
H <sub>d</sub>	3.23	2.46	J <sub>bc</sub> = 1.6
H <sub>e</sub>	3.03	2.21	J <sub>bd</sub> = 1.9
H <sub>f</sub>	2.18	2.21	J <sub>c-Me</sub> = 1.5 <sup>*</sup>
CH <sub>3</sub>	1.83	1.07	J <sub>ef</sub> = 18.0
			J <sub>e-Me</sub> = 0.8 <sup>*</sup>
			J <sub>f-Me</sub> = 0.8 <sup>*</sup>

<sup>a</sup> downfield shift from TMS as internal standard<sup>b</sup> 60 MHz in acetone-d<sub>6</sub><sup>\*</sup> 100 MHz only<sup>\*\*</sup> invoked coupling constant

fractional crystallization and three peaks attributable to the dimethylfulvene adduct.

The relative amounts of each adduct were obtained from the integrated nmr spectrum of the mixture. Peaks were selected which did not overlap with other absorptions and which could be assigned unequivocally to a particular proton in each adduct. The absorptions selected on this basis were the triplet at 6.88  $\delta$ , the broadened peak at 5.63  $\delta$  and the seven line multiplet centered at 6.09  $\delta$  corresponding to adducts VI, VIII, and VII respectively. Replicate determinations yielded  $11.4 \pm 2.2\%$  VI,  $28.9 \pm 1.3\%$  VIII, and  $58.5 \pm 3.2\%$  VII. The protonation experiment yielded 90.5% (IV + V) and 9.5% II which showed 92.2% (VII + VIII) and 7.8% VI after trapping with TCNE to form the Diels-Alder adducts. Another experiment yielded 87.0% (IV + V) and 13.0% II which showed 87.4% (VII + VIII) and 12.6% VI for the protonation and trapping respectively.



## EXPERIMENTAL

Nmr spectra were recorded on either a Varian Associates T-60 spectrometer at 37° equipped with a T-6059 Spin Decoupler or a HA-100 spectrometer at 27° equipped with a V3521A Integrator-Decoupler. Chemical shifts are relative to tetramethylsilane (TMS) as an internal standard. All spectra were recorded in a frequency sweep mode. Infrared spectra were recorded with a Beckman 521 double beam recording spectrometer. Melting points (uncorrected) were determined on a Thomas-Hoover Capillary Melting Point Apparatus in sealed capillaries. Elemental analyses of previously unreported compounds were performed by Galbraith Laboratories, Knoxville, Tennessee.

## Synthesis of Dimethylfulvene

Dimethylfulvene was synthesized by reacting equimolar (0.06 mole) quantities of freshly distilled cyclopentadiene with acetone using the basic form of an anion exchange resin as a catalyst. This was essentially the procedure developed by McCain (16).

The basic form of the resin was generated by stirring 23 g of quaternary ammonium (polystyrene) type anion exchange resin (Amberlite CG-400) in 20% potassium

hydroxide for 30 minutes. The resin was filtered, washed with deionized water until the filtrate was neutral, washed with methanol, and dried briefly in an oven.

Dicyclopentadiene was monomerized immediately before use and the distilled cyclopentadiene was stored at 0° under a nitrogen atmosphere. The acetone (36 g) and resin were added rapidly and simultaneously to the chilled cyclopentadiene (40 g) and mechanically stirred for one hour under a nitrogen bleed. The resin was filtered and washed with diethyl ether until no additional yellow color appeared in the wash solution. Low boilers were removed under reduced pressure and the dimethylfulvene was collected at 54-56° at 8 mm Hg under a nitrogen atmosphere [literature (17) 66-68° at 25 mm Hg]. Analysis of the distillate by gas-liquid partition chromatography (glpc) showed less than 1% dicyclopentadiene present. Typical yield of dimethylfulvene based on cyclopentadiene was approximately 50%. The procedure of Freiesleben (18) yielded dimethylfulvene contaminated by 8-9% dicyclopentadiene. The method of McCain allows formation of dimethylfulvene without an extensive quantity of dicyclopentadiene. Pure dimethylfulvene is easily obtainable using preparative glpc.

The nmr spectrum of dimethylfulvene in carbon tetrachloride showed a singlet at 2.00  $\delta$  and a broadened singlet

at 6.39  $\delta$  assigned to the isopropylidenic and olefinic protons respectively (13). The nmr spectrum in acetone- $d_6$  showed a downfield shift of 4.0 cps for both absorptions.

#### Kinetically Controlled Protonation of the Dimethylfulvenide Anion

Dimethylfulvene (5.9 g) was added to a slurry of an equivalent amount (0.053 mole) of potassium tert-butoxide in bis(2-methoxyethyl) ether (diglyme). Immediately upon addition to the base, the solution became brown-red and homogeneous. The solution was added to aqueous acetic acid, and the protonated isomers were extracted into carbon tetrachloride. The carbon tetrachloride layer was washed thoroughly with water to remove the diglyme. Analysis by glpc showed two peaks corresponding to 80% 1- and 2-isopropenyl-1,3-cyclopentadiene and 20% dimethylfulvene (Apiezon L, 110°). The time elapsed between protonation and analysis was about 45 minutes. This procedure is analogous to that developed by Hine and Knight (10).

#### Synthesis of 5,5,6,6-Tetracyanonorbornene (XIII)

Freshly distilled cyclopentadiene (0.5 g) was added to an approximately equimolar amount of previously sublimed tetracyanoethylene (0.008 mole) dissolved in toluene in a 100 ml three necked round bottom flask. The mixture was mechanically stirred under a nitrogen atmosphere. A dark

transient color was observed followed by the formation of white crystals in quantitative yield. Recrystallization from acetone at 0° yielded white crystals melting at 218° [literature (19) 224°]. The infrared spectrum showed a weak band at 2250 cm<sup>-1</sup> (15). The nmr spectrum in acetone-d<sub>6</sub> consisted of a triplet pattern at 6.70  $\delta$  (olefinic protons), a five line multiplet at 4.32  $\delta$  (bridgehead protons), and an AB quartet showing additional splitting. The doublets of the AB quartet were centered at 2.26 and 2.09  $\delta$  (bridge protons) (20).

Synthesis of 7-Isopropylidene-  
5,5,6,6-Tetracyanonorbornene (VI)

Dimethylfulvene (1.0 g) was added to an approximately equimolar quantity of previously sublimed tetracyanoethylene (0.09 mole) dissolved in toluene in a three necked flask equipped with a nitrogen bleed. A transient dark color was observed, but a clear solution resulted. The solution was mechanically stirred for several minutes with no observed increase in temperature. The resulting solid adduct was recrystallized from acetone at 0° to yield white crystals melting at 133° [literature (13) 138°]. The infrared spectrum showed a weak absorption at 2250 cm<sup>-1</sup> (C $\equiv$ N). The nmr spectrum in acetone-d<sub>6</sub> consisted of peaks attributable to olefinic, bridgehead, and isopropylidenic

protons. Nmr information is detailed under Discussion and Analysis of Spectra.

Trapping the Isomer Mixture  
with Tetracyanoethylene in Acetone

The carbon tetrachloride solution of the isomers was added with mechanical stirring to an approximately equimolar amount (0.05 mole) of tetracyanoethylene (purified by sublimation) dissolved in reagent grade acetone under a nitrogen atmosphere at 0°. The immediate formation of a transient dark color was observed. The solvents were removed by vacuum distillation depositing 9.5 g of green paste which were stirred in 100 ml of pentane for 70 hours. After 70 hours, the green paste had become a very pale yellow solid which was filtered, washed with pentane, and dried. A yield of 8.4 g of yellow solid was obtained which melted at 65-75°, 120-125°, and turned dark brown up to 200°.

The pale yellow solid was washed several times with portions of a mixture of 12:1 pentane-toluene solution until a sizable quantity of solid had dissolved. Vacuum distillation of the filtrate deposited 2.4 g of pale yellow paste. Approximately 0.05 g of insoluble material was removed. The paste was dissolved in 6 ml of methylene chloride and stored at 0°. Pale yellow crystals formed (m.p. 140-170°) which after recrystallization from

methylene chloride melted at  $196^{\circ}$  (TCNE). Addition of various proportions of methylene chloride-petroleum ether failed to produce crystals, and the solvents were removed under reduced pressure. The solid was dissolved in 5 ml of toluene, and 6 ml of petroleum ether was added until the cloud which formed just disappeared. The solution was stored at  $0^{\circ}$ . White crystals (0.1 g) of compound VIII formed which melted at  $92-93^{\circ}$ . The infrared spectrum contained a weak band at  $2250\text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ) but showed no absorption in the region  $880-910\text{ cm}^{-1}$  generally attributed to terminal vinyl protons. The nmr spectrum in acetone- $\text{d}_6$  was consistent with the structure and is detailed under Discussion and Analysis of Spectra. Elemental analysis yielded 71.80% C, 4.33% H, and 23.97% N which compared favorably with the calculated values of 71.76% C, 4.31% H, and 23.92% N.

The pale yellow solid ( $\sim 6\text{ g}$ ) remaining was dissolved in acetone. After several attempts at recrystallization from acetone-pentane failed, the solvents were removed under reduced pressure. The solid was stirred in 125 ml of methylene chloride, filtered, and 2.4 g of insoluble material were isolated which melted at  $196^{\circ}$ . Addition of a large excess of pentane to the filtrate caused a brown oil to form which was dissolved in 5 ml of acetone. Approximately 6 ml of petroleum ether ( $60-90^{\circ}$ ) was added until the

solution was slightly turbid. The solvents were allowed to evaporate at room temperature and white crystals of VII formed (0.1 g) which melted at 156-157°. The infrared spectrum showed weak absorptions at 2250 (C≡N), 1620 and 832  $\text{cm}^{-1}$  (trisubstituted olefin), and a strong absorption at 910  $\text{cm}^{-1}$  (terminal olefinic protons). The nmr spectrum in acetone- $\text{d}_6$  was consistent with the structure and is detailed under Discussion and Analysis of Spectra. Elemental analysis yielded 71.49% C and 4.30% H which compared favorably with the calculated values of 71.79% C and 4.27% H.

#### Trapping the Isomer Mixture with Tetracyanoethylene in Tetrahydrofuran

The carbon tetrachloride solution containing the protonated isomers was added directly to an approximately equimolar amount of tetracyanoethylene (0.04 mole) dissolved in tetrahydrofuran under a nitrogen atmosphere. A transient dark brown color was observed and the temperature increased to approximately 50°. The solution was cooled rapidly to 0°. The solvents were removed by vacuum distillation at 1 mm Hg to yield 9.7 g of a dark chartreuse paste which were washed with approximately 100 ml of petroleum ether (60-90°). On evaporation of petroleum ether the solution yielded 0.03 g of white crystals (m.p. 92-94°).

The remaining paste was dissolved in excess methylene chloride leaving a small amount of insoluble residue. As

the volume of methylene chloride solution was reduced by vacuum distillation, white crystals formed, and the solution was stored under a nitrogen atmosphere at 0°. The white crystals were filtered and dried (m.p. 191-195° with darkening).

Petroleum ether (60-90°) was added to the methylene chloride filtrate. A brown oily layer formed which was separated and stored under a nitrogen atmosphere at 0°. The formation of white crystals was observed, and 0.8 g was isolated (m.p. 115-117° partially melted, 138-140° entirely melted; both melts were pale brown). The white crystals were dissolved in 1:1 acetone-petroleum ether, and the solution was stored under a nitrogen atmosphere at 0°. A yield of white crystals (0.17 g) was obtained, filtered, and dried (m.p. 125-130°). Nmr spectroscopy indicated a mixture of 7-isopropenylidene-5,5,6,6-tetracyanonorbornene (VI) and 2-isopropenyl-5,5,6,6-tetracyanonorbornene (VIII). The filtrate was allowed to evaporate at room temperature and approximately 0.1 g of white crystals of VIII was isolated (m.p. 156-157°).

