

THE ^{13}C NMR SPECTRA OF CONJUGATED CARBANIONS
AND
PREPARATION AND THERMAL BEHAVIOR OF 3-VINYLCYCLOOCTADIENYL ANION

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PREPARATION AND THERMAL BEHAVIOR OF
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ABSTRACT

The first ^{13}C chemical shifts and $^{13}\text{C-H}$ coupling constants of pentadienyl and 3-vinylpentadienyl anions are obtained by the INDOR method and by direct measurement. The chemical shifts provide the best evidence to date regarding the electron density distribution in these anions. The results indicate high density at the odd-numbered carbons in these anions in accordance with molecular orbital theory. The chemical shift of the central carbon in cyclic pentadienyl anions is greater than that of the end carbons, suggesting higher electron density at the central atom, in accordance with certain chemical results and some molecular orbital calculations.

The cross-conjugated anion 3-vinylcyclooctadienyl anion was prepared. Unlike cyclooctadienyl anion, it did not cyclize on heating; possible reasons for this difference are discussed.

PART I

THE ^{13}C NMR SPECTRA OF CONJUGATED CARBANIONS

INTRODUCTION

The major goal of this research project was to measure the ^{13}C chemical shifts and ^{13}C -H spin-spin coupling constants of pentadienyl and related carbanions. The coupling constants give an indication of the hybridization of the ^{13}C (expected to be sp^2 in these anions), and the electron density at ^{13}C can be determined from the ^{13}C chemical shift (1,2).

In 1957 the first nuclear magnetic resonance of a ^{13}C nucleus was reported by Lauterbur (3). His work was done with natural abundance ^{13}C (1%). He listed ^{13}C chemical shifts and coupling constants for over 100 organic compounds.

An NMR technique useful for getting ^{13}C spectra indirectly in cases in which protons are attached to the carbons of interest was introduced by Baker in 1962 (4) and has become known as the INDOR (Inter-nuclear Double Resonance) method. The INDOR method employs a proton-stabilized frequency sweep spectrometer, a ^{13}C -region frequency synthesizer, a frequency counter, and an X-Y recorder. While the spectrometer is held on a ^{13}C satellite absorption peak in the proton spectrum, the frequency synthesizer, at lower radio frequency power output, is used to sweep through the absorption frequencies of ^{13}C . If H and ^{13}C are spin coupled, the intensity of the H transition will change as the resonance frequencies of ^{13}C are traversed. If the power level of the ^{13}C radio frequency is suitably adjusted, these intensity changes

of the H line will duplicate the actual ^{13}C spectrum. The INDOR method provides ^{13}C chemical shifts and ^{13}C -H coupling constants. Because of the much greater intensity of H NMR signals as compared to ^{13}C NMR signals and the relative simplicity of the equipment required, the INDOR method is sometimes the method of choice for obtaining such parameters.

^{13}C Chemical Shifts

The chemical shift of a specific nucleus "a" depends on the field experienced at that nucleus. Generally speaking, the chemical shift value increases as the electron density increases. Theoretical treatments of ^{13}C chemical shifts have been offered by several workers (5,6,7). Hoffmann (8) has made calculations using the extended Huckel theory for ^{13}C chemical shifts. His calculations are in agreement with the chemical shifts observed by Olah (9,10). Karplus and Pople formulated a molecular orbital theory giving reasonable agreement with experimental values of ^{13}C chemical shifts for conjugated hydrocarbons (11). Olah has used the well-established relationship of ^{13}C chemical shifts to electron density for studying alkyl carbonium ions, hydroxyl carbonium ions, phenyl and cyclopropyl carbonium ions, and others (9).

^{13}C -H Coupling Constants

The $J_{\text{C-H}}$ value for protons directly bonded to ^{13}C is related to the hybridization of the C-H bond in some cases, such as alkanes, alkenes, alkynes, and aromatic hydrocarbons, as indicated in Table 1 (12).

Table 1. ^{13}C -H Coupling Constants vs. Hybridization.

Bond	$J_{\text{C-H}}$, Hz
sp^3	124-126
sp^2	154-160
sp	248-251

Olah has used experimentally determined ^{13}C -H coupling constants to describe the ^{13}C hybridization in several cations. The J values of norbornyl and related compounds are discussed in terms of particular C-H bonds. In the case of 2-norbornyl cation, the coupling constant for carbon number 1 is 125 (13), as expected for sp^3 hybridization. He concluded from this J value that 2-norbornyl cation has a nonclassical structure.

Olah has reported the coupling constants for several alkyl cations (14). For instance, isopropyl cation has a coupling constant of 168, which implies (using standard numbers slightly different than those in Table 1) that the carbon-hydrogen bond of the central carbon has 33.6% s-hybridization, while in the case of diphenylmethinyl cation the methinyl carbon-hydrogen bond has a coupling constant of 164 and 32.8% s-hybridization. These results extend the validity of the linear relationship between ^{13}C -H coupling constants and fractional s-character.

However, Olah has changed his point of view on the relationship of J_{C-H} to the hybridization of ^{13}C . The carbon-hydrogen coupling mechanism is sensitive not only to bond hybridization (15), but also to bond polarization, variation in the carbon-hydrogen bond distance, and variation in the mean excitation energy (16).

Pentadienyl Anions

Pentadienyl anions are of special interest because they are intermediates in several chemical reactions. In many of these reactions, it appears that protonation and alkylation occur primarily at the central carbon. For example, in the Birch reduction of aromatic compounds, the protonation of the central carbon atom of a cyclohexadienyl anion has been postulated at the last step (17). Forsythe has studied the alkylation of pentadienyl anion and found the reaction at the central carbon of the anion favored over alkylation to form the conjugated product (18). Bates, Carnighan, and Staples studied the protonation of cyclohexadienyl anion, in which case the central carbon atom is preferentially protonated (19).

It has been suggested that protonation and alkylation occur at the central carbon atom rather than the end carbon atom because of greater electron density at the central carbon atom (17). Although simple Huckel MO calculations predict an equal charge density at carbons 1, 3, and 5 in pentadienyl anion (20), more sophisticated calculations can give either greater or lesser charge on the central atom, depending on the bond lengths selected (21).

An alternate explanation for the central protonation of cyclohexadienyl anion is offered by Hine (22). The principle of least motion, attributed to Rice and Teller (23), is used to explain the experimental observations. According to this principle, those elementary reactions will be favored that involve the least change in atomic positions and electronic configurations. The necessity of greater change in the internal geometry may cause the activation energy to be greater for the formation of 1,3-cyclohexadiene than for the formation of 1,4-cyclohexadiene.

EXPERIMENTAL

The apparatus used for the INDOR measurements is shown schematically in Figure 1. The ^{13}C satellites in the proton spectra were obtained at 100 MHz using a Varian Associates Model HA-100 spectrometer. The frequency required for ^{13}C irradiation was generated using the first upper side band created by modulating the $\sim 25,150,000$ MHz crystal frequency of an NMR Specialties HD-60 decoupler with the output of a Wavetek Model 131 VCG generator. The irradiating frequency was swept using a voltage ramp (Figure 2) and monitored with a Hewlett-Packard 5248L electronic frequency counter. The voltage ramp had provisions for sweeping in either direction at different speeds and the sweep could be stopped at any point (24). The INDOR spectra were recorded on an F. L. Moseley Company Model 2D-2A X-Y recorder.

For obtaining INDOR spectra, the HA-100 spectrometer was operated on the internal lock, frequency sweep mode and the first upper side band of internal TMS was used for the lock signal. Typical settings were: R.F. field attenuation = 10, sweep frequency = 1.0, sweep width = 250 or 500, sweep time = 500 seconds, and output = 0.4. Less noise was introduced if the signal height was increased by minimizing the R.F. field attenuation and maximizing the sweep frequency and spectrum amplitude rather than the output. The R.F. phase was critical: a slope far from horizontal in the output line can make "sitting" on a ^{13}C satellite difficult, and in some cases completely obscure the satellite.

