SIGMATROPIC REARRANGEMENTS OF PENTADIENYLLITHIUMS

by

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I hereby recommend that this dissertation prepared under my direction by William Henry Deines

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be accepted as fulfilling the dissertation requirement of the degree of DOCTOR OF PHILOSOPHY

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SIGNED: William H. Deines

TO HELEN

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ABSTRACT

Positional isomerization reactions of several pentadienyllithiums are shown to be consistent with Woodward-Hoffmann selection rules for [1,6] sigmatropic hydrogen shifts. It is demonstrated that these transformations are intramolecular, that the thermal shifts proceed antarafacially, and that the photochemical shifts, observed for the first time, proceed suprafacially.

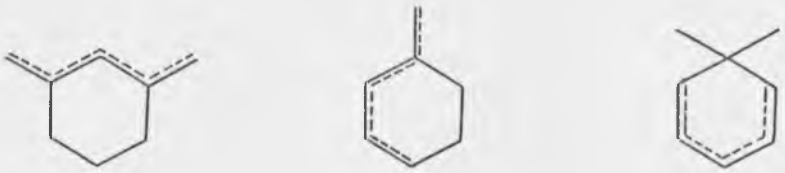
It is demonstrated that thermal equilibrium is established in two systems of pentadienyllithiums.

INTRODUCTION

The study of pentadienyl anions has been active since they were proposed as short-lived intermediates in base catalyzed isomerizations of 1,3- and 1,4-dienes (Birch 1950; Birch, Shoukry, and Stansfield 1961; Krapcho and Bothner-By 1959), in Birch reductions of aromatics, and in nucleophilic aromatic substitution by the addition-elimination mechanism (Bunnet and Zahler 1951, Miller 1963). Recent preparations of stable 20% solutions of cyclic and acyclic pentadienyllithiums (Bates, Gosselink, and Kaczynski 1967a; Bates et al. 1969) have made this class of compounds available for intensive study. It was the purpose of the work presented here to study proposed [1,6] sigmatropic hydrogen shifts in several pentadienyllithiums. In this introduction a brief discussion of related studies of pentadienyllithiums will first be presented, followed by a summary of reported positional isomerizations in pentadienyllithiums. Finally, a summary of Woodward-Hoffmann selection rules (Woodward and Hoffmann 1965, 1970), as applied to proposed [1,6] sigmatropic hydrogen shifts in pentadienyllithiums, will be presented.

Pentadienyl Anions

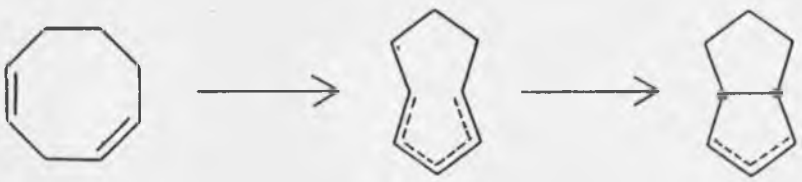
Bates, Gosselink, and Kaczynski (1967a,b) reported the preparation and nuclear magnetic resonance (NMR) study of pentadienyllithium. Studies by Gosselink (1966) of anions (1), (2), and (3) made available data on the NMR spectra of pentadienyl anions of restricted shape. Of



(1) (2) (3)

the three possible planar shapes of pentadienyllithium (U, sickle, and W), it was found that the W-shape was preferred at room temperature and that the U-shape was not detected. This was also found to be the general case for a series of acyclic pentadienyllithiums studied by Potter (1969). Gosselink (1966) and Potter (1969) also showed that rotation about the C_{2-3} and C_{3-4} bonds of acyclic pentadienyllithiums is sufficiently facile to permit at least transitory formation of U-shaped anions, provided steric hindrance is not too great.

The studies by Bates and McCombs (1969) of cyclooctadienyllithium (4) have shown additionally that pentadienyl anions can exist in a distorted U-shape. In this case, unlike anion (3), five adjacent sp^2 hybridized carbons of the pentadienyl anion system cannot possibly be coplanar with their p-orbitals perpendicular to this plane for maximum overlap and stability.



(4)

McCombs (1969) has recently reported the preparation of concentrated solutions of cyclic pentadienyllithiums. Heptatrienyllithium (5) was observed to electrocyclize quantitatively to cycloheptadienyllithium (6) at -30°, and several substituted cycloheptadienyllithiums were also prepared in this manner. It is again significant to note that these cyclic pentadienyllithiums are stable but are constrained to a bent U-shape. Again, the five adjacent sp^2 hybridized carbons cannot attain coplanarity, and less than maximum overlap of the p-orbitals results.

(5) (6)

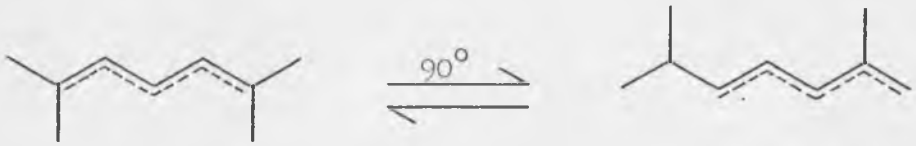
Positional Isomerizations of Pentadienyl Anions

Recently Potter (1969) reported a new positional isomerization reaction occurring in three acyclic pentadienyllithiums [(7), (9), and (11)], and it was proposed that these transformations involved [1,6] sigmatropic hydrogen shifts. If these reactions are examples of sigmatropic shifts, it must be demonstrated that

a) the isomerizations are intramolecular and

b) the stereochemistry is consistent with Woodward-Hoffmann selection rules for such transformations.

It also remains to be demonstrated whether proposed equilibration of the anions is actually established in each instance.



(7) 10%

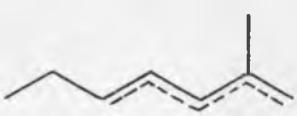
(8) 90%

(9) 48%

(10) 52%

(11) 10%

(12)



(13) 90%

Klein, Glily, and Kost (1970) observed an apparent positional isomerization reaction while studying metalations of linoleyl alcohol and linoleyl methyl ether. The substituted pentadienyllithiums formed by treatment of the alcohol and the ether with butyllithium in diethyl ether were carbonated, and the resulting carboxylic acids were esterified with diazomethane. The positions of the ester groups along the molecular chains indicated that the anions had isomerized, and the investigators proposed that the transformations involved [1,6] sigmatropic hydrogen shifts. Again, it must be established whether the proposed hydrogen shifts are intramolecular and stereochemically consistent with Woodward-Hoffmann selection rules. The investigators also concluded that the pentadienyl anion system in the alcohol and ether studied "is protected from the solvent during the isomerization by coiling the chain around it" and that "the fact that this isomerization stopped at the positions 6 and 15 at one and the other end of the molecule, respectively, requires a minimum number of 14 carbons in the chain to make this process observable" (Klein et al. 1970, p. 1283).

Woodward-Hoffmann Selection Rules for Sigmatropic Hydrogen Shifts

"Sigmatropic" reactions were defined by Woodward and Hoffmann (1965, p. 2511) in the following way: "A sigmatropic change of order [i,j] is the migration of a σ bond, flanked by one or more π electron systems, to a new position whose termini are i-1 and j-1 atoms removed from the original bonded loci, in an uncatalyzed intramolecular process." Orbital symmetry relationships must play a part in the

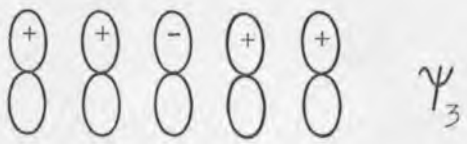
course of these transformations (Hoffmann and Woodward 1968, Woodward and Hoffmann 1970).

In the sigmatropic migration of a hydrogen from C_1 to C_5 within the all-cis-diene framework of 14, for example, there are two distinct ways of effecting the change. In a suprafacial process, the migrating

$$R_2C{=}CH{-}CH{=}CH{-}CHR'_2 \qquad R_2CH{-}CH{=}CH{-}CH{=}CR'_2$$

(14)

hydrogen atom is associated at all times with the same face of the π system, and in an antarafacial process, the hydrogen atom is passed from the top of one carbon terminus to the bottom of the other. The transition state in the example (14) is envisioned as being the combination of the orbital of a hydrogen atom with those of a radical containing five π electrons. The highest occupied orbital of the framework system possesses the symmetry shown in 15. In order to maintain positive overlap



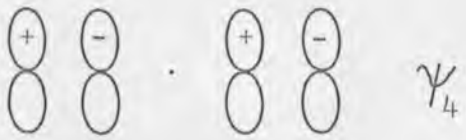
ψ_3

(15)

between the framework orbital and the migrating hydrogen orbital, the thermal [1,5] sigmatropic hydrogen shift could take place in a symmetry-allowed suprafacial manner. Many examples of thermal [1,5] shifts have been observed (Glass, Boikess, and Winstein 1966).