#### Trapping the Isomer Mixture with Tetracyanoethylene in Acetone-d<sub>6</sub>

The isomer mixture (0.003 mole) was added to an equimolar amount of tetracyanoethylene dissolved in acetone-d<sub>6</sub> (0.5 ml) in an nmr tube. A transient dark brown color was



observed. The nmr spectrum of the adduct mixture was determined (Figure 1).

#### Kinetic Study

The isomer mixture obtained by protonation of the dimethylfulvenide anion changed with time. Additional peaks appeared in the nmr spectrum at the expense of the isomer peaks. These additional peaks were tentatively assigned to products arising from Diels-Alder addition of the isomers with themselves and with each other. It was of interest to ascertain the rate of this addition.

The protonation of the dimethylfulvenide anion was carried out as described previously, and the carbon tetrachloride solvent was removed by vacuum distillation. Gas-liquid partition chromatography (glpc) showed 76.2% of isomer IV and V, 23.8% II, and essentially zero percent dicyclopentadiene. The isomer mixture was added to an nmr tube and the sample was flushed with nitrogen, sealed, and stored in the nmr spectrometer at 37°. The nmr spectrum was determined at time intervals of 0, 4, 17, 52, 114, and 280 hours. Analysis of the nmr spectrum revealed that the cross and lineally conjugated isomers disappeared more rapidly than dimethylfulvene. The lineally conjugated isomer reacted more rapidly than the cross conjugated isomer, since after four hours 58% of the former and 38% of the latter had disappeared.

A pure sample of dimethylfulvene was observed under the same conditions, and a sizeable quantity remained after 4.5 months.

## DISCUSSION AND ANALYSIS OF SPECTRA

Hine and Knight (10) have reported that the protonation of the isopropenylcyclopentadienyl anion (I) yields a mixture of dimethylfulvene (II), 1-isopropenyl-1,3-cyclopentadiene (IV), and 2-isopropenyl-1,3-cyclopentadiene (V). They also reported that 5-isopropenyl-1,3-cyclopentadiene (III) could possibly have formed but rearranged prior to analysis. The isomers very likely undergo Diels-Alder addition with themselves and with each other and are also susceptible to oxidation. It was necessary to develop a procedure to trap the mixture to provide compounds which were more amenable to separation and analysis, since it had been observed that 1- and 2-isopropenyl-1,3-cyclopentadiene could not be separated by fractional distillation or by preparative gas-liquid partition chromatography (glpc).

Tetracyanoethylene (TCNE) proved to be a suitable reagent for rapidly trapping the isomer mixture since it yielded stable solid adducts. These adducts represented the state of the isomer mixture at the time of trapping. Any rearrangements or other reactions which occurred prior to trapping would not be detected. Trapping of the isomers in acetone- $d_6$  in an nmr tube yielded a mixture of  $11.4 \pm 2.0\%$  of the adduct derived from dimethylfulvene (VI),  $28.9 \pm 1.3\%$  of the adduct derived from

2-isopropenyl-1,3-cyclopentadiene (VIII), and  $58.5 \pm 3.2\%$  of the adduct derived from 1-isopropenyl-1,3-cyclopentadiene (VII). There was no evidence of the adduct derived from 5-isopropenyl-1,3-cyclopentadiene (IX). These values are in agreement with those reported by Hine and Knight (10) for the protonation of anion I, namely 21% dimethylfulvene (II), 21% 2-isopropenyl-1,3-cyclopentadiene (V), and 57% 1-isopropenyl-1,3-cyclopentadiene (IV).

The agreement of the percentages of Diels-Alder adducts, relative to the isomers from which they were derived, indicated that tetracyanoethylene reacted with the components of the mixture at a rate which was faster than their interconversion. If the tetracyanoethylene had reacted with one isomer preferentially, these percentages would not have been internally consistent. It is known that the more highly reactive a species, the more nonselective it is in chemical reactions (21). The high reactivity of tetracyanoethylene is evidenced by its reaction rates with various dienes compared to maleic anhydride-diene reaction rates as shown in Table III (22).

There are two possible modes by which tetracyanoethylene can add by Diels-Alder addition to both IV and V. Addition can occur across the endocyclic conjugated diene system or across the conjugated diene system incorporating the isopropenyl group. The possible products are

Table III

Kinetics of the Reactions of Dienes with  
(a) Maleic Anhydride and (b) Tetracyanoethylene (22)

Diene*	(a)	(b)
	$10^8 k_2$ (at 30°C) ( $1 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ )	$10^5 k_2$ (at 20°C) ( $1 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ )
Cyclopentadiene	9 210 000	ca. 43 000 000
9,10-Dimethyl- anthracene	1 600 000	ca. 1 300 000 000
1,3-Cyclohexa- diene	13 200	7 290
Hexachlorocyclo- pentadiene	1.14	---
1,2-Dimethylene- cyclohexane	755 000	1 230 000
1,1'-Bicyclo- pentenyl	118 000	1 900 000
1-Methoxybuta- diene	84 100	598 000
2,3-Dimethyl- butadiene	33 600	24 300
<u>trans</u> -1-Methyl- butadiene	22 700	2 060
2-Methylbuta- diene	15 400	1 130
Butadiene	6 830	519
2-Chlorobutadiene	690	1.0

\* dioxane solvent

represented on page 30. Experimentally, it was observed that endocyclic addition occurred with compound V, and exocyclic addition occurred with IV as evidenced by nmr and infrared spectroscopy. It is known that Diels-Alder addition occurs with conjugated double bonds in a cis conformation (23). Klemm *et al.* (24), have reported the addition of tetracyanoethylene to a series of 1-alkyl-1-(2-naphthyl)ethenes in which they observed addition across the exocyclic diene system:

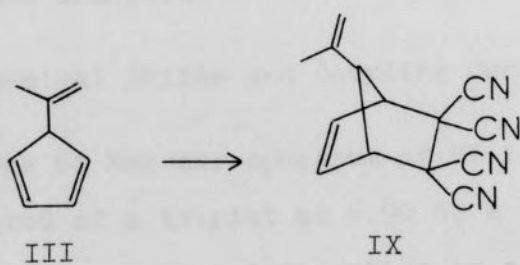
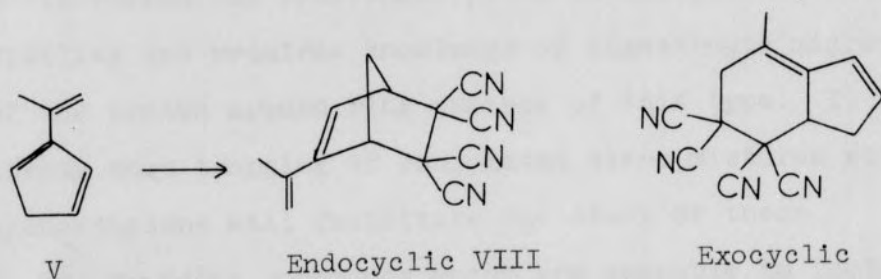
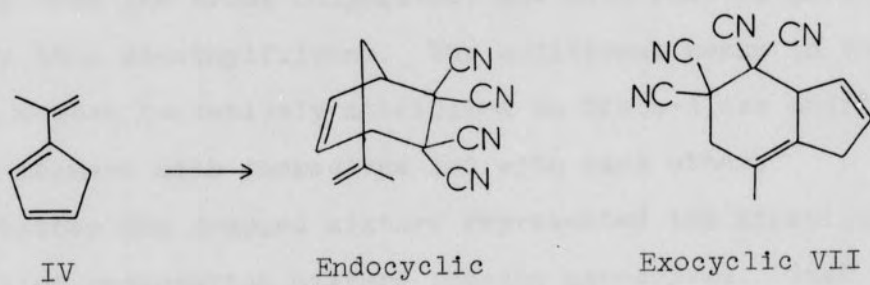
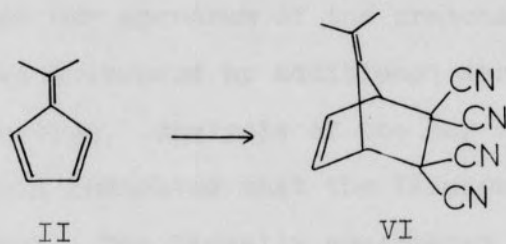


There was no conclusive evidence for the presence of the adduct derived from 5-isopropenyl-1,3-cyclopentadiene (IX). This was revealed by the composite nmr spectrum of the adduct mixture in which every peak was accounted for by the sum of the individual spectra of VI, VII, and VIII.

During the reaction of tetracyanoethylene with the isomer mixture, a dark color appeared on initial mixing but immediately disappeared. This transient color was also observed during formation of the adducts of dimethylfulvene and cyclopentadiene. This phenomenon has been reported previously (11,12) and attributed to the formation of a  $\pi$

Table IV

Possible Diels-Alder Adducts of II, IV, V, and III with TCNE



complex of tetracyanoethylene and the diene, the complex rapidly leading to adduct formation.

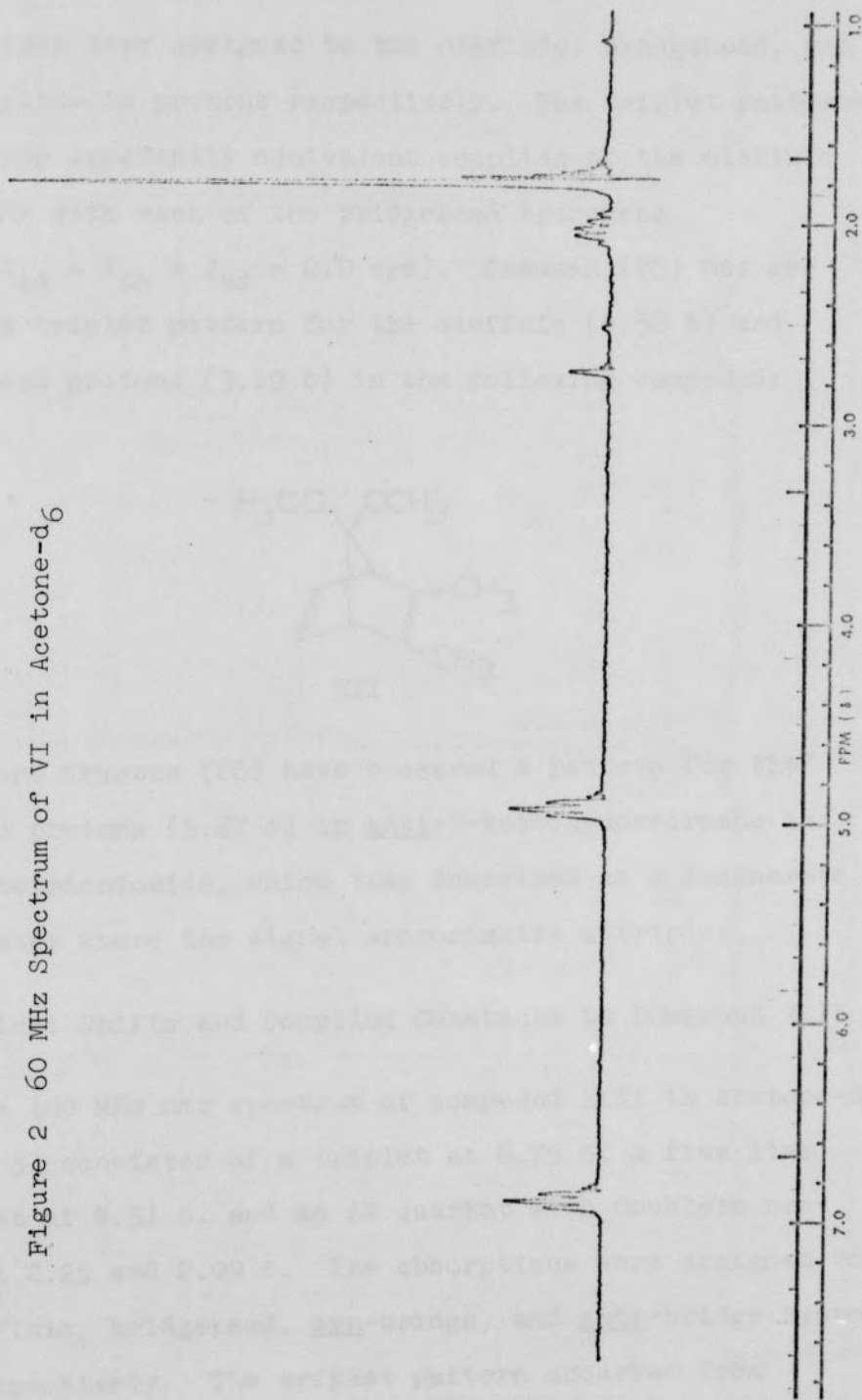
The nmr spectrum of the protonated isomers changed with time, as evidenced by additional absorptions appearing in the spectrum. Analysis of the nmr spectrum at various time intervals indicated that the isomers disappeared at different rates. The lineally conjugated isomer reacted more rapidly than the cross conjugated, and both reacted more rapidly than dimethylfulvene. The additional peaks in the spectrum were tentatively attributed to Diels-Alder addition of the isomers with themselves and with each other.