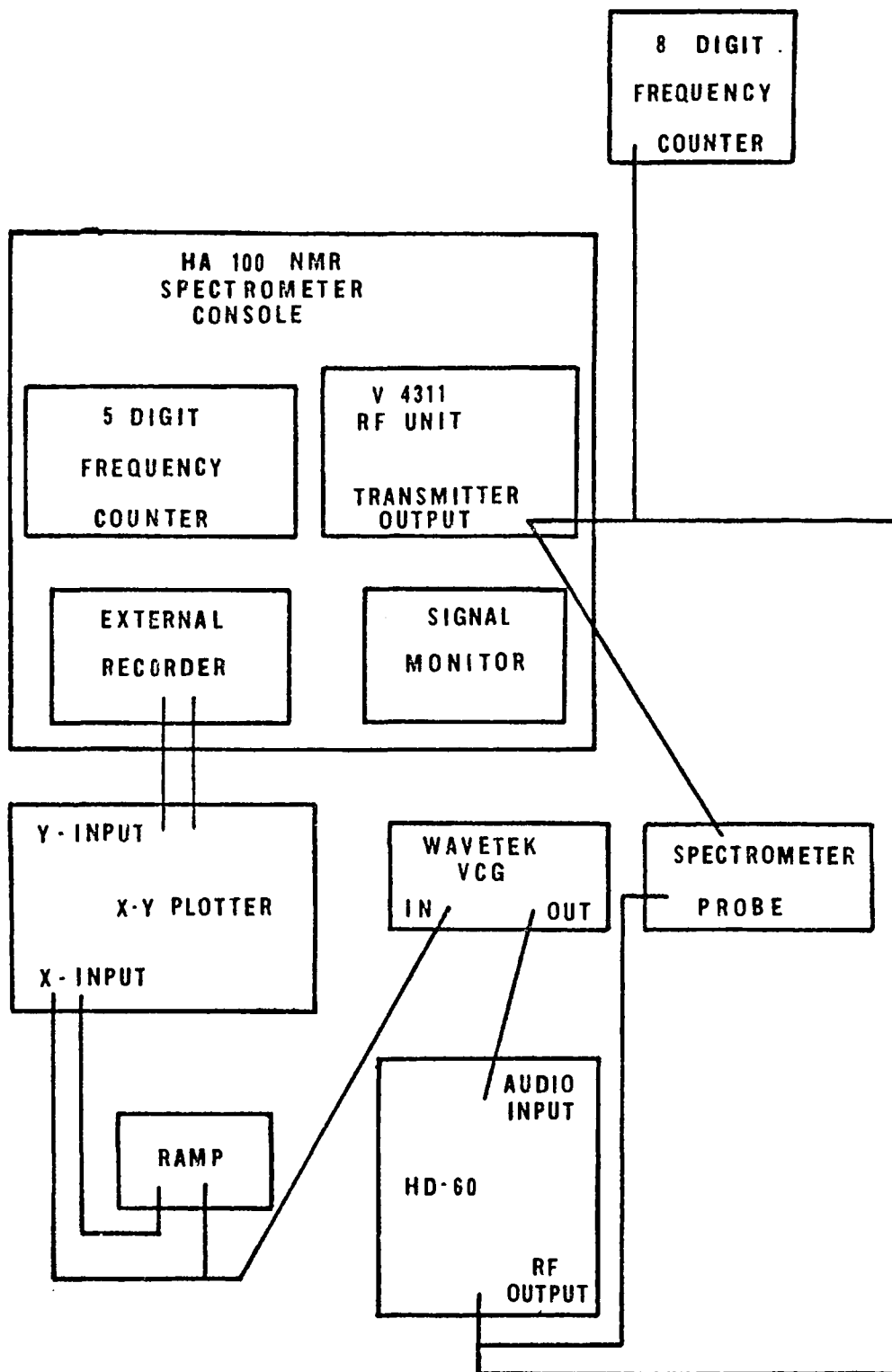
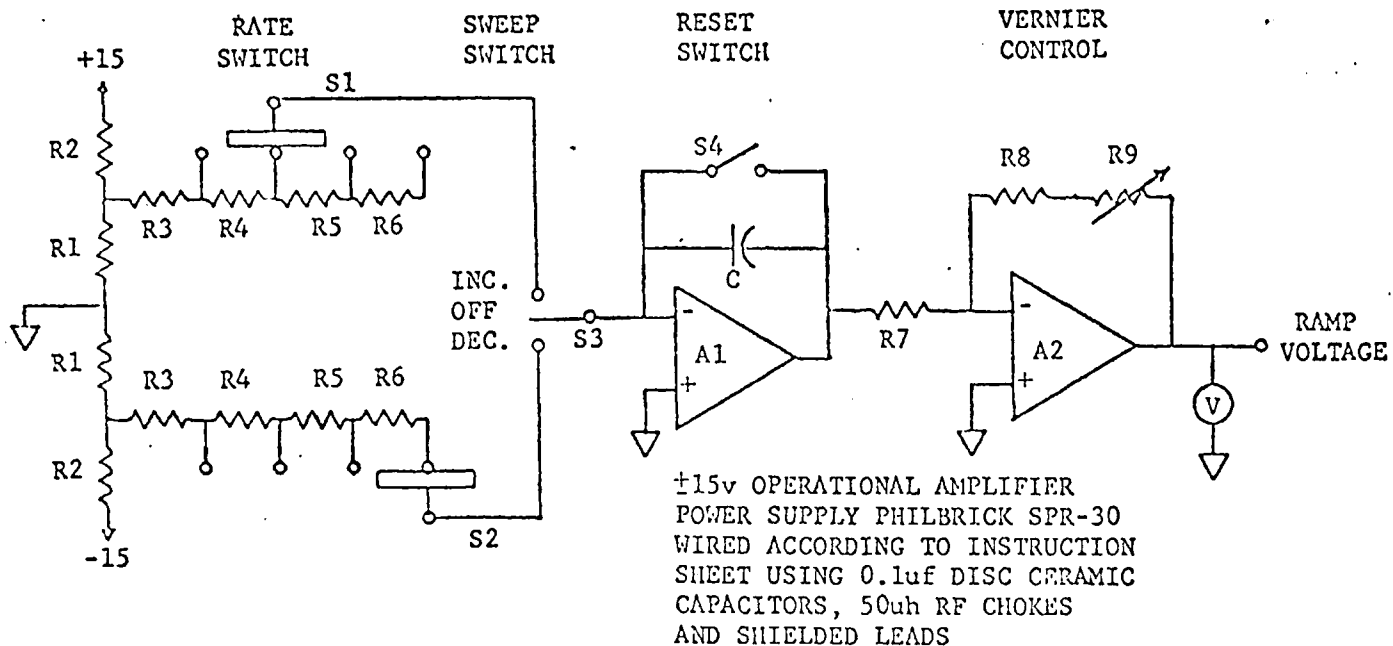


Figure 1. Schematic drawing of INDOR apparatus.



CARBON FILM RESISTORS ±1%		R9	10 KΩ W.W. LIN. TAPER
R1	100 Ω	C	10 uf POLYSTYRENE CAPACITOR
R2	15 KΩ	S1	CERAMIC ROTARY SWITCH
R3	10 "	S2	1 POLE 4 POS. SHORTING
R4	90 "	S3	LEVER SWITCH SPDT CENTER OFF
R5	900 "	S4	SPST TOGGLE SWITCH
R6	9 MΩ	V	0-2v 50 KΩ /v
R7	10 KΩ	A1	PHILBRICK OPERATIONAL
R8	1 "	A2	AMPLIFIER SP2A

Figure 2. Ramp voltage generator to control frequency sweep oscillator.

The first step was to locate the ^{13}C satellite and place the pen on the signal. The ^{13}C satellite signal was in all cases at least four mm high for INDOR spectra. Care was taken in positioning the pen at the peak of the satellite. If the pen was improperly positioned, the INDOR spectra had inflection points rather than the desired doublet, triplet, or quartet of absorption peaks.

Next, the ^{13}C satellite decoupling frequency was approximated. The approximate frequency was obtained by hand using the Wavetek and the HD-60. The HD-60 decoupler was in the upper side band setting and the audio gain was varied from 20-70 (generally close to the latter value). The carbanions studied decoupled at settings between $0.1 \times 10\text{K}$ and $0.4 \times 10\text{K}$ on the Wavetek. Also, the ^{13}C satellite signal collapsed if the audio gain setting was much above 70, due to heating phenomena. Once the signal was decoupled by hand, the approximate frequency was measured by the frequency counter. At certain frequencies, the audio gain had to be maximized to get the proper reading on the frequency counter. Also, it was found helpful to place the frequency counter 15 feet from the HD-60 in order to lessen interference.

The ramp was used to sweep the frequency region of interest at a rate of 2 Hz/sec. Once the INDOR spectrum appeared on the X-Y plotter, the audio gain of the HD-60 was adjusted for the best presentation (generally 60-70 mv).

In gathering the data for ^{13}C chemical shift calculations, the V-4311 output was measured using the eight-digit frequency counter, before and after the INDOR spectrum was recorded. It was necessary to

reduce the audio gain on the HD-60 to below 10 to read this frequency and to have a setting of less than 10 db on the V-4311. The peak positions recorded on the X-Y plotter were measured using the eight-digit frequency counter.

Finally, the lock modulation frequency was measured using the five-digit counter on the HA-100. The HA-100 signal monitor was set on "sweep frequency" and the frequency recorded with the pen still "sitting" on the satellite. In order to read the lock modulation frequency, the eight-digit frequency counter had to be off.

Calculations of ^{13}C Chemical Shifts

The chemical shifts of the carbanions are reported in ppm upfield from carbon disulfide, CS_2 , the most widely used standard. The chemical shifts of ^{13}C are known to have a range of 450 ppm, which is much greater than the range of protons.

The ^{13}C chemical shifts obtained by the INDOR method are generally first calculated with respect to tetramethylsilane (TMS), since the chemical shift of carbon disulfide cannot be measured by this technique, but that of TMS can. Then, the chemical shifts are converted using the following equation.

$$\delta^{13}\text{C}_{\text{CS}_2} = \delta^{13}\text{C}_{\text{TMS}} - 194.6 \quad (1)$$

The standard equation for calculating chemical shifts is Equation 2.

Rather than measure the INDOR spectrum of TMS each time, only the INDOR spectrum of the ^{13}C of interest is recorded, because of a modification

$$\delta^{13}\text{C}_{\text{sample}} = \frac{\nu^{13}\text{C}_{\text{sample}} - \nu^{13}\text{C}_{\text{standard}}}{\nu^{13}\text{C}_{\text{standard}}} \times 10^6 \quad (2)$$

of Equation 2 by Grant (in 25) who measured the ratio of the proton chemical shift to the ^{13}C chemical shift of TMS. The value is a constant equal to 3.9769331.

$$\nu^{1}\text{H}^{\text{TMS}} / \nu^{13}\text{C}^{\text{TMS}} = 3.9769331 .$$

The chemical shift of a sample can now be determined with respect to TMS by measuring the frequency of the TMS proton signal and the ^{13}C frequency of the sample using the INDOR method.

$$\delta^{13}\text{C}_{\text{sample}} = \frac{\nu^{13}\text{C}_{\text{sample}} - \frac{\nu^{1}\text{H}^{\text{TMS}}}{3.9769331}}{\frac{\nu^{1}\text{H}^{\text{TMS}}}{3.9769331}} \times 10^6 \quad (3)$$

Olah has used a similar equation for measuring ^{13}C chemical shifts in carbonium ions (in 10), changing Equation 3 by making algebraic manipulations and a simplifying assumption. Equation 3 was rearranged algebraically to give Equation 4. Then $^{13}\text{C}_{\text{sample}}$ was assumed

$$\delta^{13}\text{C}_{\text{sample}} = \frac{3.9769331 - \frac{\nu^{1}\text{H}^{\text{TMS}}}{\nu^{13}\text{C}_{\text{sample}}}}{\frac{\nu^{1}\text{H}^{\text{TMS}}}{\nu^{13}\text{C}_{\text{sample}}}} \times 10^6 \quad (4)$$

to be equal to $^{13}\text{C}^{\text{TMS}}$, and the denominator was replaced by 3.9769331.

Equation 5 was used by Olah to calculate ^{13}C chemical shifts (in 10).

$$\delta^{13}\text{C}_{\text{sample}} = \frac{3.9769331 - \frac{\nu^{1\text{H TMS}}}{\nu^{13}\text{C}_{\text{sample}}}}{3.9769331} \times 10^6 \quad (5)$$

In the current work, the approximation made by Olah was not used, and Equation 4 was used for the ^{13}C chemical shift calculations. In most cases, the approximation affects the chemical shift by 0.1 ppm.

Calculation of ^{13}C -H Coupling Constants

Although the ^{13}C -H coupling constants could have been taken from the INDOR spectra, it seemed that they could be measured more accurately from the proton spectra. The distance between the main proton signal and the ^{13}C satellite signal was measured. The coupling constant was equal to twice this distance. In order to accurately determine the coupling constant, the main proton signal and the ^{13}C satellite signal were recorded using the same sweep time.