Similar reasoning leads to the conclusion that the photochemical [1,5] transformation, proceeding through the first excited state with

the symmetry shown in 16 could take place in an antarafacial manner.



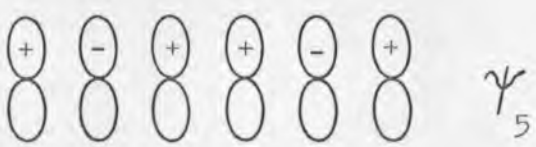
(16)

The proposed thermal [1,6] sigmatropic hydrogen shift in acyclic pentadienyllithiums would necessarily proceed antarafacially, due to the symmetry of the highest occupied orbital (17). For this transformation to occur, the anion must exist for a short time in a

(17)

helical all-cis form. Some distortion of the π system of the anion would result, but it has been shown (Bates and McCombs 1969, McCombs 1969) that pentadienyl anions can exist in a distorted U-shape.

The highest occupied orbital of cycloheptadienyl anion possesses the same symmetry as the acyclic system (17), so a thermal antarafacial [1,6] hydrogen shift is predicted. However, the rigid geometry of the ring prohibits antarafacial rearrangement. In considering the orbital symmetry of the first excited state (18), a suprafacial [1,6]



(18)

shift could be photochemically induced. The same argument applies to photochemical sigmatropic rearrangements involving [1,7] hydrogen shifts in cycloheptatrienes, and several such rearrangements have been reported (ter Borg and Kloosterziel 1965, Murray and Kaplan 1966, Jones and Jones 1967, 1968).

EXPERIMENTAL

The procedures used for the preparations of cyclic and acyclic pentadienyllithiums in this study are essentially those of previous authors (Gosselink 1966, Bates et al. 1967a, Potter 1969, McCombs 1969). Perdeuterotetrahydrofuran (THF-d_8) (Stohler Isotope Chemicals) and n-butyllithium (Foote Mineral Company, 1.6 M in hexane) were used in all nuclear magnetic resonance (NMR) tube scale anion preparations.

The NMR spectra were recorded at 60 MHz on a Varian A-60 spectrometer and at 100 MHz on a Varian HA-100 spectrometer. The Varian variable temperature control unit, used when spectra were recorded on the HA-100 spectrometer at temperatures other than the normal probe temperature of 33°, was calibrated using ethylene glycol for high temperatures and methanol for low temperatures. All chemical shifts are reported in τ units and coupling constants in Hertz. Internal standards used for anion spectra were cyclohexane (τ 8.57) and the α-protons in THF (τ 6.4). The NMR spectra of the pentadienyllithiums are not described in the Experimental section, but reproductions of them can be found in the Discussion section.

All vapor phase chromatography (VPC) was done on a Varian Aerograph Model 90-P. All mass spectral data were obtained on a Hitachi-Perkin-Elmer RMU-6E Double Focusing Mass Spectrometer. All infrared (IR) spectra were recorded on a Perkin-Elmer Model 337 Grating Infrared Spectrophotometer.

1,1-Dimethylpentadienyllithium (9)

The anion (9) was prepared as described by Potter (1969) by mixing 5-methyl-1,4-hexadiene (Chemical Samples Company, 0.100 g, 1.04 mmol), THF-d_8 (0.20 ml, 2.4 mmol), and n-butyllithium solution (0.80 ml, 1.3 mmol) in an NMR tube at -78°. The sample was placed in the NMR probe at 40°, and quantitative anion formation and separation of layers were complete after 45 min. The yellow upper layer contained hexane and THF-d_8 and was removed. The red lower layer was found by NMR to contain hexane, THF-d_8, and a mixture of anion (9) (48%) and 1,4-dimethylpentadienyllithium (10) (52%). The sample was warmed to 60° in the probe for 30 min and then cooled to 40°. The NMR spectrum again showed 9 and 10 in the above ratio.

2-Methyl-1,4-hexadiene

3-Acetoxy-5-methyl-5-hexene. Acetic anhydride (8.7 g, 0.085 mol), pyridine (7.1 g, 0.09 mol), and 5-methyl-5-hexen-3-ol (Chemical Samples Company, 8.0 g, 0.07 mol) were mixed at room temperature in a 50-ml flask fitted with a magnetic stirrer, reflux condenser, and drying tube. The reaction mixture was stirred and refluxed overnight. Ether (50 ml) was added, and the solution was washed twice with water, four times with cold 10% hydrochloric acid, and twice more with water. The ethereal solution was dried over anhydrous magnesium sulfate and the ether was removed. The resulting colorless liquid (10.3 g, 94.3% yield) was identified as the desired acetate by its NMR spectrum in ether solution which contained a triplet at τ 9.14 (3 H, C_1 hydrogens), a multiplet at τ 8.52 (2 H, C_2 hydrogens), a singlet at τ 8.30 (3 H,

vinyl methyl), a singlet at τ8.12 (3 H, acetoxy methyl), a multiplet at τ7.82 (2 H, C_4 hydrogens), an absorption at τ5.32 (2 H, C_6 vinyl hydrogens), and a multiplet at τ5.08 (1 H, C_3 hydrogen). The IR spectrum showed no residual alcohol.

Pyrolysis of 3-Acetoxy-5-methyl-5-hexene. A solution of 3-acetoxy-5-methyl-5-hexene (10.3 g, 0.066 mol) in anhydrous ether (75 ml) was passed through a Pyrex pyrolysis column packed with glass beads at 480-485° under a nitrogen atmosphere. The resulting yellow ether solution was washed five times with cold saturated sodium bicarbonate solution and three times with water. The ethereal solution was dried over anhydrous magnesium sulfate, and the solvent was partially evaporated. Five components were collected by VPC (20% of a 20% solution of silver nitrate in polypropylene glycol on 60/80 Chromosorb W) at 70°. The desired products, trans-2-methyl-1,4-hexadiene (15%) and cis-2-methyl-1,4-hexadiene (6%) were the first and second components collected, respectively, and were identified by their mass spectra (parent m/e values of 96) and NMR spectrum (Figure 1; see Discussion of Results for all figures). The third component was trans-2-methyl-1,3-hexadiene (56%) as identified by its NMR spectrum in carbon tetrachloride which contained a triplet at τ9.0 (3 H, C_6 hydrogens), a singlet at τ8.22 (3 H, vinyl methyl), a multiplet at τ7.90 (2 H, C_5 hydrogens), a sharp absorption at τ5.24 (2 H, C_1 vinyl hydrogens), a multiplet at τ4.42 (1 H, C_4 vinyl hydrogen), and a doublet at τ3.94 (1 H, C_3 vinyl hydrogen). The fourth and fifth components were, respectively, trans-2-methyl-2,4-hexadiene (16%) and cis-2-methyl-2,4-hexadiene (8%), as identified by

their NMR spectra. The product ratios were determined by integration of the VPC trace. No unreacted acetate was detected.

1,4-Dimethylpentadienyllithium (10)

In an NMR tube at -78°, THF-d_8 (0.30 ml, 3.4 mmol), 2-methyl-1,4-hexadiene (71% trans) (0.154 g, 1.6 mmol), and n-butyllithium (1.05 ml, 1.7 mmol) were thoroughly mixed and stored for 39 days at that temperature. The sample was then placed in the probe at 20°, and spectra were recorded every 10 min for 2 hrs. Layer separation occurred after 1 hr at 20°. The NMR spectra show that anion (10) is formed initially (Figure 2), but it equilibrates with anion (9) after 90 min.

The ratio of 9 to 10 at 40° was 48:52 (Figure 3). The sample was then warmed to 60° for 30 min. A final spectrum was recorded at 40° and showed the same equilibrium mixture of 9 and 10.