Whether the trapped mixture represented the kinetically controlled protonation mixture remains unresolved. That isomer III formed but rearranged prior to analysis is still a possibility and requires knowledge of sigmatropic migration of the proton around ring systems of this type. It is very likely that trapping of conjugated diene mixtures with tetracyanoethylene will facilitate the study of these systems by providing compounds which are amenable to isolation and analysis.

#### Chemical Shifts and Coupling Constants in Compound VI

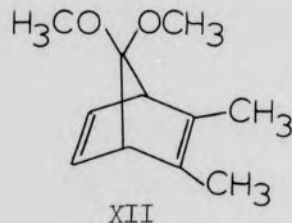
The 60 MHz nmr spectrum of VI in acetone- $d_6$  (Figure 2) consisted of a triplet at 6.90  $\delta$ , a triplet at 4.96  $\delta$ , and a singlet at 1.85  $\delta$  integrating in a ratio of 1:1:3. The



Figure 2 60 MHz Spectrum of VI in Acetone-d<sub>6</sub>

absorptions were assigned to the olefinic, bridgehead, and isopropylidene protons respectively. The triplet patterns arose from apparently equivalent coupling of the olefinic hydrogens with each of the bridgehead hydrogens

( $J_{ac} = J_{ad} = J_{bc} = J_{bd} = 2.0$  cps). Gassman (25) has reported a triplet pattern for the olefinic (6.58  $\delta$ ) and bridgehead protons (3.19  $\delta$ ) in the following compound:

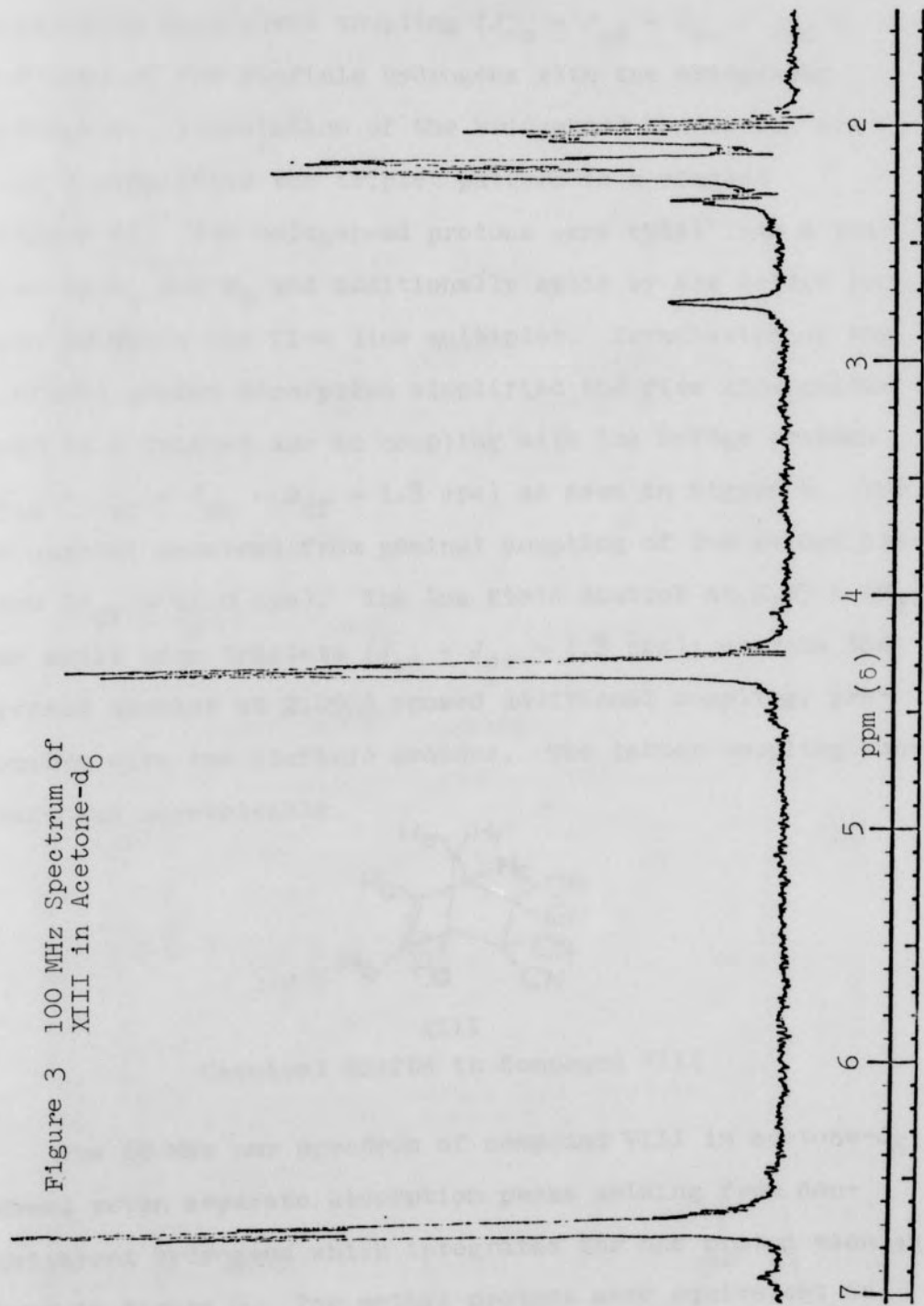


Snyder and Franzus (26) have observed a pattern for the olefinic protons (5.87  $\delta$ ) in anti-7-acetoxynorbornene in carbon tetrachloride, which they described as a degenerate  $A_2X_2$  system where the signal approximates a triplet.

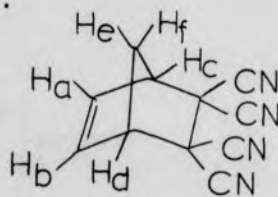
#### Chemical Shifts and Coupling Constants in Compound XIII

The 100 MHz nmr spectrum of compound XIII in acetone- $d_6$  (Figure 3) consisted of a triplet at 6.75  $\delta$ , a five line multiplet at 4.31  $\delta$ , and an AB quartet with doublets centered at 2.25 and 2.09  $\delta$ . The absorptions were assigned to the olefinic, bridgehead, syn-bridge, and anti-bridge hydrogens respectively. The triplet pattern occurred from

Figure 3 100 MHz Spectrum of  
XIII in Acetone-d<sub>6</sub>



apparently equivalent coupling ( $J_{ac} = J_{ad} = J_{bc} = J_{bd} = 2.0$  cps) of the olefinic hydrogens with the bridgehead hydrogens. Irradiation of the bridgehead absorption at 4.31  $\delta$  simplified the triplet pattern to a singlet (Figure 4). The bridgehead protons were split into a triplet by  $H_a$  and  $H_b$  and additionally split by the bridge protons to yield the five line multiplet. Irradiation of the olefinic proton absorption simplified the five line multiplet to a triplet due to coupling with the bridge protons ( $J_{ce} = J_{cf} = J_{de} = J_{df} = 1.8$  cps) as seen in Figure 5. The AB quartet occurred from geminal coupling of the bridge protons ( $J_{ef} = 11.0$  cps). The low field doublet at 2.25  $\delta$  ( $H_e$ ) was split into triplets ( $J_{ce} = J_{de} = 1.8$  cps); whereas the upfield doublet at 2.09  $\delta$  showed additional coupling, presumably with the olefinic protons. The latter coupling constant was unresolvable.



XIII

## Chemical Shifts in Compound VIII

The 60 MHz nmr spectrum of compound VIII in acetone- $d_6$  showed seven separate absorption peaks arising from non-equivalent hydrogens which integrated for one proton each as shown in Figure 6. The methyl protons were equivalent as