Pentadienyllithium INDOR Sample

Tetrahydrofuran- d_8 (0.09 ml, Norell Chemical Company) and 1,4-pentadiene (0.35 ml, 0.0035 mol, Aldrich Organic Chemical Company) were introduced into an NMR tube and cooled to -78° . Commercial (Foote Mineral Company, 1.6 M in hexane solvent) n-butyllithium (0.7 ml, 0.001 mol) was added and the tube flushed with argon. The reactants were thoroughly mixed and allowed to warm to room temperature. There was a separation of layers after 5 min. The orange-yellow lower layer was found by NMR to contain pentadienyllithium (35% by weight),

tetrahydrofuran (49% by weight), and hexane (16% by weight). A procedure for making pentadienyllithium reported by Potter (26) produced 20% by weight pentadienyllithium. Several efforts to locate and decouple the ^{13}C satellites in a 20% pentadienyllithium sample were unsuccessful. However, they were located and decoupled on a 35% sample. The yellow upper layer, which contained tetrahydrofuran, excess 1,4-pentadiene and hexane, was not removed but was retained to protect the anion in the lower layer from decomposing. The NMR tube was shaken several times over a 6-hr period, and a small amount of TMS was then added to provide an internal standard for the INDOR experiments. The tube was flushed with argon and sealed before examining by NMR. The satellites used are shown in Figures 3 and 4, and the INDOR spectra of this anion are shown in Figures 5 through 7.

3-Vinylpentadienyllithium INDOR Sample

The procedure used was identical to the pentadienyllithium procedure, substituting trivinylmethane generously provided by Cole (27) for 1,4-pentadiene. The satellites used are shown in Figures 8 and 9, and the INDOR spectra are shown in Figures 10 and 11.

Cycloheptadienyllithium INDOR Sample

Cycloheptadienyllithium was prepared from commercial (Chemical Samples Company) 1,3,6-heptatriene using the procedure described for pentadienyllithium. The satellites for C_2 are shown in Figure 12, and the INDOR spectrum of C_2 in this anion is shown in Figure 13.

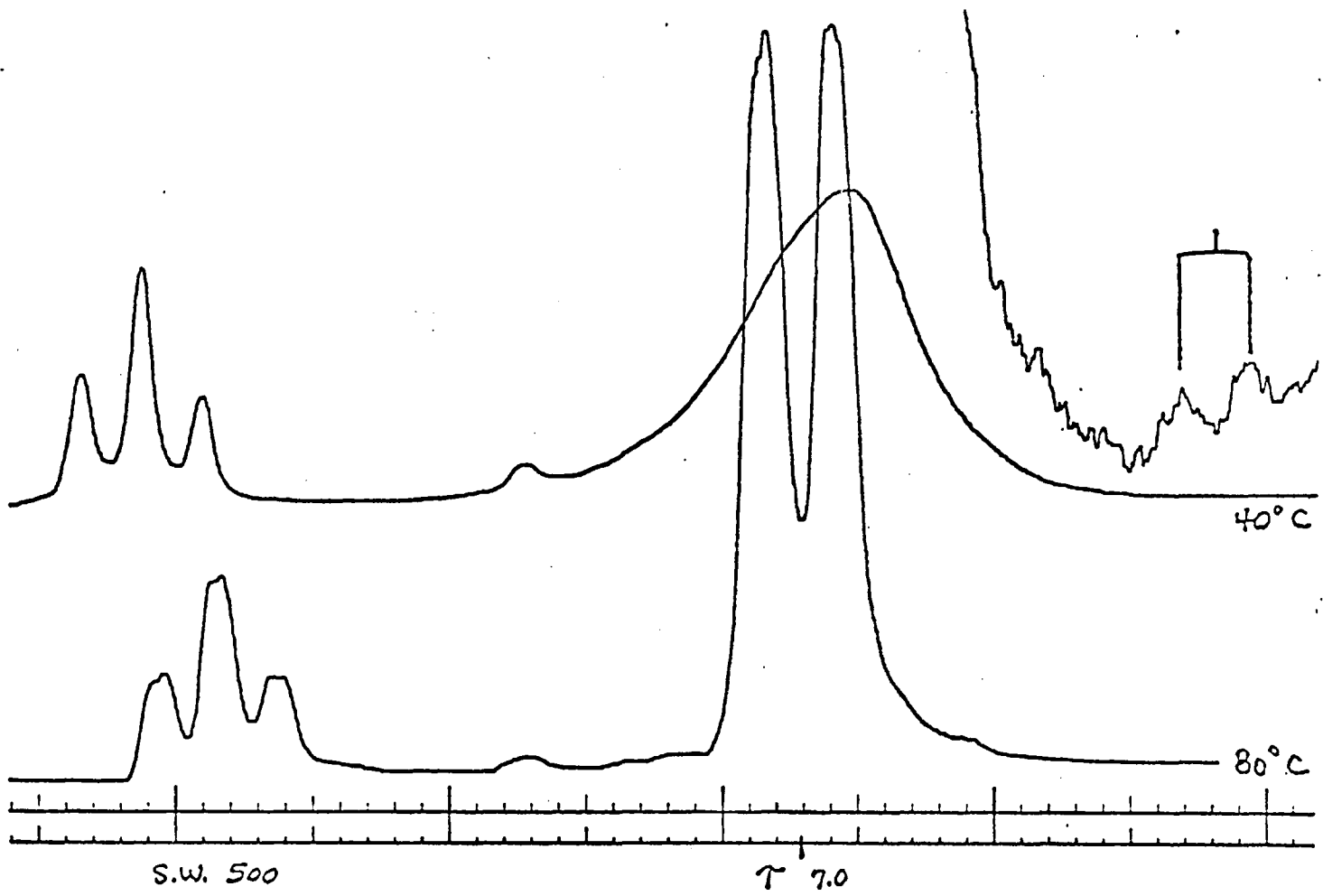


Figure 3. Satellites used for INDOR spectra of C_1 in pentadienyl anion.

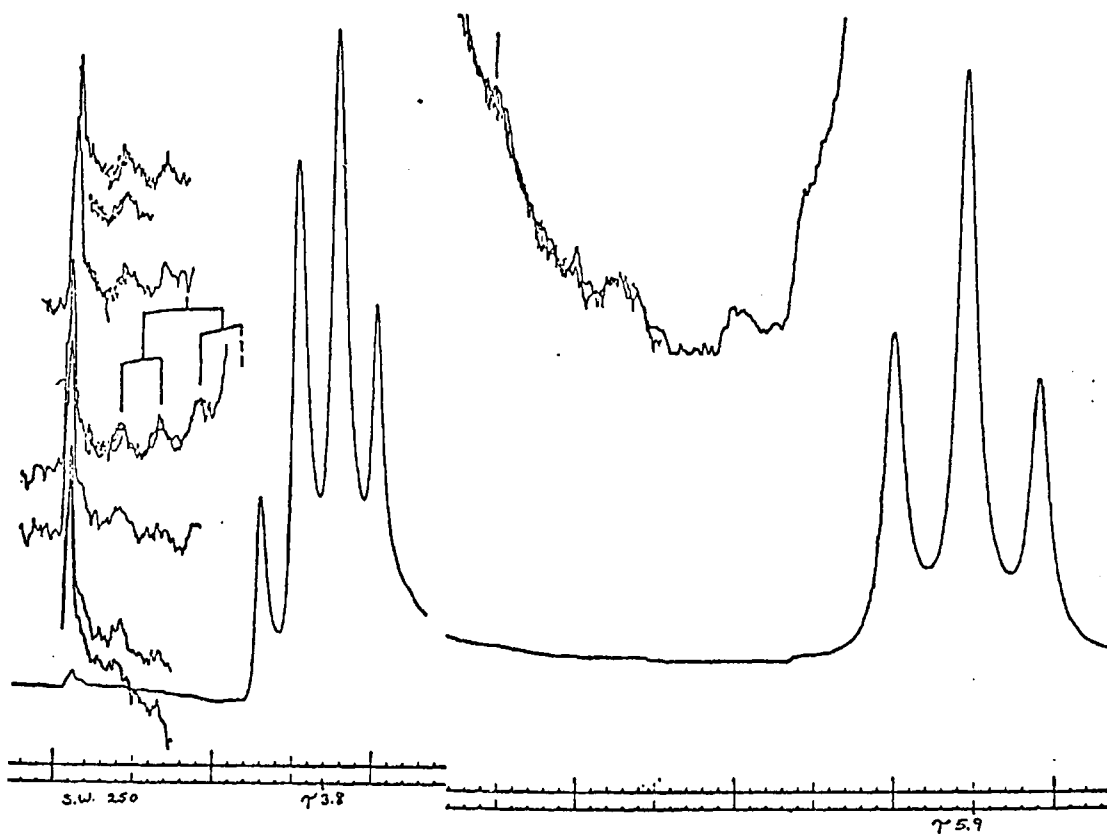


Figure 4. Satellites used for INDOR spectra of C_2 and C_3 in pentadienyl anion.

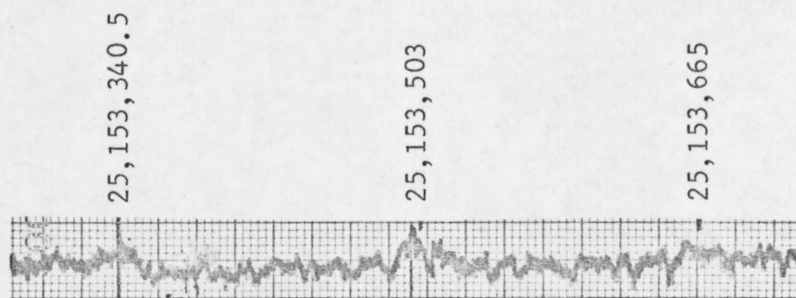


Figure 5. INDOR spectrum of C₁ in pentadienyl anion.

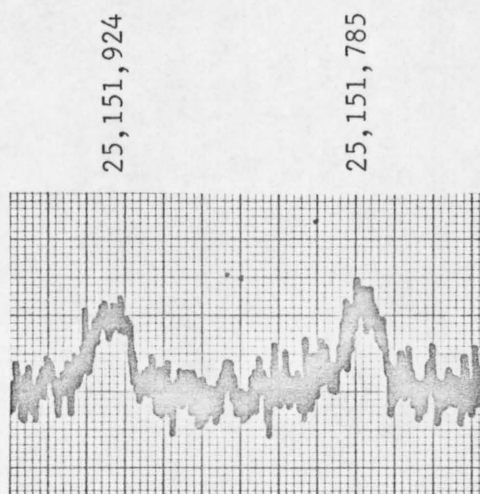


Figure 6. INDOR spectrum of C₂ in pentadienyl anion.