6-Methyl-1,4-heptadiene

Methyl-6-methyl-5-oxoheptanoate. The general procedure of Nazarov (1956) was followed for the preparation of 2,2-dimethyl-1,3-cyclohexanedione. Anhydrous potassium carbonate (124 g, 0.90 mol), 1,3-cyclohexanedione (Aldrich Chemical Company, 100 g, 0.89 mol), methyl iodide (383 g, 2.7 mol), acetone (750 ml), and water (375 ml) were mixed at room temperature in a 2-liter flask fitted with an ice-water condenser and a magnetic stirrer. The reaction mixture was stirred and refluxed for 18 hr. After cooling, the white solid was filtered off, and the acetone was distilled from the red filtrate. The remaining aqueous solution was extracted three times with ether, and the ether layers were

dried over anhydrous magnesium sulfate and filtered. The ether was removed, leaving a red liquid (74.1 g, 55% yield) consisting of three components. The first component was the desired ester (45%), and it was identified by its NMR spectrum which contained a doublet at τ8.97 (6 H, gem-dimethyl), a singlet at τ6.42 (3 H, methyl ester), a five line multiplet at τ8.22 (2 H, C_3 hydrogens), and unresolved multiplets from τ7.5 to τ7.9 (5 H; C_2, C_4, and C_5 hydrogens). As discussed by Stetter (1955), this product probably arises from basic cleavage of the β-diketone, 2,2-dimethyl-1,3-cyclohexanedione, followed by methylation of the carboxylate group. The second component was 2,2-dimethyl-1,3-cyclohexanedione (30%), and it was identified by its NMR spectrum which contained a singlet at τ8.80 (6 H, gem-dimethyl) and multiplets from τ7.4 to τ7.8 (6 H; C_4, C_5, and C_6 hydrogens). The third component was apparently 2-methyl-1,3-cyclohexanedione (25%), and it was identified by its NMR spectrum which contained a doublet at τ8.92 and a singlet at τ7.94 (3 H, methyl hydrogens of keto and enol forms) and multiplets from τ7.4 to τ7.8 (the remaining hydrogens). The hydroxy hydrogen was not detected.

Reduction of Methyl-6-methyl-5-oxoheptanoate. Anhydrous ether (1000 ml) and lithium aluminum hydride (25.0 g, 0.66 mol) were mixed at 0° in a 3-liter flask fitted with an air-stirrer, an ice-water condenser, and a drying tube. To this was added dropwise with stirring the crude mixture of methyl-6-methyl-5-oxoheptanoate, 2,2-dimethyl-1,3-cyclohexanedione, and 2-methyl-1,3-cyclohexanedione (74.1 g, 0.50 total moles) in anhydrous ether (500 ml) over 45 min. The reaction mixture

was stirred overnight at room temperature. Then, in the following order, water (25 ml), aqueous sodium hydroxide (25 ml, 15%), and water (90 ml) were added dropwise to the reaction mixture with stirring at 0°. The resulting white suspension was extracted with five 300-ml portions of ether, and the combined ether extracts were dried over anhydrous magnesium sulfate. The solvent was removed, leaving a colorless viscous liquid (62.0 g, 90% yield). The IR spectrum of the crude product mixture showed no residual carbonyl absorption. A carbon-carbon double bond absorption appeared at 1660 cm^{-1}, and this was possibly due to 2-methyl-2-cyclohexenol. This product could have arisen from an elimination reaction during the reduction of 2-methyl-1,3-cyclohexanedione (Richer and Clarke 1964).

6-Methyl-1,5-diacetoxyheptane. The above crude mixture of alcohols (62.0 g, approximately 0.45 mol of alcohols and 0.8 mol of hydroxyl), acetic anhydride (110 g, 1.06 mol), and pyridine (89.4 g, 1.13 mol) were refluxed overnight with stirring in a 500-ml flask fitted with a reflux condenser and drying tube. The reaction mixture was worked up as described for 3-acetoxy-5-methyl-5-hexene. The ether was removed to yield the mixture of acetates (74.2 g, 78% yield). The IR spectrum of the crude product showed no hydroxyl absorption.

Pyrolysis of 6-Methyl-1,5-diacetoxyheptane. The above crude mixture of acetates (74.2 g) in anhydrous ether (150 ml) was pyrolyzed at 485-495°. The resulting yellow solution was worked up as described for 3-acetoxy-5-methyl-5-hexene, and the ether was removed to yield the crude product (28.2 g). Three components were collected by VPC

(Carbowax 20M on 50/60 firebrick) at 95°. The first component collected was the desired product, trans-6-methyl-1,4-heptadiene (41% of the product mixture as determined by integration of the VPC trace), and was identified by its NMR spectrum (Figure 5) and mass spectrum (parent m/e 110). The second component collected, 6,6-dimethyl-1,4-cyclohexadiene (32% of the product mixture), was identified by comparison of its NMR spectrum with that of an authentic sample. The third component was toluene (27% of the product mixture) and was identified by its NMR spectrum and by coinjection with toluene.

1-Isopropylpentadienyllithium (11)

The anion (11) was prepared as described by Potter (1969) by mixing THF-d_8 (0.20 ml, 2.4 mmol), trans-6-methyl-1,4-heptadiene (0.130 g, 1.17 mmol), and n-butyllithium (0.80 ml, 1.3 mmol) in an NMR tube at -78°. The sample was warmed to room temperature, layer separation occurred after 20 min, and the upper layer was removed. The NMR spectrum of the lower layer at 40° (Potter 1969) showed that there had been quantitative anion formation. In addition to 11, a detectable amount of 1-ethyl-4-methylpentadienyllithium (13) was also present. The probe temperature was then raised from 40° to 90° in 10° intervals, and a spectrum was recorded at each temperature after warming for 15 min at that temperature. A final spectrum recorded at 40° (Potter 1969) showed a mixture of 11 (10%) and 13 (90%). No 1,1,5-trimethylpentadienyllithium (12) was detected.

2-Methyl-2,5-heptadiene

6-Methyl-5-hepten-2-ol. Anhydrous ether (200 ml) and lithium aluminum hydride (3.50 g, 0.092 mol) were mixed under a nitrogen atmosphere at 0° in a one-liter flask fitted with a nitrogen inlet tube, an ice-water condenser, an air stirrer, and a dropping funnel. To this mixture 6-methyl-5-hepten-2-one (Givaudan Corp., 31.55 g, 0.25 mol) in anhydrous ether (50 ml) was added dropwise with stirring at 0°. The reaction mixture was stirred overnight at room temperature and then worked up as described for 6-methyl-1,5-heptanediol. The ether was removed, and the IR spectrum of the colorless viscous liquid (30.0 g, 93.5% yield) showed no residual carbonyl absorption.

2-Acetoxy-6-methyl-5-heptene. Pyridine (33.4 g, 0.42 mol), acetic anhydride (40.6 g, 0.40 mol), and 6-methyl-5-hepten-2-ol (30.0 g, 0.23 mol) were refluxed overnight in a 250-ml flask fitted with a reflux condenser and drying tube. The reaction mixture was then cooled and worked up as described for 3-acetoxy-5-methyl-5-hexene. The ether was removed to yield the desired product (38.3 g, 96.3% yield). The IR spectrum of the product showed no hydroxyl absorption.

Pyrolysis of 2-Acetoxy-6-methyl-5-heptene. A solution of 2-acetoxy-6-methyl-5-heptene (38.3 g, 0.225 mol) in anhydrous ether (75 ml) was pyrolyzed at 485-495°. The reaction mixture was worked up as described for 2-methyl-1,4-hexadiene, and the solvent was removed to yield the crude product (20.8 g, 83.9% yield). Two components were collected by VPC (Carbowax 20M) at 88°. The first component collected was 6-methyl-1,5-heptadiene (61% of the diene mixture as determined by

integration of the VPC trace). The diene was identified by its mass spectrum (parent m/e 110) and by its NMR spectrum which contained broadened singlets of equal areas at τ8.33 and τ8.42 (6 H, vinyl methyls), a multiplet at τ7.95 (4 H, C_3 and C_4 hydrogens), a multiplet at τ5.05 (1 H, C_1 cis-hydrogen), a multiplet at τ 5.13 (1 H, C_1 trans-hydrogen), a broadened triplet at τ 4.90 (1 H, C_5 vinyl hydrogen), and a multiplet at τ 4.25 (1 H, C_2 vinyl hydrogen). The second component collected, cis- and trans-2-methyl-2,5-heptadiene (39% of the diene mixture), was identified by its mass spectrum (parent m/e 110) and its NMR spectrum (Figure 6). No unreacted acetate was detected.

1,1,5-Trimethylpentadienyllithium (12)

In an NMR tube THF-d_8 (0.36 ml, 4.1 mmol), 2-methyl-2,5-heptadiene (0.22 g, 2.0 mmol), and n-butyllithium (1.35 ml, 2.16 mmol) were thoroughly mixed at -78°. The sample was then placed in the NMR probe at 35°, and spectra were recorded at 15-min intervals for 4 hr. During this time it was observed that 12 formed (Figure 7) and then rearranged to 13. Layer separation occurred after 2.4 hr. The upper layer was removed after 4 hr, and the tube was sealed. The sample was then warmed in the probe from 40° to 90° in 10° increments. A spectrum was recorded at each temperature after warming for 15 min at that temperature. A final spectrum at 40° (Figure 8) showed an equilibrium mixture of 11 (10%) and 13 (90%).