Figure 4 Irradiation of Bridgehead Protons in XIII

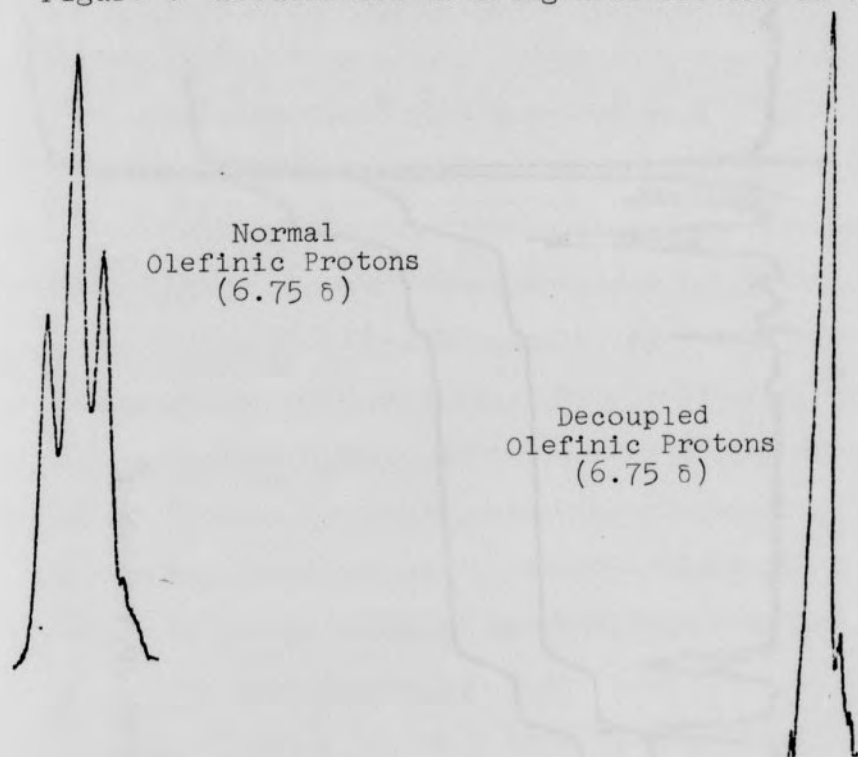


Figure 5 Irradiation of Olefinic Protons in XIII

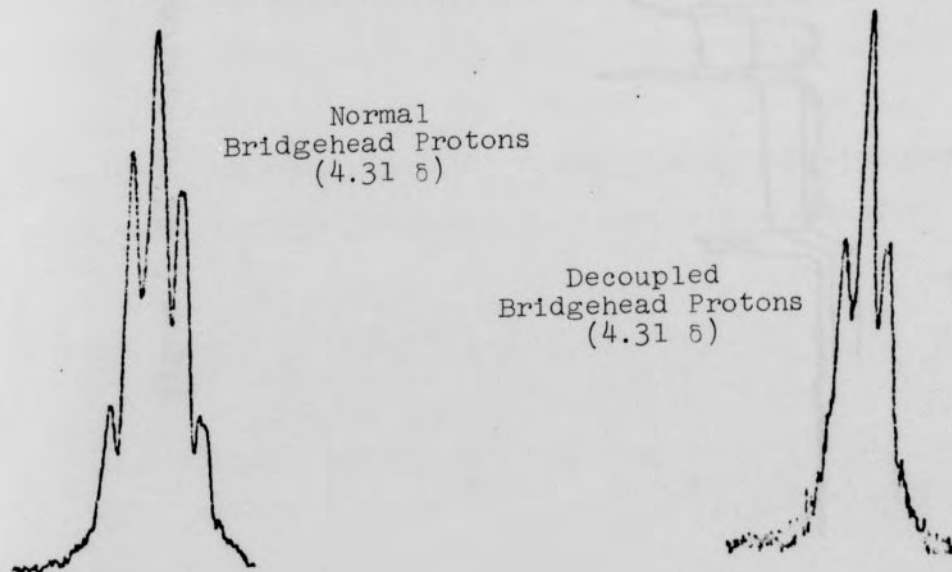
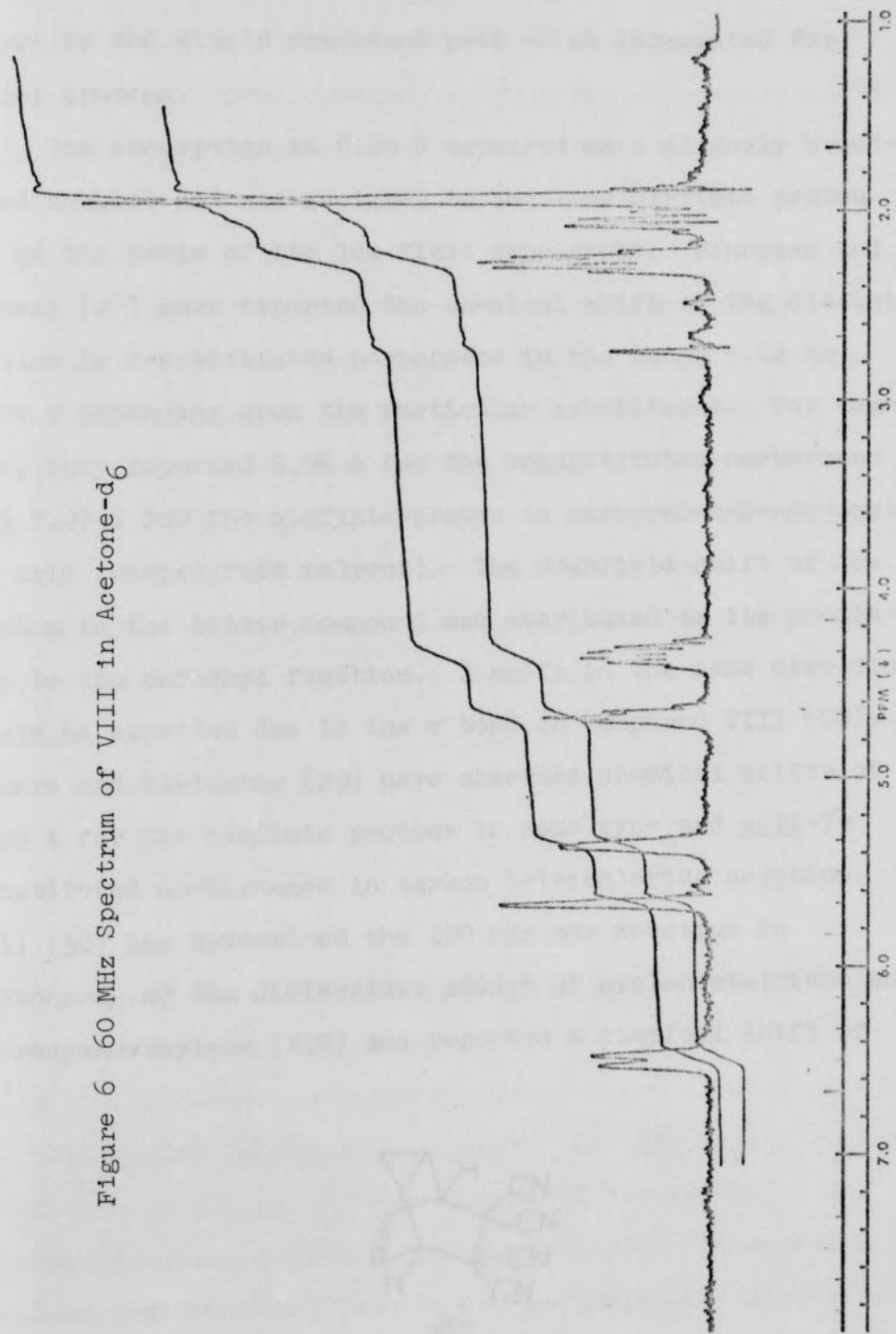
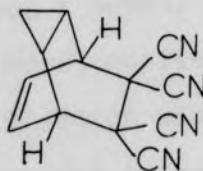


Figure 6 60 MHz Spectrum of VIII in Acetone-d<sub>6</sub>

shown by the single resonance peak which integrated for three protons.

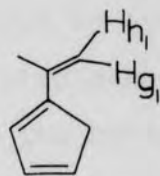
The absorption at 6.50  $\delta$  appeared as a slightly broadened doublet and was assigned to the lone olefinic proton  $H_a$  on the basis of its low field appearance. Finnegan and McNeese (27) have reported the chemical shift of the olefinic proton in 2-substituted norbornene in the range 5.42 to 7.07  $\delta$  depending upon the particular substituent. For example, they reported 5.94  $\delta$  for the unsubstituted norbornene and 7.07  $\delta$  for the olefinic proton in norbornene-2-carboxylic acid (unspecified solvent). The downfield shift of the proton in the latter compound was attributed to its proximity to the carbonyl function. A shift in the same direction would be expected due to the  $\pi$  bond in compound VIII (28). Sauers and Hawthorne (29) have observed chemical shifts of 6.00  $\delta$  for the olefinic protons in some syn- and anti-7-substituted norbornenes in carbon tetrachloride solution. Wall (30) has determined the 100 MHz nmr spectrum in acetone- $d_6$  of the Diels-Alder adduct of cycloheptatriene and tetracyanoethylene (XIV) and reported a chemical shift of



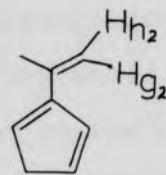
XIV

6.23  $\delta$  for the two olefinic protons. Davis and Van Auken (31) have examined the 56.4 MHz nmr spectra of the endo- and exo-5-cyanonorbornenes in carbon tetrachloride solution and reported chemical shifts in the range 6.03 and 6.30  $\delta$  for the olefinic protons. The 60 MHz nmr spectra in acetone- $d_6$  of the Diels-Alder adducts of tetracyanoethylene with dimethylfulvene and cyclopentadiene yielded olefinic proton absorptions at 6.90 and 6.75  $\delta$  respectively (VI, XIII).

The broad absorption peaks at 5.63 and 5.33  $\delta$  were attributed to  $H_g$  and  $H_h$ , respectively, on the basis of chemical shift data reported by Hine and Knight (10) in the 100 MHz spectra of 1- and 2-isopropenylcyclopentadiene (IV, V) in carbon tetrachloride solution:



IV



V

They reported chemical shifts for the terminal vinyl protons of  $H_{h_1}$  (4.77  $\delta$ ),  $H_{g_1}$  (5.09  $\delta$ ),  $H_{h_2}$  (4.96  $\delta$ ), and  $H_{g_2}$  (5.21  $\delta$ ), and attributed the downfield appearance of  $H_g$  to the deshielding of the ring  $\pi$  bonds. On this basis, it was consistent to assign the more downfield absorption to the terminal olefinic proton  $H_g$  which was nearer the  $\pi$  bond of the ring and therefore expected to be deshielded more than  $H_h$  (32). The widths at half height of the  $H_g$  and  $H_h$  peaks



were 2.8 and 3.8 cps respectively. This supports the chemical shift assignments, since coupling of the methyl proton with the cis proton ( $J \simeq 1.4$ ) was reported to be greater than coupling ( $J \simeq 0.7$ ) with the trans proton (33). These coupling constants were not resolvable in compound VIII.

The five line multiplet at 4.69  $\delta$  was attributed to  $H_d$ . The six line multiplet at 4.33  $\delta$  was assigned to the other bridgehead proton  $H_c$ . Finnegan and McNees (27) have determined the 60 MHz spectrum of the methyl ester of norbornene-2-carboxylic acid (Figure 7) and observed multiplets at 3.69 and 3.24  $\delta$  which they assigned to  $H_d$  and  $H_c$  respectively. They based their assignments on the greater degree of splitting expected for  $H_c$  and the downfield displacement of the  $C_1$  proton due to its proximity to the carboxyl group. This downfield displacement and lesser splitting would be expected for the bridgehead proton adjacent to the isopropenyl substituent in compound VIII. Wall (30) has reported a bridgehead proton shift of 4.23  $\delta$  in acetone- $d_6$  for the adduct of tetracyanoethylene and cycloheptatriene (XIV).

An AB pattern was present in the 100 MHz nmr spectrum in acetone- $d_6$  (Figure 8) within the region 2.0 to 2.4  $\delta$  with a chemical shift difference and coupling constant of 19.0 and 11.5 cps respectively. Each peak of the AB quartet showed fine splitting indicating spin-spin coupling with additional protons. The center of each doublet was at 2.35

Figure 7 60 MHz Spectrum  
of the Methyl  
Ester of  
Norbornene-2-  
Carboxylic Acid  
(27)

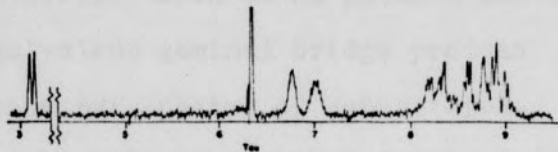
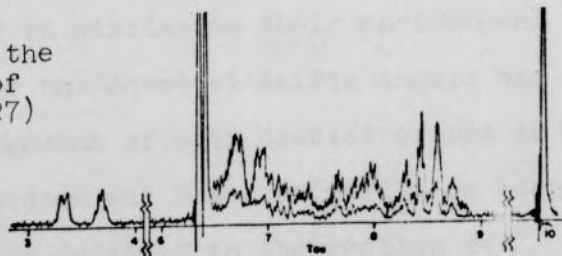


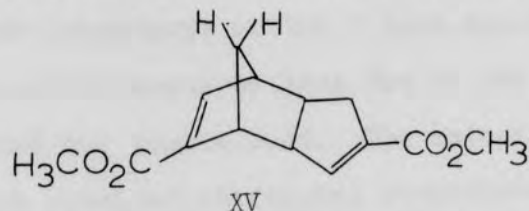
Figure 8 100 MHz Spectrum of  
AB Pattern in VIII



Figure 9 NMR Spectrum of the  
Dimethyl Ester of  
Thiele's Acid (27)



and 2.16  $\delta$ ; these absorptions were attributed to the resonances of  $H_e$  and  $H_f$  respectively. Such an AB pattern due to coupling between the nonequivalent geminal bridge protons has been observed in numerous nmr spectra of substituted norbornenes (20,27,31,34,35,36,37). Laszlo and Schleyer (20) have reported chemical shifts of 1.78 and 2.00  $\delta$  for the methylene bridge protons of trans-5,6-dichloronorbornene in carbon tetrachloride solution. Finnegan and McNees (27) have reported chemical shifts of 1.66 and 1.37  $\delta$  for the bridge protons in the dimethyl ester of Thiele's acid (XV) in an unspecified solvent (Figure 9). The nmr



spectrum in acetone- $d_6$  of 5,5,6,6-tetracyano-2-norbornene (XIII) (Figure 3) prepared in this laboratory showed absorptions of the bridge protons at approximately 2.00  $\delta$ . It is reasonable that the magnetic environment of the geminal protons in the above compound is similar to their environment in compound VIII; therefore the chemical shifts should be similar as observed. Assignment of each doublet of the AB quartet to the indicated proton was based primarily on long range coupling which will be detailed in the section describing coupling constants.