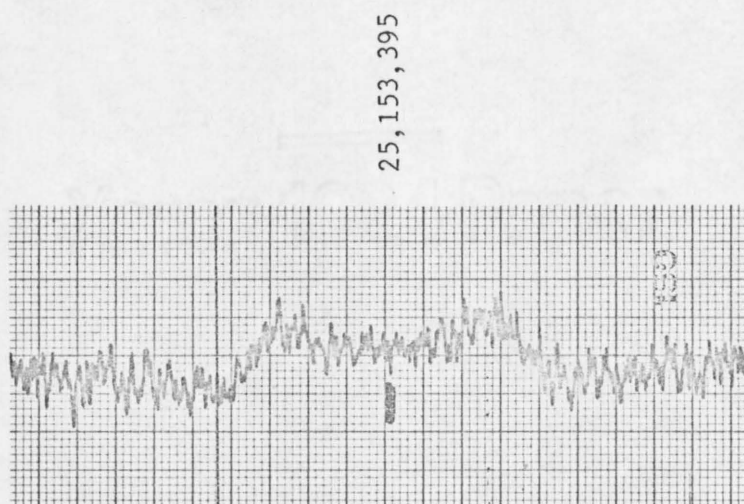


Figure 7. INDOR spectrum of C₃ in pentadienyl anion.

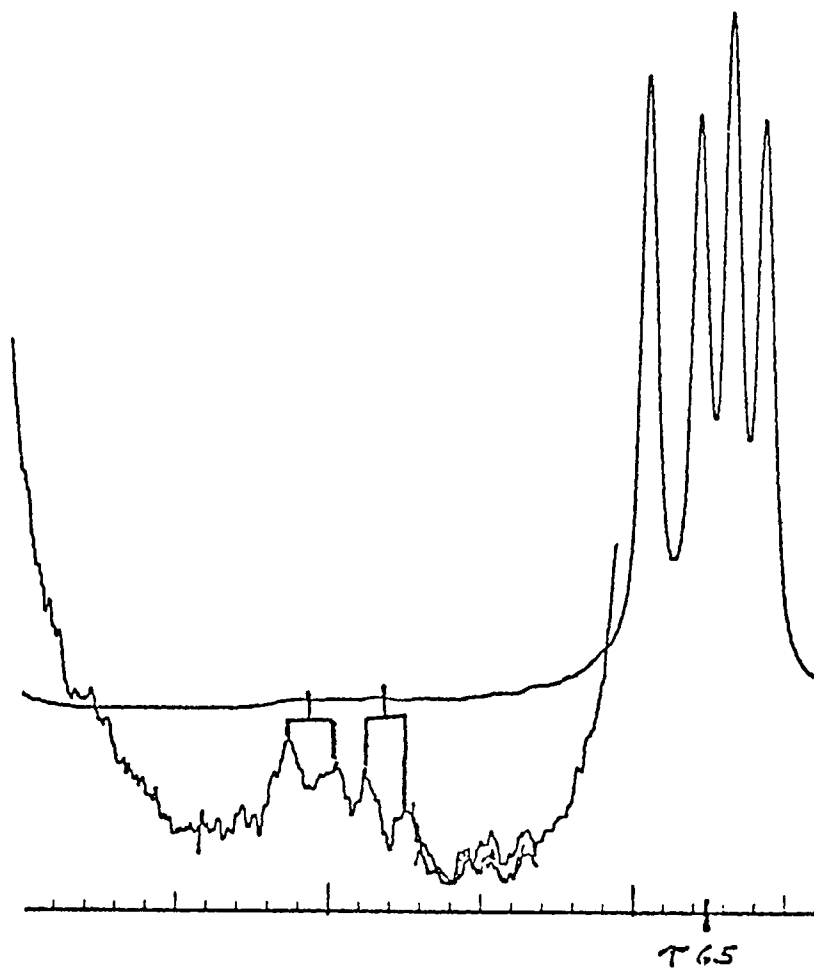


Figure 8. Satellites used for INDOR spectra of C_1 in 3-vinylpentadienyl anion.

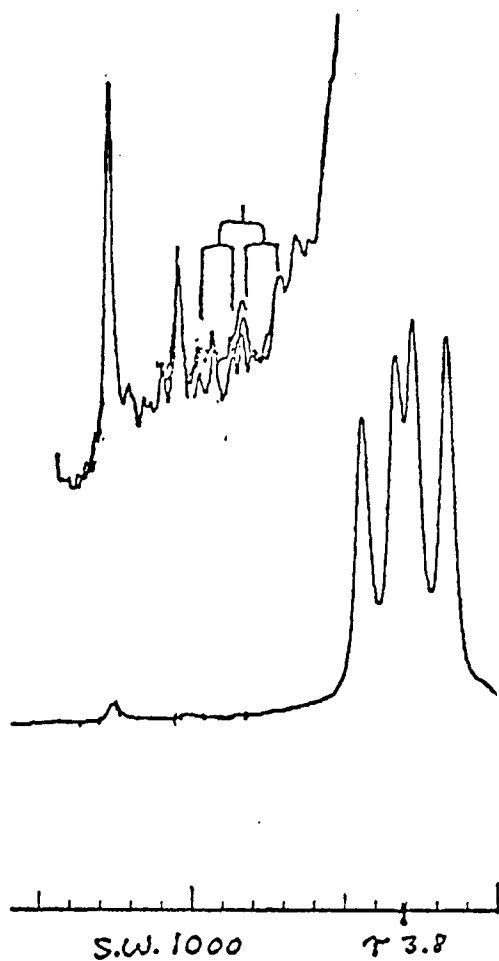


Figure 9. Satellites used for INDOR spectra of C_2 in 3-vinylpentadienyl anion.

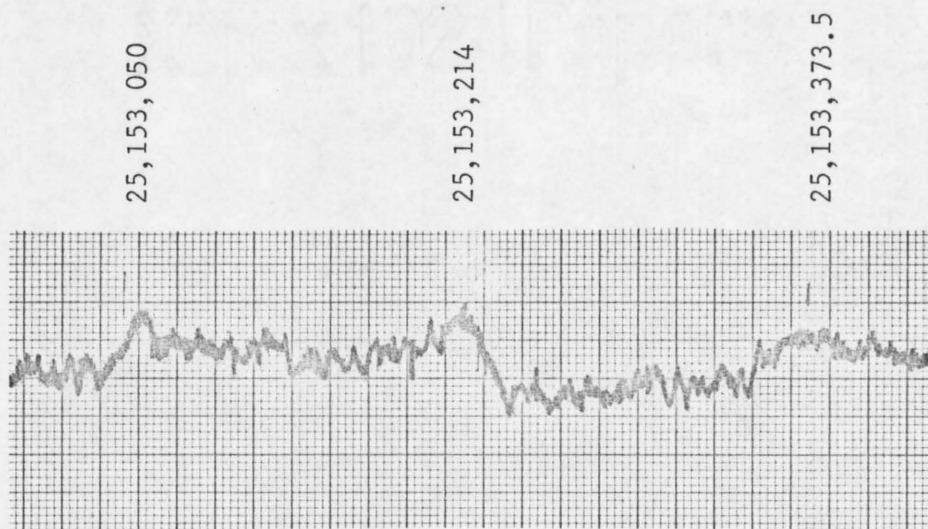


Figure 10. INDOR spectrum of C₁ in 3-vinylpentadienyl anion.

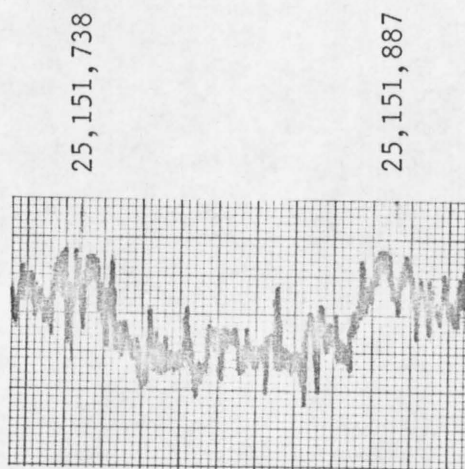


Figure 11. INDOR spectrum of C₂ in 3-vinylpentadienyl anion.

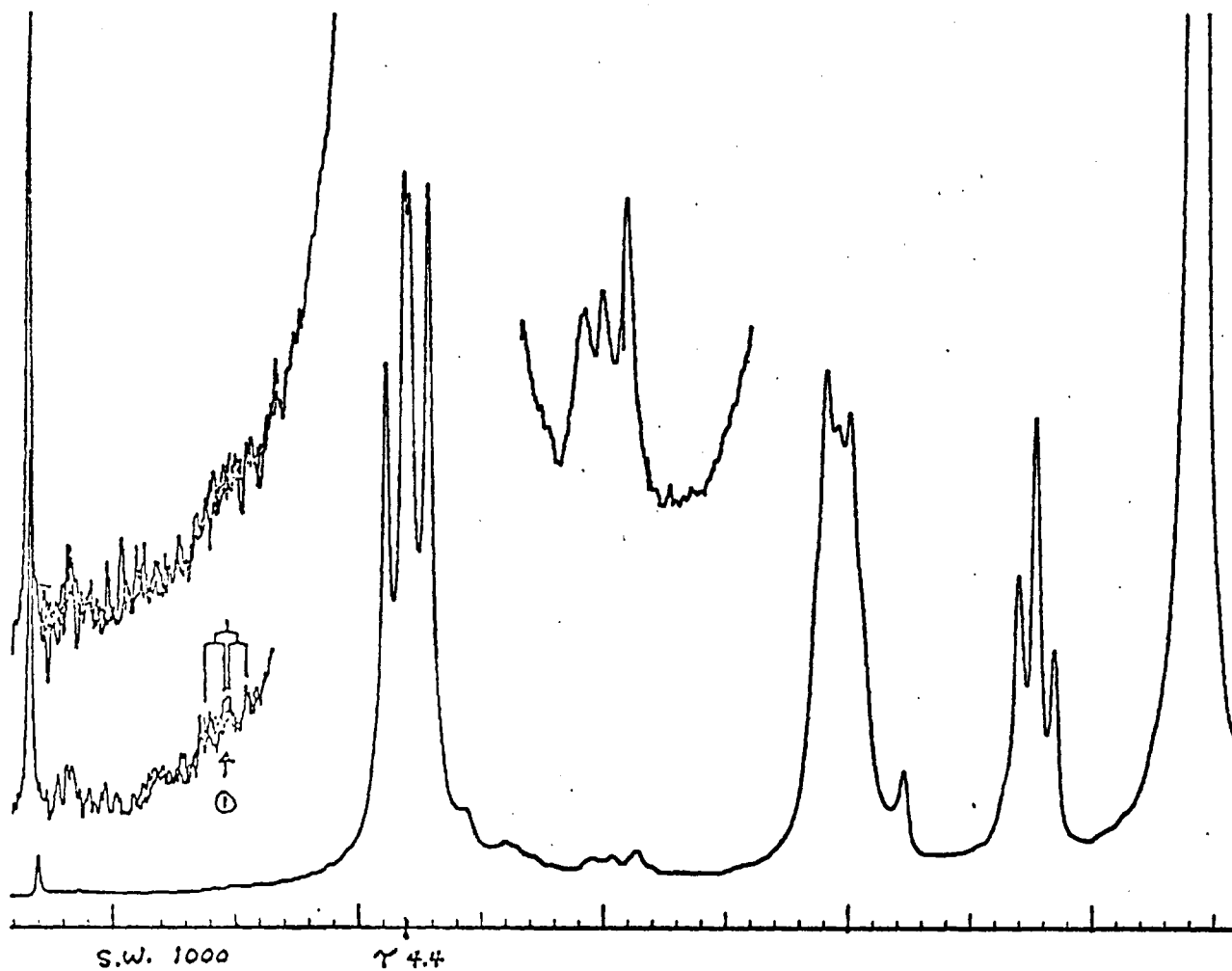


Figure 12. Satellites used for INDOR spectra of C_2 in cycloheptadienyl anion.