2-Methyl-5,7,7,7-tetradeutero-2,5-heptadiene

6-Methyl-1,1,1,3,3-pentadeutero-5-hepten-2-one (Methylheptenone-d_5). Dry THF (5.5 ml), 6-methyl-5-hepten-2-one (methylheptenone) (Givaudan Corp., 9.5 g, 0.075 mol), deuterium oxide (10.2 g, 0.56 mol), and sodium hydroxide (0.2 g) were stirred vigorously in a 200-ml flask for 24 hr at room temperature. The lower, aqueous layer was removed, and the procedure was repeated three more times. Ether (40 ml) was added and the organic layer was removed. The aqueous layer was extracted twice with ether, and the combined ether layers were dried over anhydrous sodium carbonate. The solvent was removed yielding methylheptenone-d_5 (8.4 g, 85.5% yield). The product was identified by its mass spectrum (parent m/e 131) and by its NMR spectrum which contained a strong absorption at τ 8.4 (6 H, vinyl methyls), a broadened doublet at τ 7.84 (2 H, C_4 hydrogens), and a complex triplet at τ 4.97 (1 H, C_5 vinyl hydrogen). Residual α-hydrogens were not detected in the NMR spectrum.

6-Methyl-5-hepten-2-ol-d_5. The procedure for the preparation of 6-methyl-5-hepten-2-ol was followed employing anhydrous ether (180 ml), lithium aluminum hydride (1.95 g, 0.051 mol), and methylheptenone-d_5 (16.8 g, 0.128 mol). Workup and removal of solvent yielded the desired product (15.8 g, 92.4% yield). The IR spectrum showed no residual carbonyl absorption.

2-Acetoxy-6-methyl-5-heptene-d_5. The procedure for the preparation of 2-acetoxy-6-methyl-5-heptene was followed employing pyridine (15.0 g, 0.190 mol), acetic anhydride (18.5 g, 0.181 mol), and

6-methyl-5-hepten-2-ol-d_5 (15.8 g, 0.119 mol). Workup and removal of solvent yielded the desired product (20.5 g, 98.3% yield). The IR spectrum showed no residual hydroxyl absorption.

Pyrolysis of 2-Acetoxy-6-methyl-5-heptene-d_5. The procedure for the pyrolysis of 2-acetoxy-6-methyl-5-heptene at 485-495° was followed employing ether (60 ml) and 2-acetoxy-6-methyl-5-heptene-d_5 (11.7 g, 0.067 mol). Following workup and removal of solvent, the crude product was analyzed by VPC (Carbowax 20M) at 88°. The first component, 6-methyl-1,1,3,3-tetradeutero-1,5-heptadiene (43% of the crude product as determined by integration of the VPC trace), was identified by its mass spectrum (parent m/e 114) and by its NMR spectrum which contained broadened singlets of equal areas at τ 8.33 and τ 8.42 (6 H, vinyl methyls), a broad doublet at τ 7.95 (2 H, C_4 hydrogens), a complex triplet at τ 4.88 (1 H, C_5 vinyl hydrogen), and a broad singlet at τ 4.25 (1 H, C_2 vinyl hydrogen). The second component was the desired diene, a mixture of cis- and trans-2-methyl-5,7,7,7-tetradeutero-2,5-heptadiene (29% of the crude product) as identified by its NMR spectrum (Figure 14) and mass spectrum (parent m/e 114). The third component was unreacted acetate (28% of the crude product). No unreacted acetate was observed in the undeuterated case; the difference may be due to a deuterium isotope effect in the pyrolysis.

1,1-Dimethyl-5-trideuteromethyl-4-deuteropentadienyllithium (19)

The procedure for the preparation of 1,1,5-trimethylpentadienyllithium was followed employing THF-d_8 (0.30 ml, 3.4 mmol),

2-methyl-5,7,7,7-tetradeutero-2,5-heptadiene (0.190 g, 1.66 mmol), and n-butyllithium (1.10 ml, 1.76 mmol). The sample was thoroughly mixed in an NMR tube at -78° and then placed in the probe at 33°. Spectra were recorded every 20 min for 8 hr, and layer separation occurred after 2.5 hr. As in the undeuterated case, the initially formed anion (19) rearranged to a second anion, 1-ethyl-4-methylpentadienyllithium-d_4 (20). The upper layer was then removed and the tube was sealed. The sample was warmed outside the probe from 45° to 90° in 15° intervals. The sample was warmed for 30 min at each temperature, and a spectrum was recorded at 33° after each temperature. The final spectrum (Figure 16) shows a ratio of 9:1 of anion (20) to 1-isopropylpentadienyllithium-d_4 (21).

Protonation of 1,1-Dimethyl-5-trideuteromethyl-4-deuteropentadienyllithium After Heating

The above anion solution was poured into cold, saturated aqueous ammonium chloride solution (8 ml), and the organic layer was washed 5 times with water and dried. The mass spectrum of the organic layer showed a parent m/e value of 114 and no enrichment of the P-1 and P+1 peaks as compared with the mass spectrum of the starting diene. No intermolecular scrambling of deuterium labels was detected.

Preparation of a 1:1 Mixture of 1,1,5-Trimethylpentadienyllithium and 1,1-Dimethyl-5-trideuteromethyl-4-deuteropentadienyllithium

The procedure for the preparation of 12 was followed employing THF-d_8 (0.38 ml, 4.3 mmol), 2-methyl-2,5-heptadiene (0.110 g, 1.0 mmol),

2-methyl-5,7,7,7-tetradeutero-2,5-heptadiene (0.114 g, 1.0 mmol), and n-butyllithium (1.35 ml, 2.1 mmol). The sample was thoroughly mixed in an NMR tube at -78° and then warmed to room temperature. Layer separation occurred after 3 hr, and the upper layer was removed after 4 hr.

Protonation of a 1:1 Mixture of 1,1,5-Trimethylpentadienyllithium and 1,1-Dimethyl-5-trideuteromethyl-4-deuteropentadienyllithium

One-half (0.2 ml) of the above anion solution was poured into cold saturated aqueous ammonium chloride solution (8 ml) and the organic layer was washed five times with water and dried. The mass spectrum of the organic layer showed parent m/e peaks of equal height at 110 and 114. The relative peak heights of m/e values from 109 to 115 matched those of the mass spectrum of a 1:1 mixture of the two starting dienes. No intermolecular scrambling of deuterium labels was detected.

The second half of the above anion solution was warmed at 90° for 90 min and then protonated, washed, and dried as described above. The mass spectrum of the organic layer showed parent m/e peaks of equal height at 110 and 114, and the relative peak heights of m/e values from 109 to 115 matched those of the mass spectrum of a 1:1 mixture of the two starting dienes. No intermolecular scrambling of deuterium labels was detected.

3-Methyl-1,4-cycloheptadiene

Cycloheptadienyllithium (6) was prepared by the general procedure of McCombs (1969) involving the rearrangement of the acyclic anion from 1,3,6-heptatriene. Slowly, n-butyllithium (13.5 ml, 21.6 mmol)

was added with stirring to a solution of 1,3,6-heptatriene (Chemical Samples Company, 1.88 g, 20.0 mmol) in dry THF (3.50 ml, 43.5 mmol) contained in a 25-ml flask at -78°. The mixture was warmed to room temperature, layer separation occurred after 10 min, and the upper layer was removed. Dry THF (3.5 ml) was added to the lower layer. The mixture was cooled to -78° and methyl iodide was added dropwise with stirring until the dark red anion color disappeared. Pentane (8 ml) was added at room temperature, and the organic layer was washed ten times with water. The organic layer was dried over anhydrous magnesium sulfate, filtered, and the solvent was removed. Two components were collected by VPC (Carbowax 20M) at 110°. The first component was the expected diene (76% of the diene mixture as determined by integration of the VPC trace) and was identified by its NMR spectrum (Figure 21) and mass spectrum (parent m/e 108). The second component was 5-methyl-1,3-cycloheptadiene (24% of the diene mixture) and was identified by its mass spectrum (parent m/e 108) and by its NMR spectrum which contained a doublet at τ 8.94 (3 H, methyl hydrogens), a multiplet at τ 8.22 (2 H, C_6 hydrogens), a multiplet at τ 7.75 (2 H, C_7 hydrogens), a multiplet at τ 7.60 (1 H, C_5 hydrogen), and two multiplets centered at τ 4.35 (4 H, vinyl hydrogens).