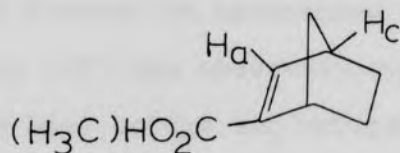
The absorption at 1.92  $\delta$  appeared as a slightly broadened multiplet integrating for three protons and was attributed to the methyl protons on the basis of the report of Hine and Knight's (10) assigned values of 1.95 and 1.99  $\delta$  for the methyl absorption in 1- and 2-isopropenylcyclopentadiene (IV,V) in carbon tetrachloride solution.

The exocyclic vinyl protons  $H_g$  and  $H_h$  absorbed at 5.56 and 5.34  $\delta$ , respectively, as broadened singlets. The more downfield absorption was assigned to  $H_g$  on the basis of the neighboring anisotropy of the ring double bond which tends to deshield protons in the plane of the olefinic bond (28,32). The anisotropy of the  $\pi$  bond would also deshield  $H_h$ , but the effect would be less due to the greater separation of  $H_h$  and the double bond. The anisotropic effects of the  $\pi$  bond on chemical shifts has been discussed at length by Fraser (32). The chemical shift assignments were also consistent with the greater width at half height of the resonance of  $H_h$  ( $W_{\frac{1}{2}} = 3.5$  cps) as compared to the resonance of  $H_g$  ( $W_{\frac{1}{2}} = 2.3$  cps).

#### Coupling Constants in Compound VIII

The olefinic proton  $H_a$  absorbed at 6.49  $\delta$  and was split into a well resolved doublet ( $J_{ac} = 3.2$  cps) by the adjacent bridgehead proton  $H_c$ . Finnegan and McNees (27) have reported  $J_{ac} = 3.0$  cps for the coupling between the lone

olefinic proton and the bridgehead proton in norbornene-2-carboxylic acid and its methyl ester (XVI). The coupling

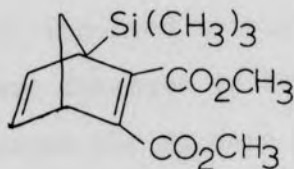


XVI

constant was also consistent with the reported values of Garbisch (38), Snyder and Franzus (26), Laszlo and Schleyer (20,39), Davis and Van Auken (31), and Moen and Makowski (40). The broadening (2.0 cps) of each peak of the  $H_a$  resonance suggested further unresolved coupling. This additional coupling, as will be shown later, was most probably due to interaction with the anti-bridge proton  $H_f$ .

The resonance of  $H_d$  (3.69  $\delta$ ) consisted of a five line multiplet due to coupling with four protons, namely  $H_c$ ,  $H_e$ ,  $H_f$ , and a proton in the isopropenyl group. The constant due to coupling between the bridgehead-bridgehead protons ( $J_{cd}$ ) was 1.5 cps, between the bridgehead-bridge protons ( $J_{de}$ ,  $J_{df}$ ), 1.6 and 1.5 cps respectively, and for a proton in the isopropenyl group, 1.5 cps. Garbisch (38) has reported coupling constants due to interaction between the bridgehead protons in norbornene and norbornadiene of 1.12 and 1.85 cps respectively. Ramey et al. (41), have reported

bridgehead-bridgehead coupling of 1.0-1.6 cps in norbornene derivatives. The assignment of  $J_{dc} = 1.5$  cps was consistent with these previously recorded four-bond couplings between the bridgehead protons in norbornene and norbornane derivatives. Gassman (25) has observed coupling of 1.3 cps between the methylene bridge and bridgehead hydrogens which was in agreement with the values of 1.6 and 1.5 cps found for compound VIII. It should be noted that the multiplicity of  $H_d$  required that  $J_{ad} = 0$  cps. Such a lack of coupling has been reported by Ashe (42) for the  $^3J$  [coupling over three bonds (43)] vinyl-allylic coupling in a trimethylsilyl norbornene (XVII). The width of each line ( $< 0.5$  cps) of



XVII

the five line multiplet indicated very little interaction between  $H_d$  and other protons in the molecule.

The resonance of  $H_c$  consisted of a six line multiplet at 4.33  $\delta$  due to coupling with the bridgehead proton  $H_d$  ( $J_{cd} = 1.5$  cps), the two bridge protons  $H_e$  and  $H_f$  ( $J_{ce} = 1.6$  cps,  $J_{cf} = 1.5$  cps), and the lone olefinic proton  $H_a$  ( $J_{ca} = 3.2$  cps). The different coupling constants of the bridgehead protons with each bridge proton was consistent

with the coupling observed by Davis and Van Auken (31) for endo- and exo- norbornene derivatives ( $J_{1,7s} = 1.8-1.9$  cps,  $J_{1,7a} = 1.3-1.4$  cps).

The bridge protons  $H_e$  and  $H_f$  exhibited an AB spectrum with a geminal coupling constant of 11.5 cps (Figure 8). The downfield doublet of the AB quartet was assigned to  $H_e$  (2.35  $\delta$ ) which was additionally coupled with  $H_c$  ( $J_{ec} = 1.6$  cps) and  $H_d$  ( $J_{ed} = 1.6$  cps) to yield a well resolved triplet pattern in each peak of the doublet. The upfield half of the AB quartet was assigned to  $H_f$  (2.16  $\delta$ ) primarily due to the observation of additional splitting which was attributed to the interaction of  $H_f$  with the lone olefinic proton  $H_a$  (26,31,36). It was because of this additional splitting, that the well resolved triplets in the absorption attributed to  $H_e$  were not observed in the  $H_f$  resonance. The coupling constants observed for  $H_f$  were  $J_{cf} = 1.5$  cps,  $J_{df} = 1.5$  cps, and estimating  $J_{af} \simeq 0.5$  cps (39).

The AB pattern observed for  $H_e$  and  $H_f$  was similar to that reported by Laszlo and Schleyer (20) in the spectrum of trans-5,6-dichloronorbornene in which the bridge protons split each other into doublets with  $J = 9.1$  cps. They also observed that each peak of the AB quartet was additionally split by the olefinic protons and the protons on  $C_5$  and  $C_6$ . Finnegan and McNees (27) also observed an AB pattern for the bridge protons in the dimethyl ester of Thiele's acid (XV)

(Figure 9) with chemical shift differences of 18 cps and  $J = 9$  cps. Subramanian *et al.* (36), have reported an AB quartet for the geminal bridge protons in 5,6-dihalogenated norbornenes. In the exo-cis isomer (Figure 10), the bridge proton syn to the double bond was reported to be upfield from the anti-bridge proton; whereas in the endo-cis compound (Figure 11), the proton anti to the double bond was upfield.

The most convincing corroboration for the assignment of the AB quartet was obtained from the 100 MHz spectrum in acetone- $d_6$  of an authentic Diels-Alder addition product of tetracyanoethylene and cyclopentadiene (XIII) (Figure 3). The same pattern was observed for the bridge protons, namely an AB quartet ( $J = 11.0$  cps) with a chemical shift difference of 31.0 cps between the centers of the two doublets. The downfield doublet was additionally split into well resolved triplets ( $J_{ec} = J_{ed} = 1.6$  cps); whereas the upfield doublet was broadened and the multiplicity unresolvable. Comparison of the  $W_{\frac{1}{2}}$  of the upfield doublet in each compound indicated a substantial broadening in the latter adduct ( $W_{\frac{1}{2}} = 6.0$  and 8.0 cps respectively). The additional broadening of the upfield doublet in the cyclopentadiene adduct was attributed to coupling of two olefinic protons with the anti-bridge proton as opposed to one olefinic proton in compound VIII. This supported the assignment of the anti-proton



Figure 10 NMR Spectrum of exo-cis-5,6-Dibromo-2-Norbornene (36)

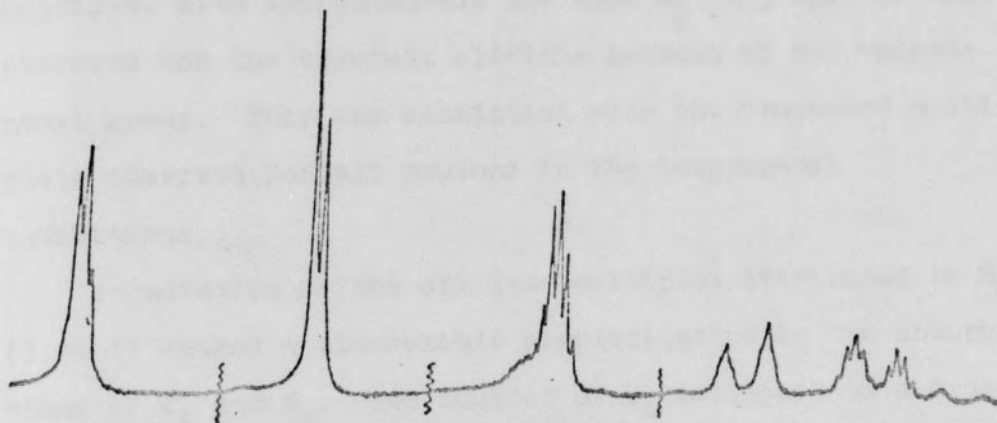


Figure 11 NMR Spectrum of endo-cis-5,6-Dibromo-2-Norbornene (36)



$H_f$  to the upfield doublet in the AB quartet of compound VIII.

The absorption due to the methyl protons in the exocyclic isopropenyl group appeared at 1.92  $\delta$  as a broadened multiplet with approximately the same  $W_{\frac{1}{2}}$  ( $\sim 3$  cps) as that observed for the terminal olefinic protons of the isopropenyl group. This was consistent with the broadened multiplets observed for all protons in the isopropenyl substituent.

Irradiation of the six line multiplet attributed to  $H_c$  (3.24  $\delta$ ) caused a discernible simplification in the absorptions of  $H_a$  and  $H_e$ . The doublet of  $H_a$  collapsed to a broadened singlet ( $W_{\frac{1}{2}} = 3.0$  cps) (Figure 12), and the triplets of  $H_e$  simplified to doublets ( $J_{de} = 1.5$  cps) (Figure 13). A small but unresolvable distortion was observed in the absorptions of  $H_d$  and  $H_f$ .

Irradiation of the absorption due to  $H_e$  (2.35  $\delta$ ) resulted in a distortion of the  $H_c$  and  $H_d$  absorptions. The effect of the irradiation on  $H_f$  was indefinite due to interference of the beat pattern of the irradiating frequency.

#### Chemical Shifts in Compound VII

The 60 MHz nmr spectrum in acetone- $d_6$  of compound VII (Figure 14) had well resolved multiplets in the region 6.53-5.98  $\delta$  and complex absorptions centered at 4.21, 3.82-2.90, and 1.83  $\delta$ .