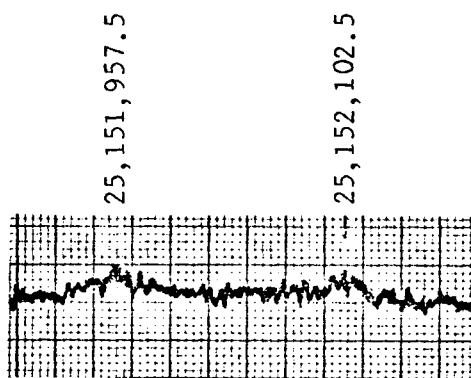


Figure 13. INDOR spectrum of C_2 in cycloheptadienyl anion.

Direct ^{13}C Spectra

Spectra of pentadienyllithium, 3-methylpentadienyllithium, 6,6-dimethylcyclohexadienyllithium, cycloheptadienyllithium, and 3-vinylpentadienyllithium in THF containing hexane were very kindly run by Dr. G. E. Maciel of Colorado State University on a Bruker spectrometer at 22.635 MHz. An external standard (hexafluorobenzene) was present for locking purposes, but for the measurement of ^{13}C chemical shifts, the farthest upfield peak of hexane [114.82 ppm upfield from benzene (28)] was used. Using a value of 65.0 ppm for the chemical shift of benzene relative to CS_2 (28), ^{13}C chemical shifts in ppm upfield from CS_2 were calculated for all of the carbons in the above anions.

DISCUSSION

The ^{13}C chemical shifts obtained for the five conjugated anions studied are given in Figure 14. There are minor discrepancies between the values obtained by INDOR and directly, with the former values generally being about 7 ppm higher. Small differences between INDOR and direct ^{13}C chemical shifts have also been found for carbonium ions (29). A possible source of difference is the temperature at which the spectra were measured; in this connection, it should be noted that the INDOR shift for the end carbons in pentadienyllithium was measured at an elevated temperature to avoid complexities due to exchange phenomena, and not at the ordinary probe temperature at which all of the other values were measured. The INDOR values were very helpful in unambiguously assigning peaks in the direct spectra to particular carbon atoms.

Assuming correlation of electron density with ^{13}C chemical shift (9), the electron density is greatest at the end and central carbons in these anions, as predicted by MO theory (20). The end and central atoms absorb in the 93.6-128.3 ppm range, whereas the other carbons of the conjugated system gave peaks in the 45.6-64.6 ppm range [this is the lower end of the range for ordinary alkenes (29)].

The differences in ^{13}C chemical shifts between end and central carbons are smaller, but nevertheless are large enough to show an interesting trend. The end shift values are higher for the acyclic anions and lower for the cyclic anions. They are higher by 8.2-27.9

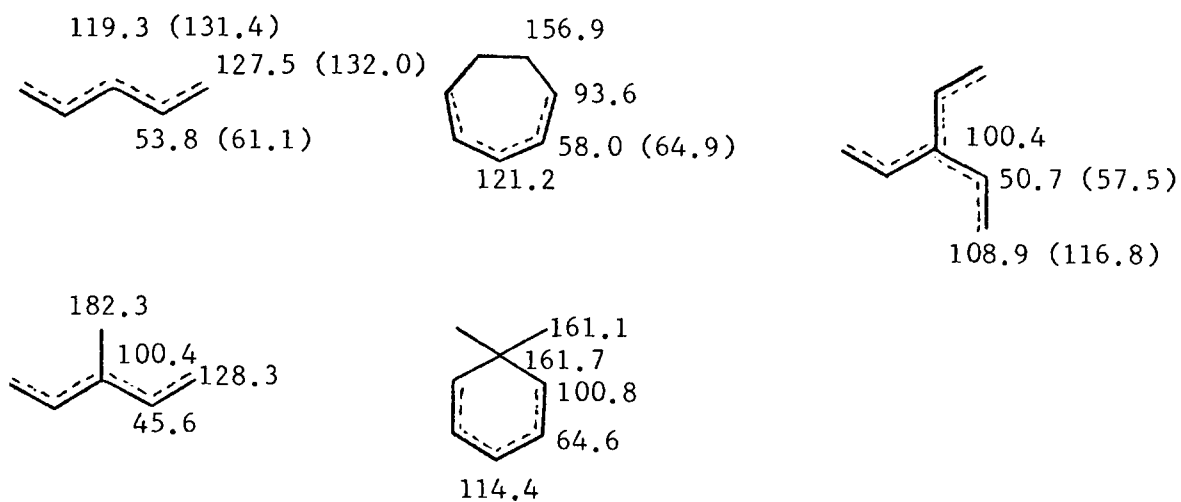


Figure 14. ^{13}C Chemical shifts for conjugated carbanions by direct measurement and, in parentheses, INDOR, in ppm upfield from CS_2 .


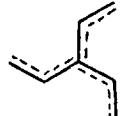
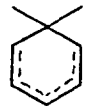

ppm in the former and lower by 13.6-27.6 in the latter. This is no doubt partly due to all of the end carbons being primarily in the acyclic anions and secondary in the cyclic anions. The effect of this difference is twofold: (1) In general, primary groupings absorb up-field from corresponding secondary groupings (28); (2) In these anions, charge redistribution can occur when a primary grouping is made secondary; as primary carbons are better able to carry negative charge than are secondary carbons, this effect should operate in the same direction. These effects are also seen in comparing the two acyclic pentadienyl anions. In 3-methylpentadienyl anion the central atom (tertiary instead of secondary) absorbs lower than in pentadienyl anion by 18.9 ppm, whereas the end carbons each absorb higher by 0.8 ppm.

The results of several reactions of these conjugated anions are summarized in Table 2. These reactions, like the ^{13}C chemical shifts, are probably governed to some extent by the electron distribution in the anions, so it seems worthwhile to look for some correlation between the reactions and the chemical shifts. In the cyclic anions, the central atom is favored more in these reactions than in the acyclic anions, and thus the correlation apparently exists.

It should be noted that in 3-vinylpentadienyl anion, unlike the other four anions, the charge is distributed over more atoms (three end atoms and a central one), and the chemical shifts of these atoms would be expected to be generally lower, as is observed.

In the ^{13}C -H coupling constants observed (Figure 15), parallelism in the values obtained is evident, but the significance of the values is presently unknown.

Table 2. Percentages for Reaction at the Central Atom of the Conjugated System in Conjugated Anions.

Anion	Reactant		
	Water	Methyl iodide	Ethylene oxide
	10 (30) ^a	35 (31)	65 (32)
	--	--	77 (32)
	60 (30)	100 (33)	--
	25 (34)	100 ^b	100 (21)

a. Numbers in parentheses are reference numbers.

b. Although this reaction has not been run, the finding of 100% reaction at the central atom for compounds with one less carbon in the ring (entry above in the table) and one more (31) makes this value likely.

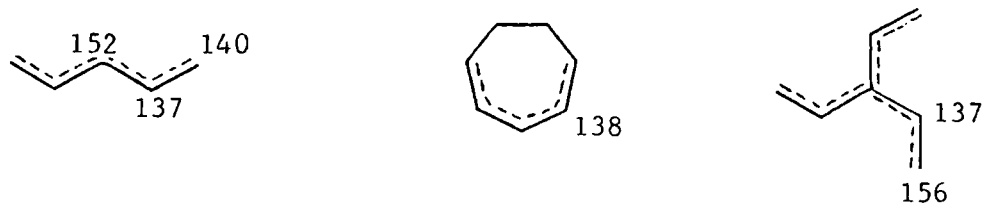


Figure 15. ^{13}C -H Coupling constants for conjugated carbanions, Hz.

PART II

PREPARATION AND THERMAL BEHAVIOR OF 3-VINYLCYCLOOCTADIENYL ANION

INTRODUCTION

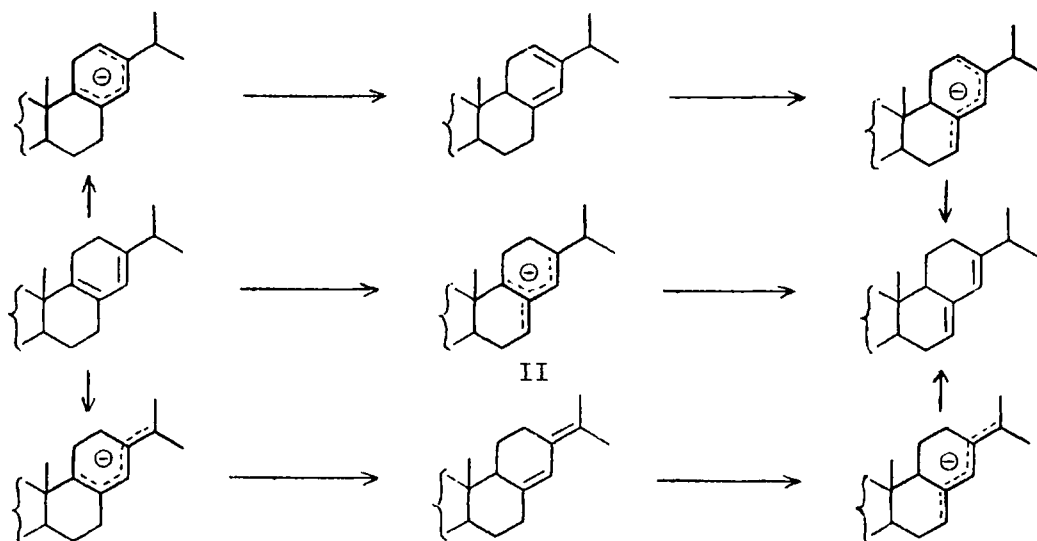
The major goal of this part of the research was to prepare a 2-vinylallyl anion and observe its properties. The anion was to be observed by NMR spectroscopy and its abstraction of protons monitored.