3-Methylcycloheptadienyllithium (22)

The procedure for the preparation of 1,1,5-trimethylpentadienyllithium was followed employing THF-d_8 (0.44 ml, 5.0 mmol), 3-methyl-1,4-cycloheptadiene (0.26 g, 2.4 mmol), and n-butyllithium (1.55 ml, 2.5 mmol). The sample was thoroughly mixed in an NMR tube at -78° and

then warmed to room temperature. Layer separation occurred after 15 min, the upper layer was removed from the dark green anion layer, and the tube was sealed. The NMR spectrum (Figure 22) of the sample showed complete conversion of the starting diene to 3-methylcycloheptadienyllithium (22).

6-Methylcycloheptadienyllithium (23)

The general procedure of McCombs (1969) for the preparation of the anion (23) was followed employing THF-d_8 (0.36 ml, 4.1 mmol), 1,3,6-octatriene [Chemical Samples Company, 0.216 g, 2.0 mmol, purified by preparative VPC (Carbowax 20M) at 110°], and n-butyllithium (1.30 ml, 2.1 mmol). The sample was thoroughly mixed in an NMR tube at -78° and then warmed to room temperature. Layer separation occurred after 5 min, the upper layer was removed from the dark green anion layer, and the tube was sealed. The NMR spectrum (Figure 24) of the sample showed complete conversion of the starting triene to 6-methylcycloheptadienyllithium (23).

1,3,5-Trimethylcycloheptadienyllithium

The general procedure of McCombs (1969) for the preparation of the anion was followed employing THF-d_8 (0.36 ml, 4.1 mmol), 2,4,6-trimethyl-1,3,6-heptatriene (Aldrich Chemical Company, 0.26 g, 1.9 mmol), and n-butyllithium (1.25 ml, 2.0 mmol). Layer separation was complete after 18 hr, the upper layer was removed from the dark red anion layer, and the tube was sealed. The NMR spectrum (McCombs 1969)

showed greater than 50% conversion of the starting triene to 1,3,5-trimethylcycloheptadienyllithium.

Heating of Anion (22), Anion (23), and 1,3,5-Trimethylcycloheptadienyllithium

The three anions in sealed NMR tubes were heated simultaneously in an oil bath from 35° to 175° at 10° intervals. The NMR spectrum of each sample was recorded at 33° after each temperature, and the samples were warmed at each temperature for 30 min. The anion spectra remained virtually unchanged up through warming at 145°. Above this temperature the spectral resolution was diminished, apparently due to sample decomposition.

Irradiation of 3-Methylcycloheptadienyllithium (22) and 6-Methylcycloheptadienyllithium (23)

The anions (22) and (23) were prepared as described above in quartz NMR tubes (Wilmad Glass Company). The upper layer was removed from each sample and the tubes were sealed. The NMR spectra of the samples showed complete conversion of the starting diene and triene to their respective anions (22) and (23). The samples were then irradiated simultaneously at 0° with a high-pressure mercury lamp (Philips HPK 125 W Type 57203B) for 580 hr. The UV lamp was placed in an inner quartz jacket, ice-water was circulated between the inner and an outer quartz jacket, and the samples were adjacent to the outer jacket and immersed in ice-water. The distance from the lamp to the samples was 1 cm. At intervals NMR spectra of the samples were recorded. Anion (23) remained virtually unchanged during the period of irradiation, as

is evidenced by its NMR spectra and additional evidence which follows. Anion (22) underwent nearly quantitative change to 2-methylcyclohepta-dienyllithium (24), as is evidenced by its NMR spectrum (Figure 27) and additional evidence which follows.

Protonation of 2-Methylcyclohepta-dienyllithium (24) and VPC Analysis of Protonation Products

The irradiated 3-methylcycloheptadienyllithium (24) was poured into cold saturated aqueous ammonium chloride solution (8 ml), and the organic layer was washed five times with water and dried. Analysis by VPC (Carbowax 20M) at 92° showed three components to be present other than hexane and THF-d_8. The second component was identified as 2-methyl-1,3-cycloheptadiene by comparison of VPC data with an authentic sample on two columns (Carbowax 20M and Silicone Rubber GE SE-30) at 90° (helium flow rate, 60 ml/min). Retention times for 2-methyl-1,3-cycloheptadiene were 8.4 min on Carbowax 20M and 6.2 min on GE SE-30. The other two expected protonation products of 24 were 1-methyl-1,3-cycloheptadiene and 2-methyl-1,4-cycloheptadiene. Although the first and third components were not identified, they were shown by comparison of VPC data with an authentic sample not to be 3-methyl-1,4-cyclohepta-diene. Protonation of 3-methylcycloheptadienyllithium (22) under the same conditions described above reproducibly gave 2-methyl-1,3-cyclo-heptadiene and 3-methyl-1,4-cycloheptadiene in a 2:1 ratio. Therefore, the absence of 3-methyl-1,4-cycloheptadiene as a protonation product of 24 further argues that 2-methyl-1,3-cycloheptadiene is indeed a product of protonation of 2-methylcycloheptadienyllithium (24).

Protonation of Irradiated 6-Methylcycloheptadienyllithium (23) and VPC Analysis of Protonation Products

The irradiated anion (23) was protonated, worked up, and dried using the same procedure as described above for 24. Analysis by VPC (Carbowax 20M) at 122° showed three components to be present other than hexane. The first component was identified as 6-methyl-1,4-cycloheptadiene by comparison of its NMR spectrum with that of an authentic sample and by comparison of VPC data with an authentic sample on two columns (Carbowax 20M, 123°, and Silicone Rubber GE SE-30, 73°) (helium flow rate, 60 ml/min). The second component, 6-methyl-1,3-cycloheptadiene, and the third component, 5-methyl-1,3-cycloheptadiene, were also identified by comparison of their NMR spectra with those of authentic samples and by comparison of VPC data with authentic samples using the same columns and conditions as described above. Retention times for components 1, 2, and 3, respectively, were 6.1, 6.7, and 7.0 min on Carbowax 20M and 10.0, 10.6, and 10.9 min on GE SE-30. The ratio of components 1 to 2 to 3 was 1:2:2, the same ratio obtained when an unirradiated sample of 23 is protonated.

DISCUSSION OF RESULTS

In this study positional isomerization reactions of several pentadienyllithiums are investigated. A new positional isomerization of a cyclic pentadienyllithium is reported, and equilibria are established in two systems of acyclic pentadienyllithiums. Evidence is presented that these positional isomerizations are intramolecular reactions, stereochemically consistent with Woodward-Hoffmann selection rules for [1,6] sigmatropic hydrogen shifts (Woodward and Hoffmann 1965, 1970).

NMR Spectra of Pentadienyllithiums

The NMR spectra of a number of starting dienes and trienes and new cyclic and acyclic pentadienyllithiums are presented in this discussion. Chemical shifts in τ units and coupling constants in Hertz (Hz) are also presented for several new anions. Tetramethylsilane (TMS, τ 10.0) is the internal standard used in all spectra of starting dienes and trienes, and cyclohexane (τ 8.57) is the standard used in the 60 MHz spectra of anions. Hexane absorptions are utilized as lock signals for 100 MHz spectra of anions. Therefore these spectra are offset toward higher field, and these offsets are indicated in Hz. In the anion spectra small absorptions at τ 6.40 and τ 8.25 are due to the residual α- and β-hydrogens of THF-d_8, respectively. The NMR spectra of several cyclic and acyclic pentadienyllithiums discussed here have been

reported previously by Potter (1969) and McCombs (1969), and will not be presented in this discussion.

The chemical shifts of hydrogens attached to the sp^2 carbons of pentadienyllithiums have been reported by Bates et al. (1967b) and McCombs (1969), and they can be related to the charge density on these carbons. Observations show that the hydrogens on carbons 2 and 4 of pentadienyllithium absorb in the normal range of olefinic hydrogens (τ4.45) and that the hydrogens on carbons 1, 3, and 5 absorb much higher (end τ7.1; central τ5.9). Theoretical calculations (Brickstock and Pople 1954) predict higher electron density on carbons 1, 3, and 5 in this anion, and these results are consistent with the generality that higher field absorption indicates higher electron density. This generality has been well substantiated by NMR studies of allyl anions (West, Purmort, and McKinley 1968), acyclic pentadienyllithiums (Potter 1969), and cyclic pentadienyllithiums (McCombs 1969). In addition, in a given acyclic pentadienyl anion system, primary hydrogens on carbons 1 and/or 5 tend to absorb at higher field than secondary hydrogens at carbons 3 and/or 5. This is reasonable because primary carbanions are generally more stable than secondary carbanions, and one might predict that there would be more negative charge at the primary carbons in such hybrid carbanions. Finally, McCombs (1969) has also observed that the hydrogens on carbons 2 and 4 of cycloheptadienyllithium absorb at lower field (τ4.4) than the hydrogens on carbons 1 and 5 (τ6.2) and carbon 3 (τ7.6).