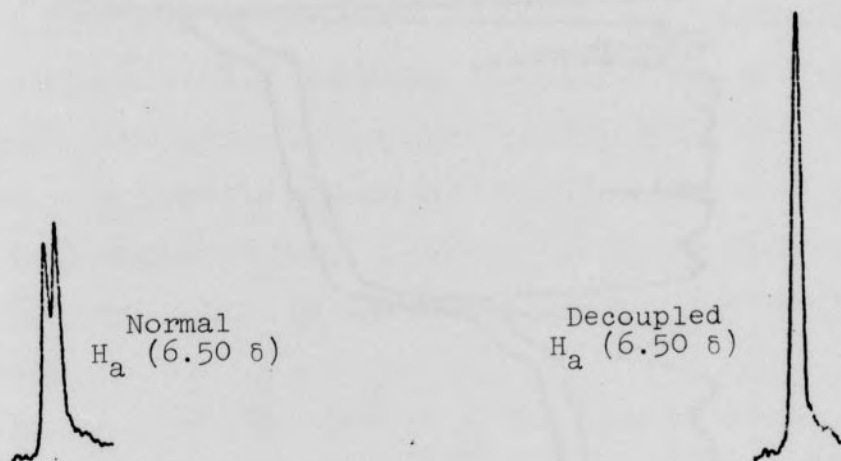
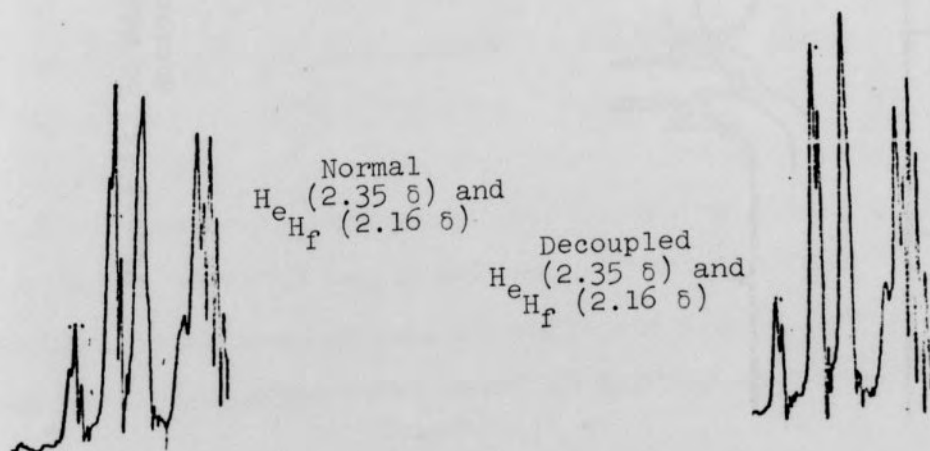
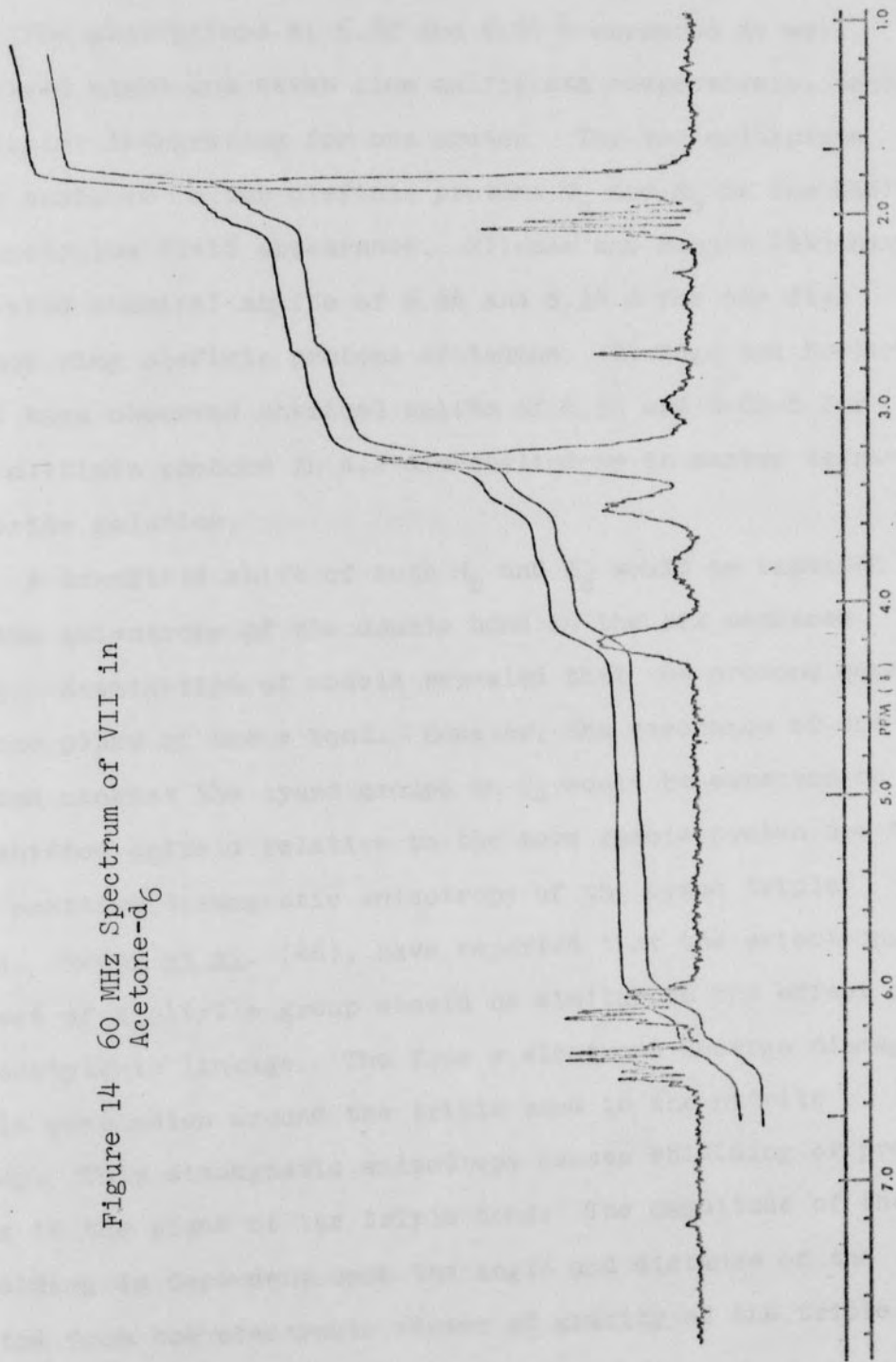
Figure 12 Decoupling of  $H_a$  from  $H_c$  in VIIIFigure 13 Decoupling of  $H_e$  and  $H_f$  from  $H_c$  in VIII

Figure 14 60 MHz Spectrum of VII in  
Acetone-d<sub>6</sub>

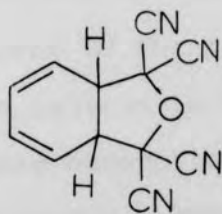


The absorptions at 6.42 and 6.09  $\delta$  appeared as well resolved eight and seven line multiplets respectively, each multiplet integrating for one proton. The two multiplets were assigned to the olefinic protons  $H_a$  and  $H_b$  on the basis of their low field appearance. Elleman and Manatt (44) have reported chemical shifts of 6.66 and 6.14  $\delta$  for the five carbon ring olefinic protons of indene. Elvidge and Foster (45) have observed chemical shifts of 6.36 and 6.82  $\delta$  for the olefinic protons in 4,7-dimethylindene in carbon tetrachloride solution.

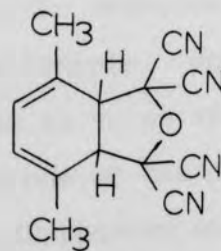
A downfield shift of both  $H_b$  and  $H_a$  would be expected by the anisotropy of the double bond in the six membered ring. Examination of models revealed that the protons were in the plane of the  $\pi$  bond. However, the resonance of the proton nearest the cyano groups on  $C_4$  would be expected to be shifted upfield relative to the more remote proton due to the positive diamagnetic anisotropy of the cyano triple bond. Reddy et al. (46), have reported that the anisotropy effect of a nitrile group should be similar to the effect of an acetylenic linkage. The four  $\pi$  electrons undergo diamagnetic precession around the triple bond in the nitrile group. This diamagnetic anisotropy causes shielding of protons in the plane of the triple bond. The magnitude of the shielding is dependent upon the angle and distance of the proton from the electronic center of gravity of the triple

bond. Davis and Van Auken (31) have reported that the eclipsed proton, whether endo or exo, adjacent to the nitrile group in 5-cyano-2-norbornene is shifted upfield relative to the corresponding proton in the isomeric compound. Cross and Harrison (47) have observed long range shielding due to the cyano substituents in 5-cyano steroids. The downfield eight line multiplet was assigned to  $H_a$ , and the seven line multiplet was assigned to  $H_b$  in agreement with the shielding due to the triple bond of the nitrile group.

The broad absorption peak at 4.21  $\delta$  showed no resolvable fine splitting and integrated for a single proton. This peak was assigned to  $H_c$  on the basis of chemical shifts in acetone- $d_6$  reported by Linn and Benson (48) for 1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran (XVIII) and 4,7-dimethyl-1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran (XIX). The tertiary protons absorbed at 4.60 and 4.58  $\delta$  respectively.



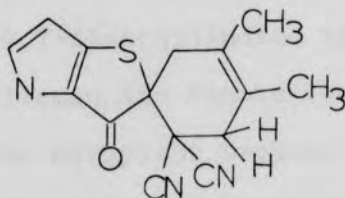
XVIII



XIX

The region between 3.82 and 2.90  $\delta$  (Figure 15) consisted of four broad peaks; the outer two peaks were

approximately equal in intensity, and the inner two peaks varied in intensity. The entire region integrated for four protons. The distance between peaks 1 and 2, and 3 and 4 was equal to 18.0 cps, and the distance between the centers of the two outer peaks was equal to 31.0 cps. Van Dyke and Snyder (49) have reported the nmr spectrum of the following geminal substituted cyclohexene (XX):



XX

They observed a chemical shift difference and coupling constant of 41 and 19 cps respectively for the methylene protons adjacent to the geminal cyano substituents. On this basis, the pattern in Figure 15 appeared to be an AB quartet with another absorption coincident with one of the peaks. Protons  $H_e$  and  $H_f$  were assigned to the AB pattern absorbing at 3.03 and 2.18  $\delta$  respectively. Inspection of models indicated that the pseudoaxial proton  $H_e$  was approximately in the plane of the triple bond of the axial cyano groups on

C<sub>4</sub> and C<sub>5</sub> and was shielded to higher field resonance. The pseudoequatorial hydrogen H<sub>f</sub> was spatially aligned approximately equidistant between the axial and equatorial groups on C<sub>5</sub> and was not in the plane of the  $\pi$  bond (28,50). This supported the assignment of the upfield doublet of the AB quartet to the resonance of H<sub>e</sub>.

The absorption at 3.23  $\delta$  integrated for approximately 2.5 protons. It contained the methylene protons H<sub>d</sub> of the five carbon ring in addition to that part of the AB pattern due to H<sub>f</sub>. This assignment was supported by the chemical shifts of 3.11  $\delta$  observed by Elvidge and Foster (45) for the methylene protons in 4,7-dimethylindene in carbon tetrachloride solution. Elleman and Manatt (44) have reported a value of 2.99  $\delta$  for the methylene protons of indene.

The broadened multiplet at 1.83  $\delta$  was assigned to the methyl protons on the basis of Linn and Benson's (48) reported value of 2.08  $\delta$  for the methyl absorptions in the isobenzofuran derivative (XIX).

#### Coupling Constants in Compound VII

The olefinic protons H<sub>a</sub> and H<sub>b</sub> showed resonance peaks at 6.42 and 6.09  $\delta$  respectively. The absorption due to H<sub>a</sub> was split by spin coupling with the methylene protons H<sub>d</sub> of the five carbon ring, the lone tertiary proton H<sub>c</sub>, and the adjacent olefinic proton H<sub>b</sub>. The coupling constants arising



from interaction between  $H_a$  and the protons  $H_b$  and  $H_c$  were obtained from double resonance experiments. The coupling constants obtained were  $J_{ab} = 6.2$  cps and  $J_{ac} = 2.4$  cps. A coupling constant of  $J_{ad} = 2.4$  cps was invoked to account for the eight line multiplicity. The absorption due to  $H_b$  was split by spin coupling with the adjacent olefinic proton  $H_a$ , the adjacent tertiary proton  $H_c$ , and the methylene protons  $H_d$  in the five carbon ring. As in the case for the  $H_a$  absorption, the coupling constants were obtained from the decoupled spectrum. The doublet due to coupling with the adjacent olefinic proton  $H_a$  ( $J_{ba} = 6.2$  cps) was split again into doublets ( $J_{bc} = 1.6$  cps) by  $H_c$  and additionally split into triplets ( $J_{bd} = 1.9$  cps) by the methylene protons  $H_d$ .

Irradiating the center of the eight line multiplet due to  $H_a$  resulted in a change in the  $H_b$  absorption. The two outer peaks of the seven line multiplet due to  $H_b$  were removed; however the beat pattern of the side band of the irradiating frequency distorted the center of the multiplet such that no additional information could be obtained. Irradiating the center of the seven line multiplet attributed to  $H_b$  caused a change in  $H_a$  similar to that observed in  $H_b$  during the irradiation of the eight line multiplet.