The simplest conjugated carbanion is 2-vinylallyl anion I. The 2-vinylallyl anion II is a proposed intermediate in a diterpene



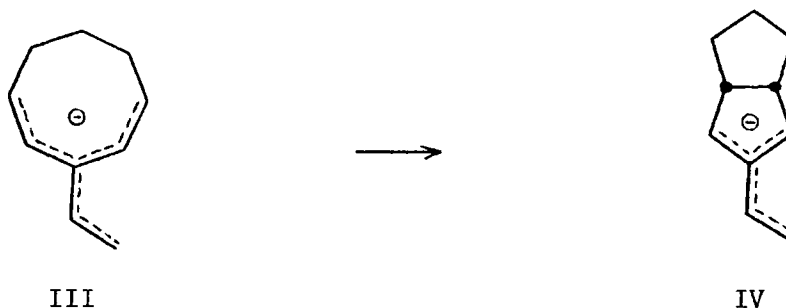
I

isomerization reaction (35), although the reaction may well proceed via linearly conjugated pentadienyl anions only:

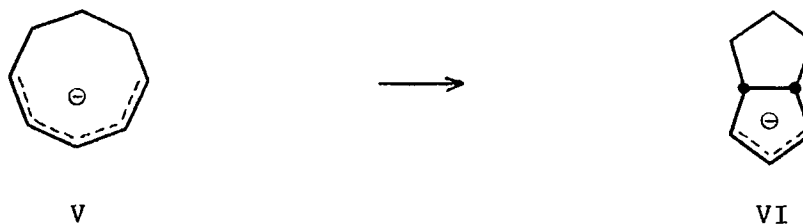


In our laboratory, an attempt to prepare 2-vinylallyl anion itself from 2-chloromethylbutadiene failed (36).

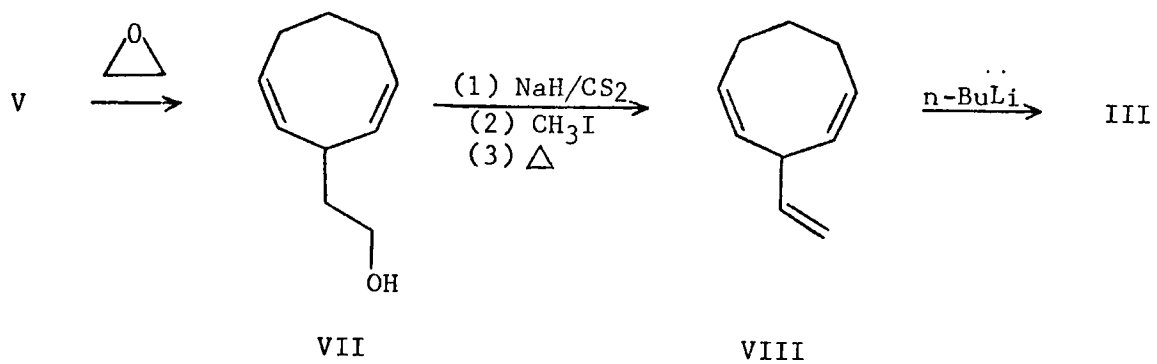
The 2-vinylallyl anion IV might be prepared by electrocyclization of III, since McCombs (in 37) found that carbanion V underwent



isomerization to the allyl anion VI at 35°.



The proposed route to 3-vinylcyclooctadienyl anion III is given below. It is patterned after the syntheses of 3-vinylpentadienyl anion itself (36) and 3-vinylcycloheptadienyl anion (23). It is critical that the ethylene oxide addition takes place before cyclooctadienyl anion (V) cyclizes to VI. Also anion III must cyclize as did V.



EXPERIMENTAL

2,4- and 2,7-Cyclooctadien-1-yl Bromides

The procedure followed was patterned after that of Moon and Ganz (38), but as somewhat higher yields were obtained than they reported, details are given below. Commercial 1,3-cyclooctadiene (260 g, 2.4 mol) (Aldrich Chemical Company), benzoyl peroxide (1.2 g) (Matheson, Coleman, and Bell Company), N-bromosuccinimide (350 g, 2.0 mol) (Eastman Organic Chemical Company), and carbon tetrachloride (800 ml) were placed in a 2-liter, 3-necked flask fitted with a mechanical stirrer and a condenser. The mixture was refluxed under nitrogen with stirring for 24 hr, and then cooled, and the succinimide removed by filtration. The filtrate was washed with three 600-ml portions of 10% NaHCO_3 and two 600-ml portions of H_2O and then dried over MgSO_4 . The solvent was removed under reduced pressure (20 mm) through a Vigreux column, and the residue was distilled through a short-path distillation column to give 208 g (58% based on N-bromosuccinimide) of a mixture of 2,7-cyclooctadien-1-yl bromide and 2,4-cyclooctadien-1-yl bromide.

1,4-Cyclooctadiene

Again, higher yields were obtained than those reported (38). A 3-liter, 3-necked flask was fitted with a condenser, an addition funnel, and a mechanical stirrer. Lithium aluminum hydride (30.0 g, 0.8 mol) (Alfa Inorganics, Inc.) was suspended in anhydrous ether (400 ml)

(Mallinckrodt Chemical Works), and the bromide mixture (208 g, 1.15 mol) was added dropwise with stirring. The mixture was refluxed 24 hr, then cooled in an ice bath, and 100 ml of H_2O was cautiously added dropwise with stirring. Sulfuric acid (20%, 200 ml) was added in a similar manner, followed by 800 ml more of the acid at room temperature. The aqueous portion was separated and extracted with two 250-ml portions of ether. The latter was added to the original organic layer and the combined extracts were washed with three 600-ml portions of 10% $NaHCO_3$, two 400-ml portions of H_2O , and dried over $MgSO_4$. The ether was removed by roto-evaporation. The crude diene mixture (128 g, 98% based on the bromide mixture) was added to 400 ml of 50% aqueous $AgNO_3$. The mixture was stirred in the dark overnight. A silver nitrate-complex formed, but not in the form of a green precipitate as reported by Moon and Ganz (38). Instead, the complex was dispersed in the aqueous layer. The aqueous layer was dissolved in 350 ml of cold concentrated NH_4OH . The ammonium hydroxide solution was extracted with three 300-ml portions of ether. The ether solution was washed with water, dried ($MgSO_4$), and concentrated by roto-evaporation. The residue, identified by NMR, was found to be 1,4-cyclooctadiene (34 g, 13% based on 1,3-cyclooctadiene used). According to the procedure of Moon and Ganz (38), the organic phases could be reextracted with 50% aqueous $AgNO_3$ to provide more 1,4-cyclooctadiene. This worker was unable to obtain additional 1,4-cyclooctadiene by reextracting the organic layer.

3-(2-Hydroxyethyl)-1,4-cyclooctadiene (VII)

Under a nitrogen atmosphere, a mixture of 1,4-cyclooctadiene (24 g, 22 mol) and tetrahydrofuran (80 ml, dried over lithium aluminum hydride, followed by distillation and storage over 4-A molecular sieves) in a 500-ml, 3-necked flask, equipped with an addition funnel and a magnetic stirrer, was cooled at -10° using a Dry Ice-acetone bath. While the solution was stirred at -10° , n-butyllithium in hexane (150 ml, 0.24 mol) (Foote Mineral Company) was added. After stirring for 1 hr at 0° , ethylene oxide (50 ml, 1.0 mol) (Eastman Organic Chemical Company) dissolved in an equal volume of pentane was added at 0° dropwise, cautiously, but as rapidly as possible to preclude loss of ethylene oxide by vaporization. The solution was then stirred at 0° for 1 hr and then kept at room temperature for another hr. Water (100 ml) was added, and the organic layer was separated and washed with three 50-ml portions of water. The combined water layers were back-extracted with two 50-ml portions of pentane. The organic portions were combined, dried with MgSO_4 , and concentrated using roto-evaporation. The crude 3-(2-hydroxyethyl)-1,4-cyclooctadiene (VII, 28 g, 84% of crude product) was not further purified.

3-Vinyl-1,4-cyclooctadiene (VIII)

The procedure followed was patterned after that used by Berger, Stogryn, and Zimmerman for trivinylmethane (32). To an ether suspension of sodium hydride (4.8 g, 0.2 mol) (Metal Hydrides, Inc.), 3-(2-hydroxyethyl)-1,4-cyclooctadiene (VII, 28 g, 0.18 mol) was cautiously added, and the mixture was refluxed for 4 hr. The solution was cooled, carbon

disulfide (30 g, 0.4 mol) (Allied Chemical Company) was added cautiously, and the mixture was refluxed for 1.5 hr. Methyl iodide (46 g, 0.32 mol) (Mallinckrodt Chemical Works) was then added, and the solution was refluxed for a final 1.5 hr. The solution was cooled to room temperature and poured over 200 ml of ice water. The organic layer was separated, dried, and ether, unreacted carbon disulfide, and methyl iodide was removed. The crude xanthate was pyrolyzed at 250-300° in a distillation apparatus, with elimination products being distilled off as they formed. Heat was provided by a Woods Metal Bath with the temperature being raised to 300° gradually over 1.5 hr. Some of the sulfur-containing by-products were removed from the distillate by passing it through an alumina column. Elution with pentane gave 20 g (82%) of crude product which by NMR was estimated to consist of 1/3 3-vinyl-1,4-cyclooctadiene (VIII, 1 proton at τ 6.3). Preparative GC on an SE-30 silicone column at 140° gave VIII (NMR, Figures 16 and 17) as the C₁₀ hydrocarbon with the shortest retention time, and IX (NMR, Figure 18) as the next substance eluted.