Equilibrium Mixtures of Acyclic Pentadienyllithiums

In reporting the positional isomerizations of anions (7), (9), and (11), Potter (1969) proposed that equilibrium had been established in each instance. In the present study, the latter two systems were studied, and the proposed equilibria were approached from anions (10) and (12), respectively.

Anion (10), 1,4-dimethylpentadienyllithium, was prepared in an NMR tube by reacting 2-methyl-1,4-hexadiene (Figure 1) in THF-d_8 with n-butyllithium in the NMR probe at 20°. A spectrum recorded after 20 min (Figure 2, 90 Hz offset) shows that anion (10) is formed initially, and the cis-isomer (10a) and trans-isomer (10b) are present in the ratio of 40:60, respectively, as determined by integration of their respective C_1 hydrogen absorptions at τ 7.50 and τ 7.26. It is also evident from Figure 2 that anion (10) has started to rearrange to anion (9) (doublet at τ 7.78, C_1 hydrogens). The diene had completely reacted after 90 min, and the sample was then warmed to 40°. A spectrum recorded at this temperature (Figure 3, 84 Hz offset) shows a mixture of 47% anion (9) and 53% anion (10). Potter (1969) reported that warming anion (9) to 40° produced a mixture of 48% anion (9) and 52% anion (10), so it is concluded that equilibrium has been established in this system (Figure 4).

The equilibrium concentrations of anions (9) and (10) at 40° indicate that anion (10) is only about 0.1 kcal/mol more stable than anion (9). This is somewhat surprising, in that carbons 1, 3, and 5 of anion (10) are 1°, 2°, and 2°, respectively, and carbons 1, 3, and 5 of

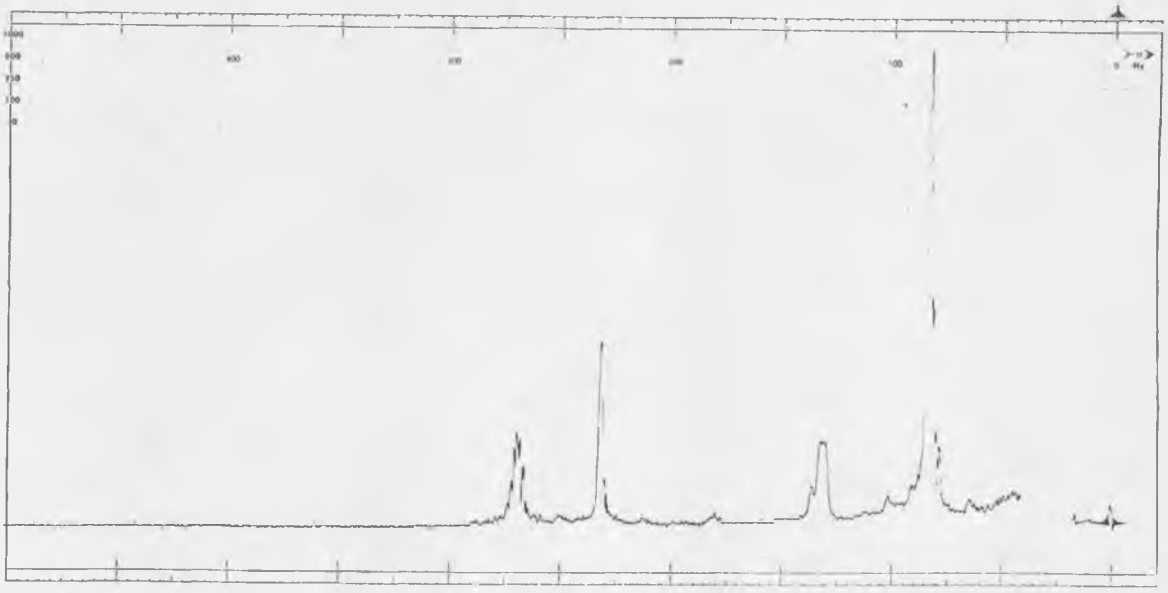


Figure 1. 100 MHz NMR spectrum of 2-methyl-1,4-hexadiene.

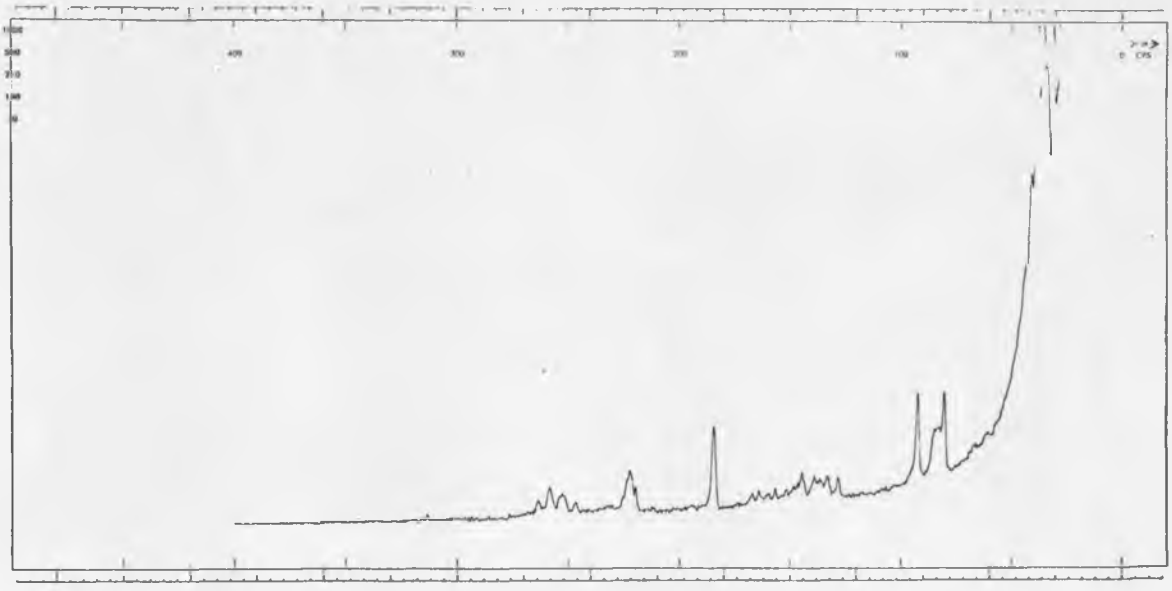


Figure 2. 100 MHz NMR spectrum of 2-methyl-1,4-hexadiene and anion (10).

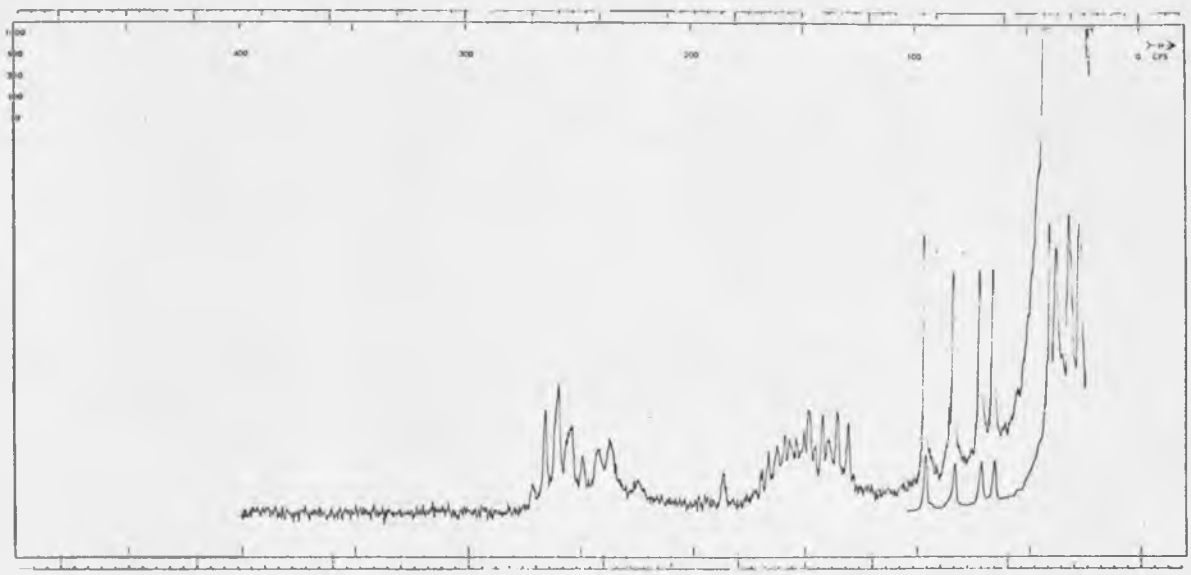


Figure 3. 100 MHz NMR spectrum of anions (9) and (10).