It was observed during irradiation of  $H_c$  (4.21  $\delta$ ) that the eight and seven line multiplets of  $H_a$  and  $H_b$  simplified to an AB pattern with each peak of the quartet split into

triplets by coupling with the protons  $H_d$  (Figure 16). The triplet pattern in the  $H_b$  doublet of the AB quartet was better resolved; whereas the triplet pattern in the  $H_a$  absorption was broadened. This was consistent with the assignment of the greater coupling constant to  $H_a-H_d$  interaction and assignment of the smaller constant to  $H_b-H_d$  interaction.

Irradiation of the absorption due to  $H_d$  (3.23  $\delta$ ) caused the complex multiplets of  $H_a$  and  $H_b$  to reduce to an ABX pattern ( $J_{ab} = 6.2$  cps,  $J_{ax} = 2.4$  cps, and  $J_{bx} = 1.6$  cps) (Figure 17). The coupling of  $H_c$  with  $H_a$  ( $J_{ac} = 2.4$  cps), where  $H_c$  is the X proton of the ABX pattern, was greater than the coupling of  $H_c$  with  $H_b$  ( $J_{bc} = 1.6$  cps).

Irradiation of  $H_e$ ,  $H_f$ , and  $CH_3$  showed no changes in the absorptions of  $H_a$  and  $H_b$ .

It should be noted that the above coupling constant assignments required that  ${}^4J$  [coupling over four bonds (43)] be greater than  ${}^3J$  (coupling over three bonds) for the  $H_a$ ,  $H_b$ ,  $H_c$  vinyl-allylic system and that  ${}^3J$  be greater than  ${}^4J$  in the  $H_a$ ,  $H_b$ ,  $H_d$  vinyl-allylic system. Such an inverse in the coupling of a vinyl-allylic system has been observed in the spectrum of 2-butenic acid- $\gamma$ -lactone (51) in which  ${}^4J$  was greater than  ${}^3J$ . Elvidge and Foster (45) have observed  ${}^4J = 2$  cps in 2-methylindene and  ${}^3J = 1.7$  cps in 3-methylindene. House and Rasmusson (52) have noted  ${}^3J > {}^4J$  in the

Figure 16 Decoupling of  $H_a$  and  $H_b$  from  $H_c$  in VII (Acetone- $d_6$ )<sup>a</sup>

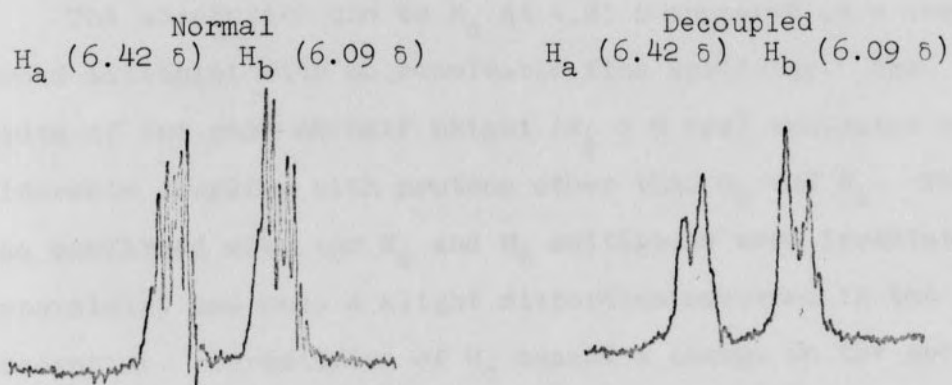
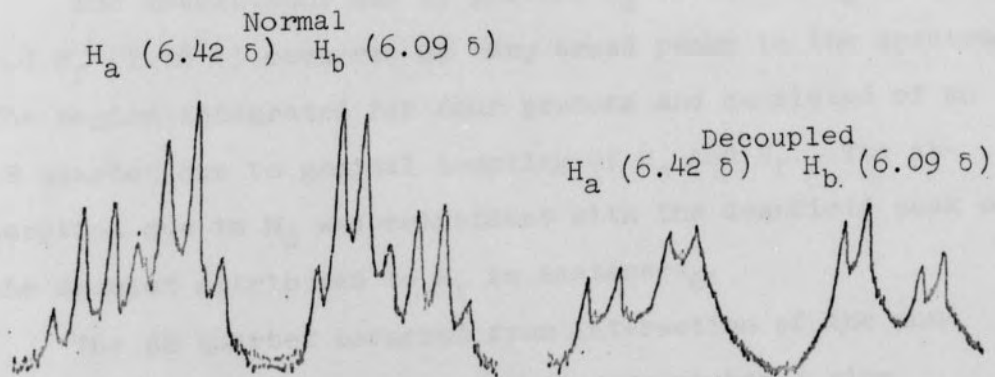


Figure 17 Decoupling of  $H_a$  and  $H_b$  from  $H_d$  in VII (Acetone- $d_6$ )<sup>a</sup>



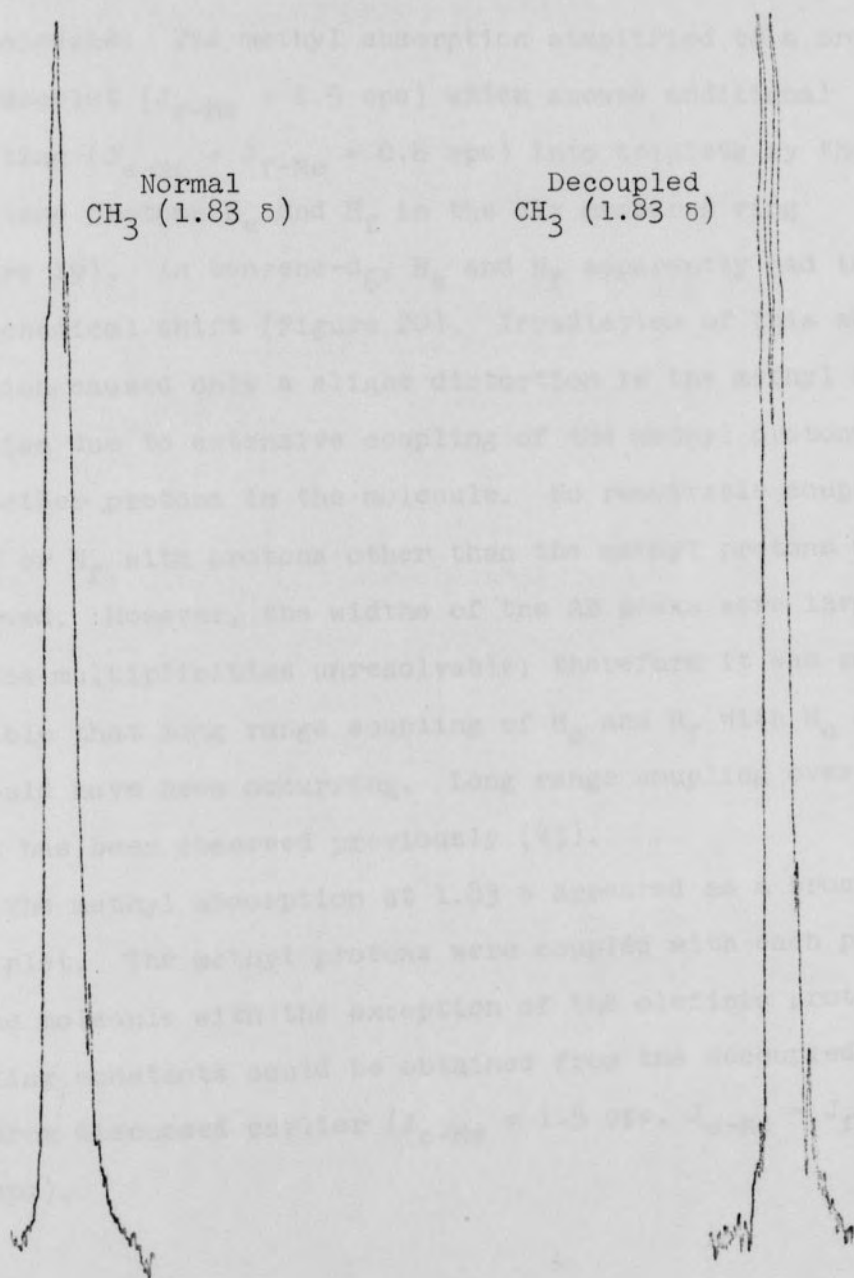
spectrum of 3a,4,7,7a-tetrahydroindene. The coupling constant magnitudes estimated from the spectrum of 2-butenic acid- $\gamma$ -lactone and reported for the indene derivatives were in agreement for the values reported for compound VII.

The absorption due to  $H_c$  at 4.21  $\delta$  appeared as a very broad multiplet with no resolvable fine splitting. The width of the peak at half height ( $W_{\frac{1}{2}} = 9$  cps) indicated considerable coupling with protons other than  $H_a$  and  $H_b$ . This was confirmed when the  $H_a$  and  $H_b$  multiplets were irradiated separately, and only a slight distortion occurred in the  $H_c$  absorption. Irradiation of  $H_c$  caused a change in the absorption of the methyl substituent. Interpretation of the change was hindered since the multiplicity of the resulting pattern was unresolvable. Indication of coupling between  $H_c$  and the methyl protons was also obtained when  $H_d$  was irradiated, and the methyl multiplet simplified to a broadened doublet ( $J_{c-Me} = 1.5$  cps) (Figure 18).

The absorptions due to protons  $H_d$  (3.23  $\delta$ ),  $H_e$  (3.03  $\delta$ ), and  $H_f$  (2.18  $\delta$ ) occurred as very broad peaks in the spectrum. The region integrated for four protons and consisted of an AB quartet due to geminal coupling of  $H_e$  and  $H_f$ . The absorption due to  $H_d$  was coincident with the downfield peak of the doublet attributed to  $H_f$  in acetone- $d_6$ .

The AB quartet occurred from interaction of the non-equivalent methylene protons in the six membered ring

Figure 18 Decoupling of  $\text{CH}_3$  from  $\text{H}_d$  in VII  
(250 Hz Sweep Width)



( $J_{ef} = 18.0$  cps). The width ( $W_{\frac{1}{2}} = 10.0$  cps) of each peak of the quartet indicated coupling with additional protons in the molecule. The methyl absorption simplified to a broadened doublet ( $J_{c-Me} = 1.5$  cps) which showed additional splitting ( $J_{e-Me} = J_{f-Me} = 0.8$  cps) into triplets by the methylene protons  $H_e$  and  $H_f$  in the six membered ring (Figure 19). In benzene- $d_6$ ,  $H_e$  and  $H_f$  apparently had the same chemical shift (Figure 20). Irradiation of this absorption caused only a slight distortion in the methyl absorption due to extensive coupling of the methyl protons with other protons in the molecule. No resolvable coupling of  $H_e$  or  $H_f$  with protons other than the methyl protons was observed. However, the widths of the AB peaks were large and the multiplicities unresolvable; therefore it was conceivable that long range coupling of  $H_e$  and  $H_f$  with  $H_c$  and  $H_d$  could have been occurring. Long range coupling over five bonds has been observed previously (43).

The methyl absorption at 1.83  $\delta$  appeared as a broadened multiplet. The methyl protons were coupled with each proton in the molecule with the exception of the olefinic protons. Coupling constants could be obtained from the decoupled spectrum discussed earlier ( $J_{c-Me} = 1.5$  cps,  $J_{e-Me} = J_{f-Me} = 0.8$  cps).