3-Vinylcyclooctadienyllithium (III)

Pentane was removed from the 3-vinyl-1,4-cyclooctadiene (VIII) by micro-Hickman distillation. To 3-vinyl-1,4-cyclooctadiene (VIII, 0.2 ml) in an NMR tube was added n-butyllithium (1.0 ml) (Foote Mineral Company). The mixture was cooled in a Dry Ice-acetone bath and perdeuterotetrahydrofuran (0.3 ml) (Norell Chemical Company) was added. The bath was removed and at ca 10° the solution became opaque and began

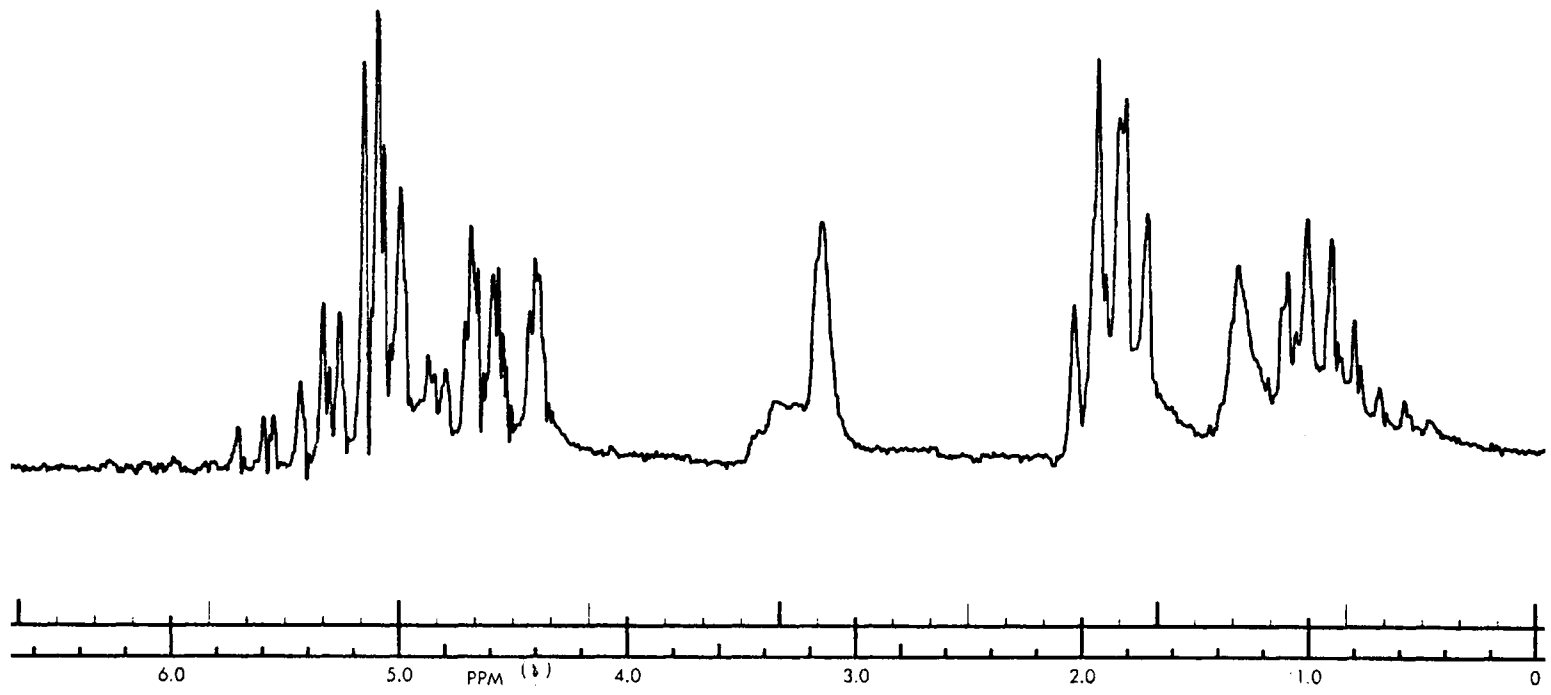
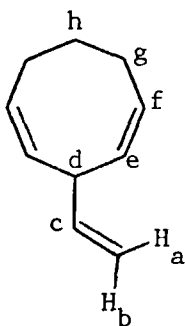


Figure 16. NMR spectrum of 3-vinyl-1,4-cyclooctadiene (VIII).



Chemical Shifts (τ)

$$H_a = 5.0$$

$$H_b = 5.1$$

$$H_c = 4.2$$

$$H_d = 6.2$$

$$H_e = 4.4$$

$$H_f = 4.6$$

$$H_g = 7.7$$

$$H_h = 8.6$$

Coupling Constants (Hz)

$$J_{ab} = 2$$

$$J_{ac} = 16$$

$$J_{bc} = 9$$

$$J_{cd} = 7$$

$$J_{de} = 4$$

$$J_{ef} = 10$$

$$J_{fg} = 6$$

$$J_{gh} = 6$$

Figure 17. NMR parameters for 3-vinyl-1,4-cyclooctadiene (VIII).

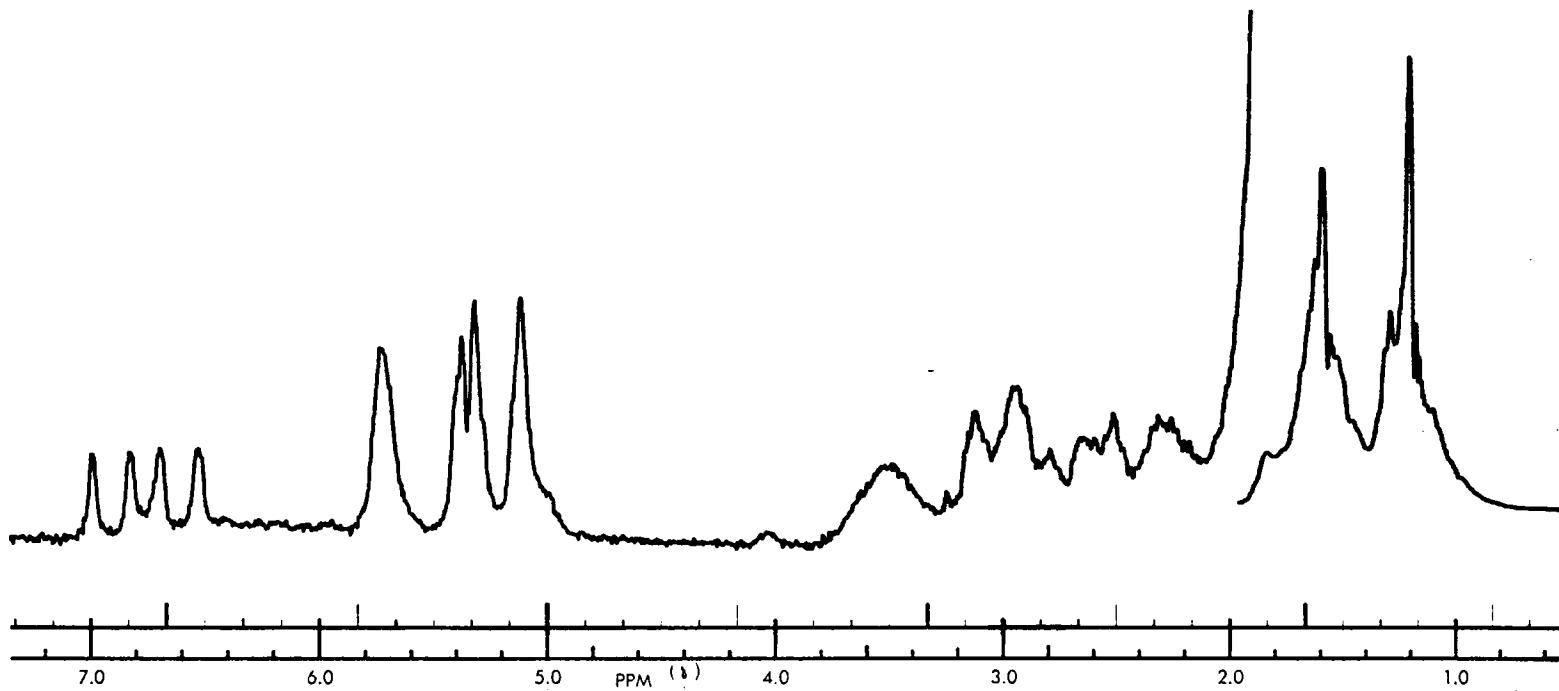


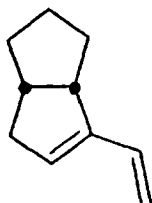
Figure 18. NMR spectrum of IX or XI in pentane.

to separate into two layers. The NMR spectra (Figures 19-22) of the lower layer show III to be the major anion present.

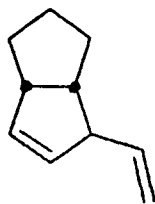
Heating of the solution containing III in the NMR probe to 75° for 30 min caused only minor changes in the NMR spectrum; III was evidently stable under these conditions.

DISCUSSION

The synthesis of 3-vinylcyclooctadiene (VIII) proceeded reasonably well as outlined in the Introduction. Cyclooctadienyl anion (V) was prepared as previously described (37) but in slightly higher yield. The ethylene oxide reaction was carried out at 0° in the hope of avoiding cyclization of V to VI, but one of the by-products (IX below) appears to have been derived from VI, presumably formed to some extent due to local heating during the ethylene oxide addition. The xanthate preparation and pyrolysis gave a good yield of crude 3-vinylcyclooctadiene (VIII), but NMR suggested the presence of only about one-third of the desired triene VIII (1 proton at τ 6.3); VIII (NMR, Figures 16 and 17) was obtained from the mixture by preparative GC. The major by-products appear to be either IX (NMR, Figure 18; presumably formed by the isomerization of X) or XI (formed by deprotonation of VII, cyclization, protonation, and the xanthate pyrolysis sequence) and either XII or XIII (formed by an undesired isomerization of either the desired product, VIII, or an expected by-product, XIV). XII or XIII was never obtained pure, but its presence was suggested by a quartet ($J = 10, 17$ Hz) for 1 proton at τ 3.7.



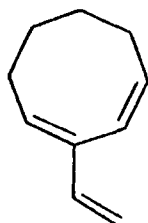
IX



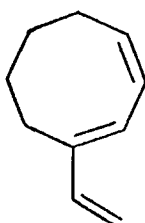
X



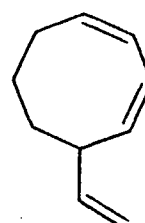
XI



XII



XIII



XIV

The metalation of VIII proceeded smoothly as expected to yield anion III, whose NMR parameters (Figures 19 and 20; these assignments were verified with the aid of the decoupling experiments shown in Figures 21 and 22) are as expected from those of the related anions V (37) and 3-vinylcycloheptadienyl anion (21).

Heating of III to 75° in the NMR probe caused no visible (NMR) cyclization to IV; instead, the spectrum of III persisted unchanged. This behavior contrasts with that of cyclooctadienyl anion (V), which cyclizes to VI at 35° with a half-life of 90 min (37). It is possible that the failure of III to close to IV under these conditions is due to a shift in the equilibrium position as compared to the V-VI system, but such a large shift seems unlikely if the changes in delocalization energies shown in Figure 23 are close to being correct. The problem seems more likely kinetic in nature; it may be possible to settle this point by re-preparing III in a thick-walled NMR tube and heating it to a temperature above 75°.