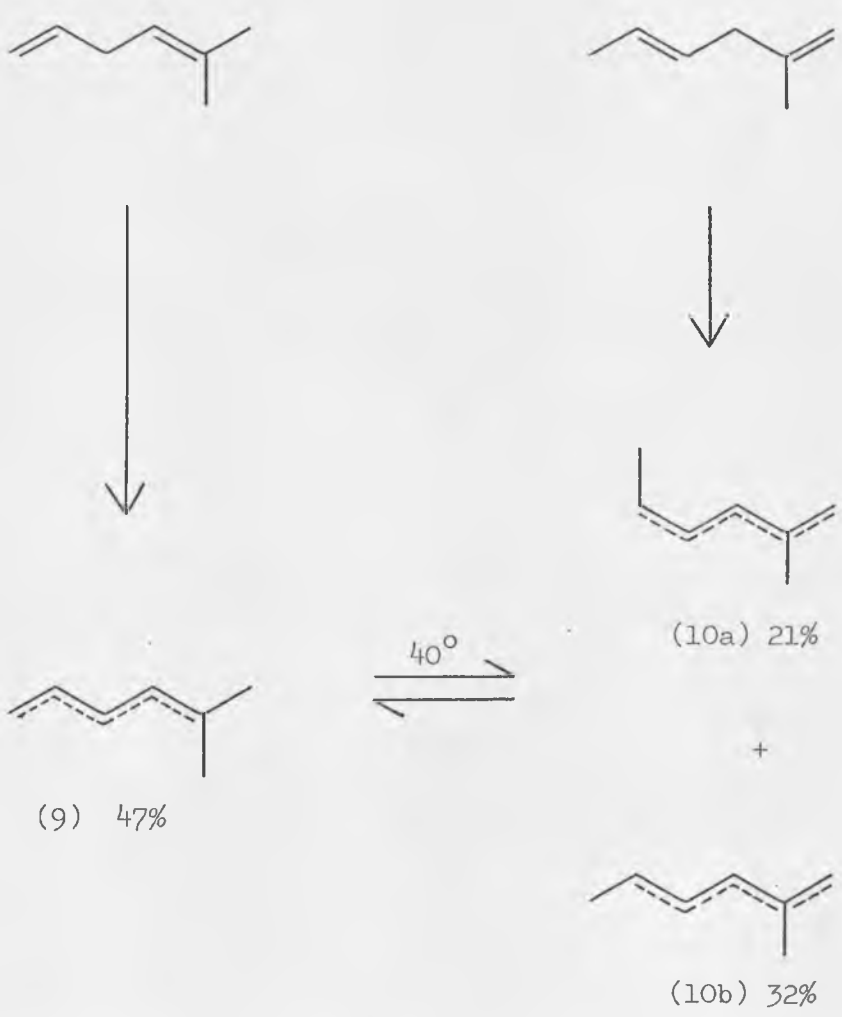


Figure 4. Equilibrium mixture of anions (9), (10a), and (10b).

anion (9) are 1^{o}, 2^{o}, and 3^{o}, respectively. The negative charge is concentrated on carbons 1, 3, and 5 in each anion, so it is expected that the tertiary carbon 5 in anion (9) would be destabilizing. Thus, other factors must be considered.

Potter (1969) concluded that a methyl group attached to carbon 2 in acyclic pentadienyllithiums tends to increase the double bond character of the C_{1-2} bond. This would occur if the methyl group twists the anion such that the sp^2 carbons 1 and 2 no longer lie in the plane of the original 5 sp^2 carbons of the pentadienyl system, and should result in less negative charge on carbon 1 of anion (10) as compared to anion (9). Indeed, this appears to be the case, because the C_1 hydrogens of anion (10) absorb at lower field than the C_1 hydrogens of anion (9). This twisting should destabilize the pentadienyl system. A second consideration is solvation of the anion. Birch et al. (1961) have postulated that alkyl substitution of pentadienyl anions destabilizes due to steric hindrance to solvation. Thus, the methyl group on carbon 2 of anion (10) could hinder solvation at both carbons 1 and 3. The above considerations provide some rationalization for the presence of anion (9) as 47% of the equilibrium mixture.

Potter (1969) proposed a second equilibrium involving anions (11), (12), and (13). This system was entered by reacting 6-methyl-1,4-heptadiene (Figure 5) in THF-d_8 with n-butyllithium at room temperature and initially forming 1-isopropylpentadienyllithium (11). Upon warming the sample to 90^{o}, it was observed that a mixture of 10% anion (11) (<u>cis</u>-isomer C_1 hydrogens at τ7.60, doublet; <u>trans</u>-isomer C_1

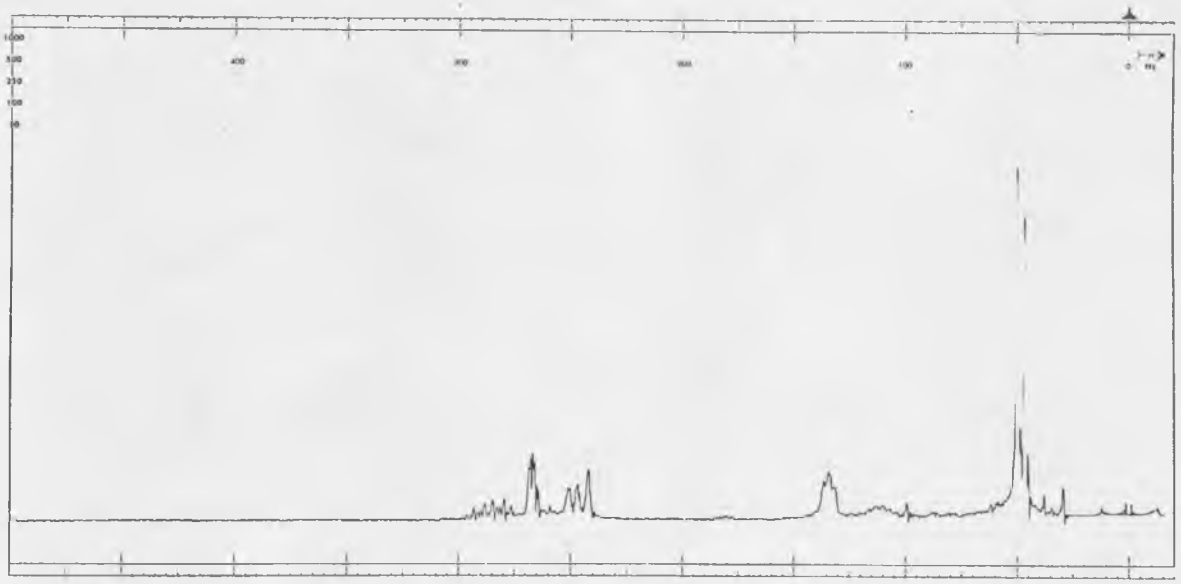


Figure 5. 100 MHz NMR spectrum of 6-methyl-1,4-heptadiene.

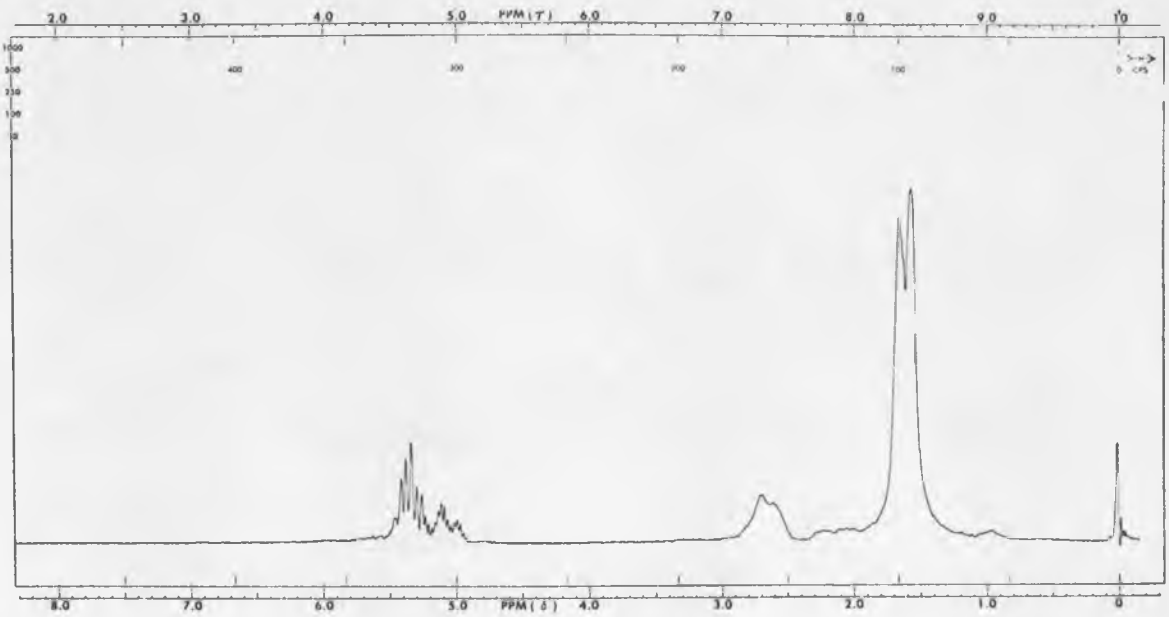


Figure 6. 60 MHz NMR spectrum of 2-methyl-2,5-heptadiene.