Figure 19 Decoupling of  $\text{CH}_3$  from  $\text{H}_d$  in VII  
(100 Hz Sweep Width)

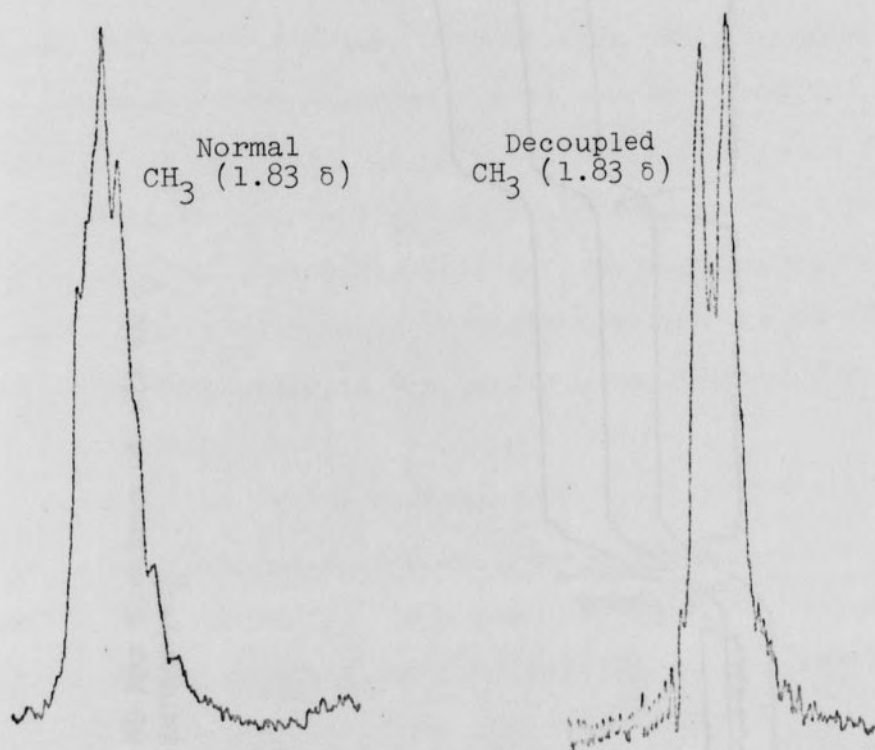
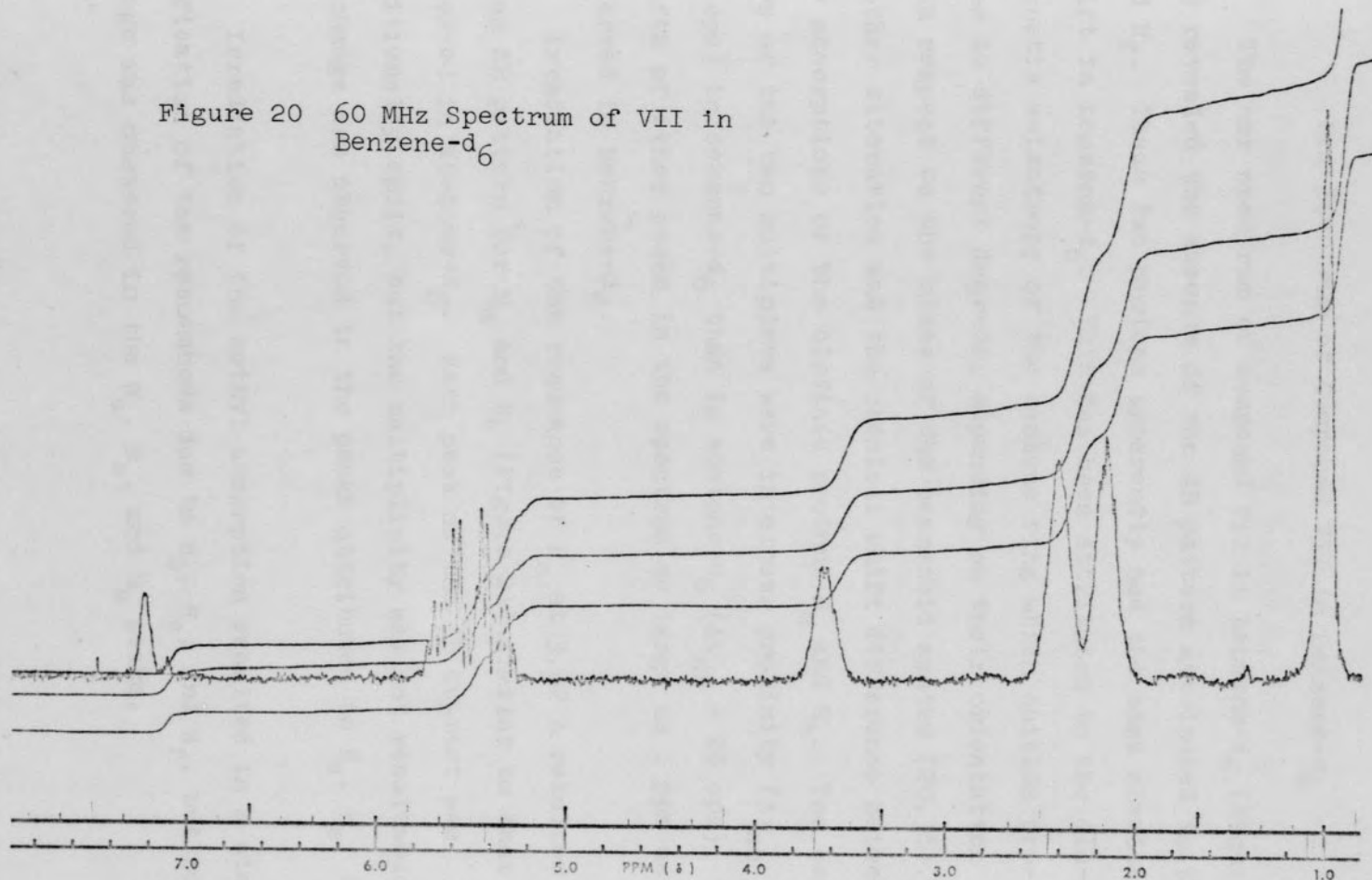


Figure 20 60 MHz Spectrum of VII in Benzene-d<sub>6</sub>





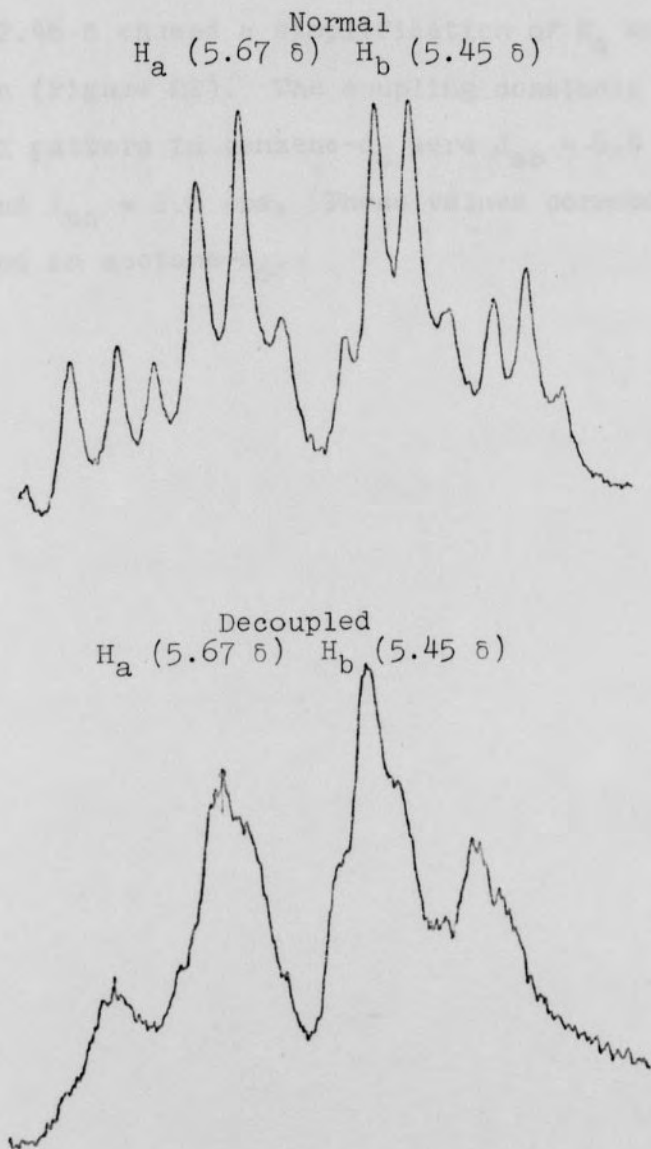
Nmr Spectrum of Compound VII in Benzene-d<sub>6</sub>

The nmr spectrum of compound VII in benzene-d<sub>6</sub> (Figure 20) revealed the absence of the AB pattern attributed to H<sub>e</sub> and H<sub>f</sub>. These two protons apparently had the same chemical shift in benzene-d<sub>6</sub>. This has been attributed to the diamagnetic anisotropy of the benzene ring which shields protons to different degrees, depending on their orientation with respect to the plane of the benzenoid system (20,36). Another alteration was the chemical shift difference between the absorptions of the olefinic protons H<sub>a</sub> and H<sub>b</sub>. The centers of the two multiplets were in closer proximity ( $\Delta\nu_{ab} = 14$  cps) in benzene-d<sub>6</sub> than in acetone-d<sub>6</sub> ( $\Delta\nu_{ab} = 20$  cps). Shifts of other peaks in the spectrum as large as 1 ppm were observed in benzene-d<sub>6</sub>.

Irradiation of the resonance of H<sub>c</sub> at 3.62  $\delta$  resulted in an AB pattern for H<sub>a</sub> and H<sub>b</sub> (Figure 21) similar to that observed in acetone-d<sub>6</sub>. Each peak of the AB quartet was additionally split, but the multiplicity was not resolvable. No change was observed in the peaks attributed to H<sub>d</sub>, H<sub>e</sub>, or H<sub>f</sub>.

Irradiation of the methyl absorption resulted in a simplification of the resonances due to H<sub>d</sub>, H<sub>e</sub>, and H<sub>f</sub>, but no change was observed in the H<sub>c</sub>, H<sub>a</sub>, and H<sub>b</sub> peaks.

Figure 21 Decoupling of  $H_a$  and  $H_b$  from  $H_c$   
in VII (Benzene- $d_6$ )

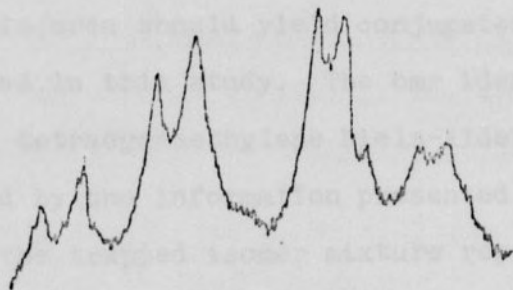


Irradiation of the peak attributed to  $H_e$  and  $H_f$  resulted in no observable change in the resonances of  $H_a$ ,  $H_b$ , or the methyl hydrogens.

Irradiation of the absorption of the methylene protons  $H_d$  at 2.46  $\delta$  caused a simplification of  $H_a$  and  $H_b$  to an ABX pattern (Figure 22). The coupling constants observed for the ABX pattern in benzene- $d_6$  were  $J_{ab} = 6.4$  cps,  $J_{ac} = 2.4$  cps, and  $J_{bc} = 1.6$  cps. These values corroborated the data obtained in acetone- $d_6$ .

Figure 22 Decoupling of  $H_a$  and  $H_b$  from  $H_d$   
in VII (Benzene- $d_6$ )

Decoupled  
 $H_a$  (5.67  $\delta$ )  $H_b$  (5.45  $\delta$ )



## SUMMARY

It is anticipated that the results obtained with tetracyanoethylene as a trapping agent for the isomer mixture will be useful in subsequent studies. The experiments planned in this area should yield conjugated dienes similar to those formed in this study. The nmr identification of the resulting tetracyanoethylene Diels-Alder adducts should be facilitated by the information presented in this thesis.

Whether the trapped isomer mixture represented the kinetically controlled protonation mixture or a mixture derived from subsequent rearrangements, remains unresolved. Additional work in this area is in progress.

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