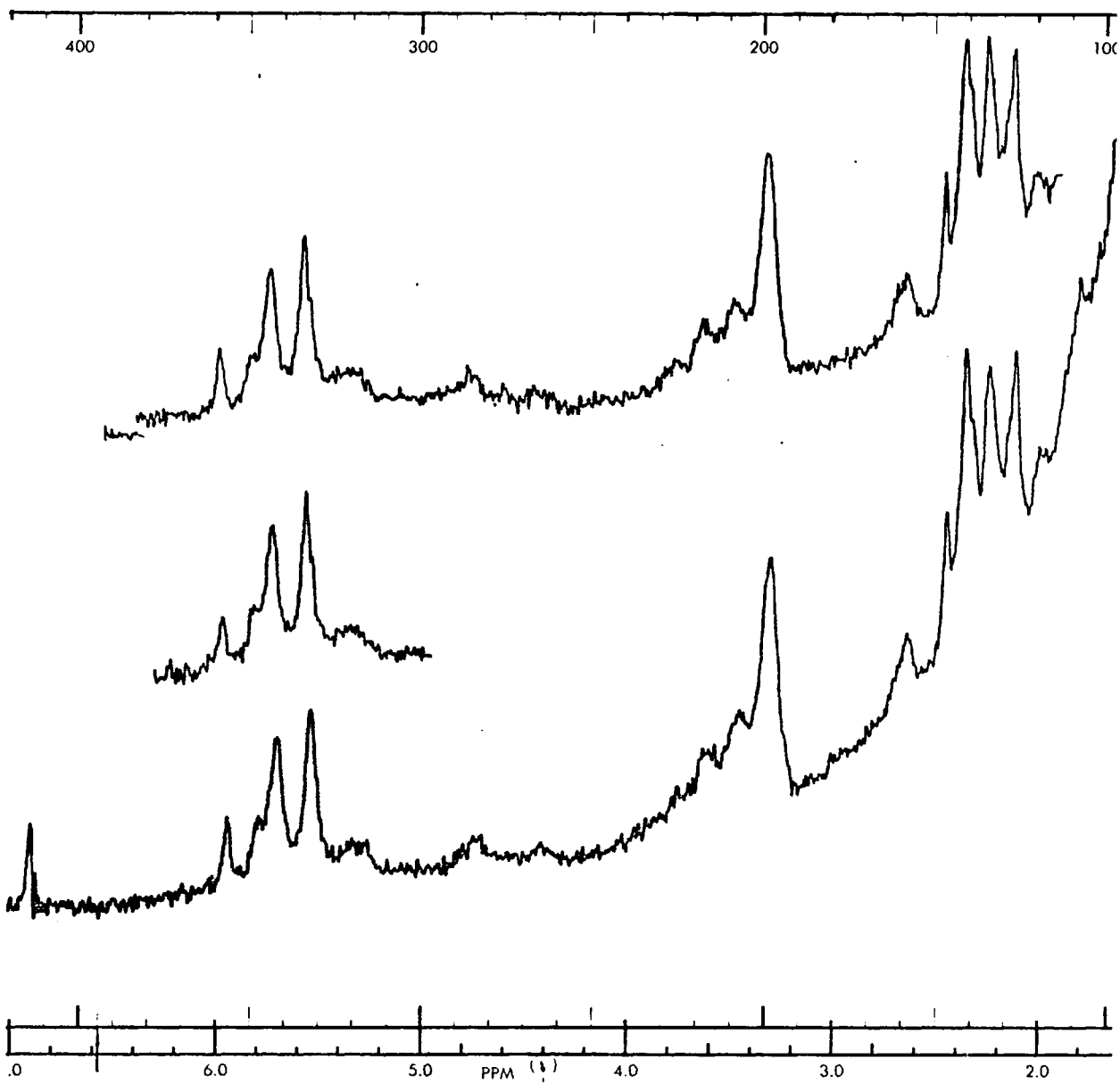
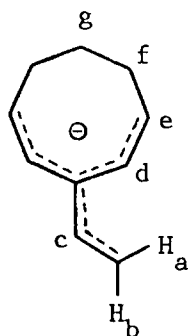


Figure 19. NMR spectrum of 3-vinylcyclooctadienyllithium (III).



Chemical Shifts (τ)

$$H_a = 7.7$$

$$H_b = 7.5$$

$$H_c = 4.0$$

$$H_d = 4.1$$

$$H_e = 6.2$$

$$H_f = 7.4$$

$$H_g = > 8.4$$

Coupling Constants (Hz)

$$J_{ac} = 15$$

$$J_{bc} = 9$$

$$J_{de} = 10$$

$$J_{ef} = 7$$

$$J_{fg} = 6$$

Figure 20. NMR parameters for anion III.

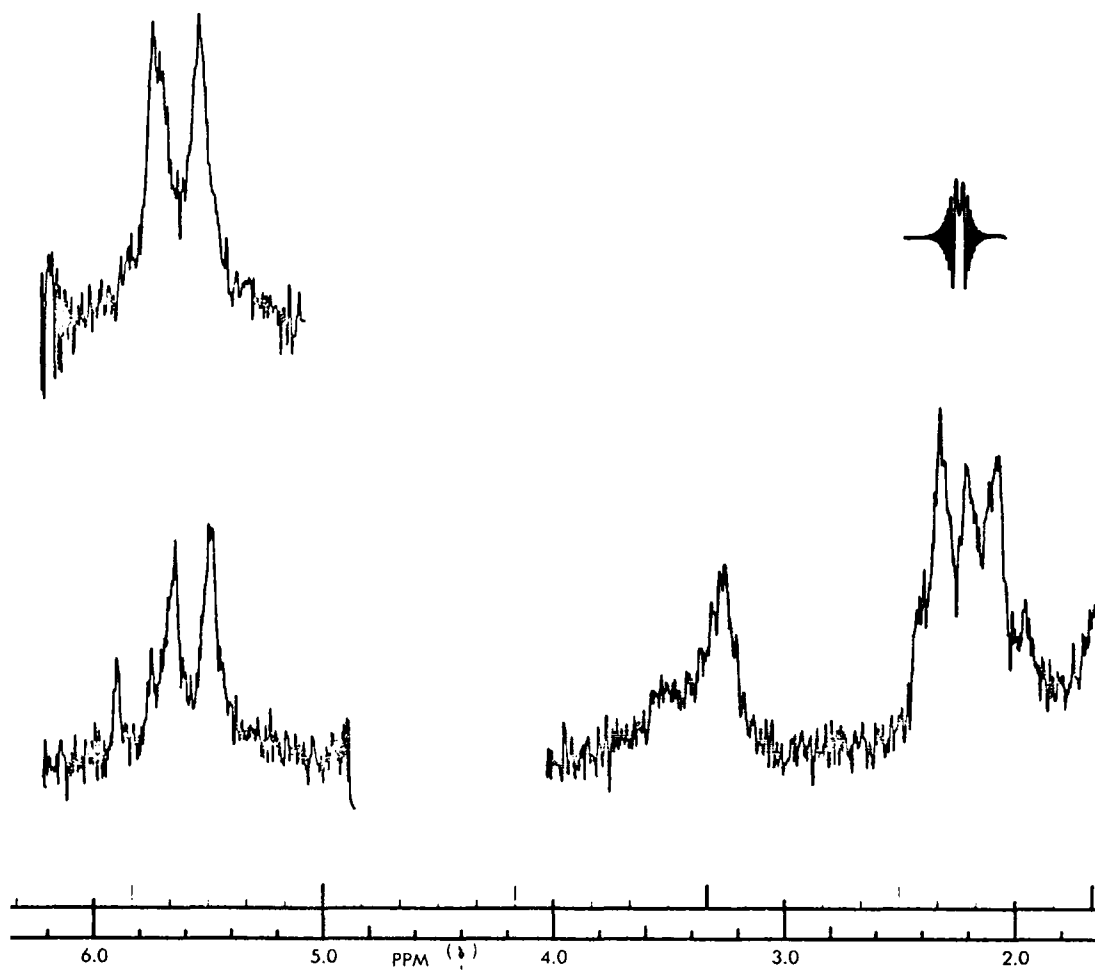


Figure 21. NMR spectrum of III with irradiation at $\tau 77.5$.

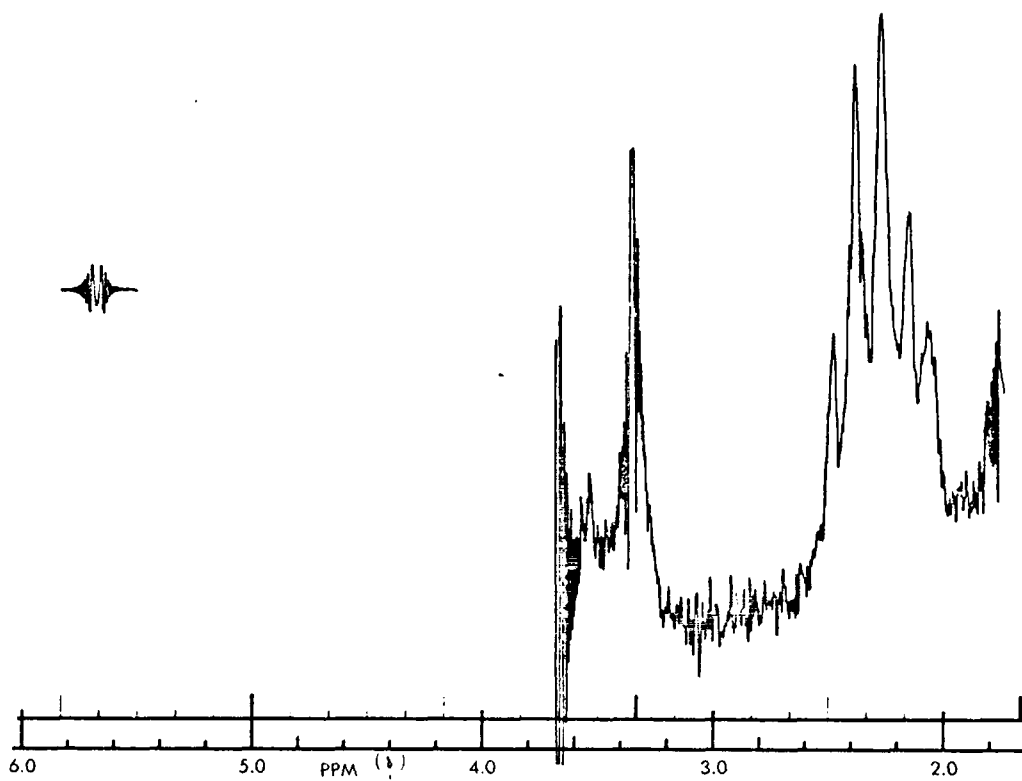
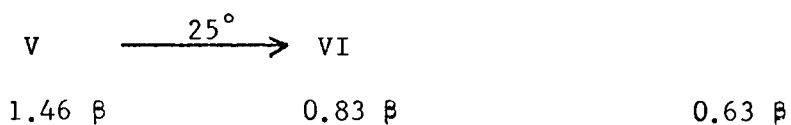


Figure 22. NMR spectrum of III with irradiation at τ 4.05.



Difference: 0.14 β [ca. 1 kcal/mol (20)]

Figure 23. Resonance energy changes calculated for some cyclizations using simple Huckel MO theory (39).

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