hydrogens at τ 7.42, doublet) and 90% anion (13) (cis-isomer C_1 hydrogens at τ 7.41; trans-isomer C_1 hydrogens at τ 7.22) resulted. Anion (12) was not detected in the mixture. In the present study, 1,5,5-trimethylpentadienyllithium (12) was prepared in an NMR tube by reacting 2-methyl-2,5-heptadiene (Figure 6) in THF-d_8 with n-butyllithium in the NMR probe at 35°. A spectrum recorded after 20 min (Figure 7, 86 Hz offset) shows that anion (12) is formed initially, and the cis-isomer (12a) and the trans-isomer (12b) are present in the ratio of 2:5, respectively. The NMR parameters for 12a and 12b are presented in Figures 9 and 10, respectively. The diene was completely reacted after 2.4 hr. During this time it was observed that anion (12) rearranged rapidly to anion (13), and after 4 hr only anion (13) was detected. The sample was then warmed to 90° in the probe, and the NMR spectrum recorded at this temperature (Figure 8, 95 Hz offset) shows a mixture of anions (11) and (13) in a 1:9 ratio. Anion (12) was not detected in the equilibrium mixture. It is concluded that equilibrium has been established in this system (Figure 11).

A potential energy curve for the above equilibrium is presented in Figure 12, and is based on NMR studies made during the formation and equilibration of the anions. The equilibrium concentrations of anions (11), (12), and (13) at 90° indicate that ΔG_1 is about 1.6 kcal/mol. Anion (12) is present as much less than 5% of this equilibrium mixture which indicates that ΔG_2 is at least 0.5 kcal/mol. Therefore, ΔG_3 is at least 2.1 kcal/mol. It is observed for the first order transformation of anion (11) to anion (13) that the half-life ($t_{1/2}$) is greater

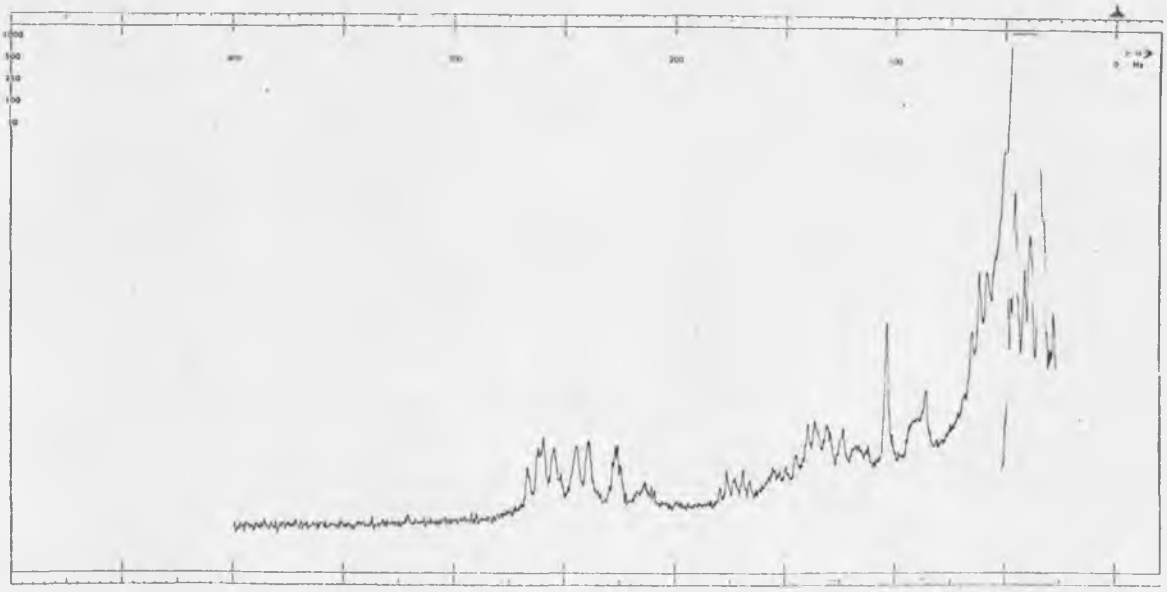


Figure 7. 100 MHz NMR spectrum of 2-methyl-2,5-heptadiene and anions (12) and (13).

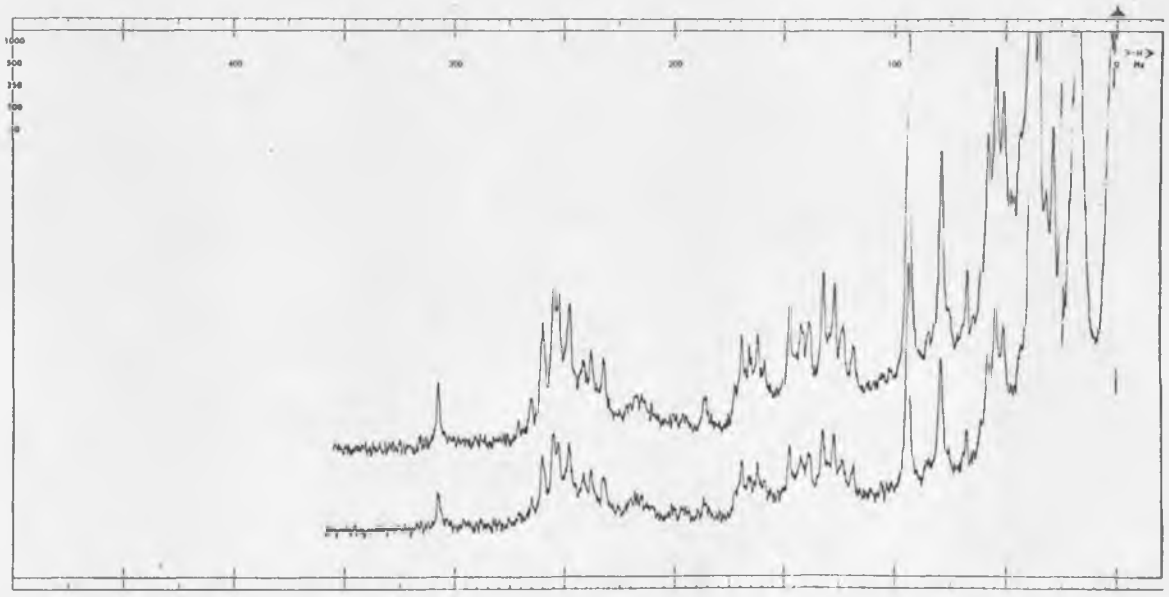
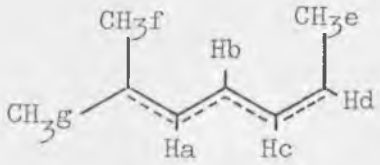
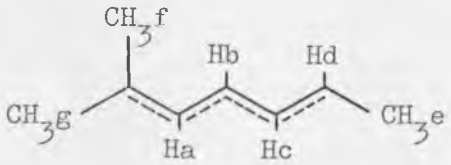


Figure 8. 100 MHz NMR spectrum of anions (11) and (13).



Chemical Shifts (τ)				Coupling Constants (Hz)	
Ha	4.35	He	~8.4	Jab	11.0
Hb	6.52	Hf	~8.4	Jbc	14.0
Hc	4.16	Hg	~8.5	Jcd	10.0
Hd	~6.9				

Figure 9. NMR parameters for anion (12a).



Chemical Shifts (τ)				Coupling Constants (Hz)	
Ha	4.37	He	~8.4	Jab	12.0
Hb	6.70	Hf	~8.4	Jbc	14.0
Hc	4.07	Hg	~8.5	Jcd	13.0
Hd	~6.6				

Figure 10. NMR parameters for anion (12b).

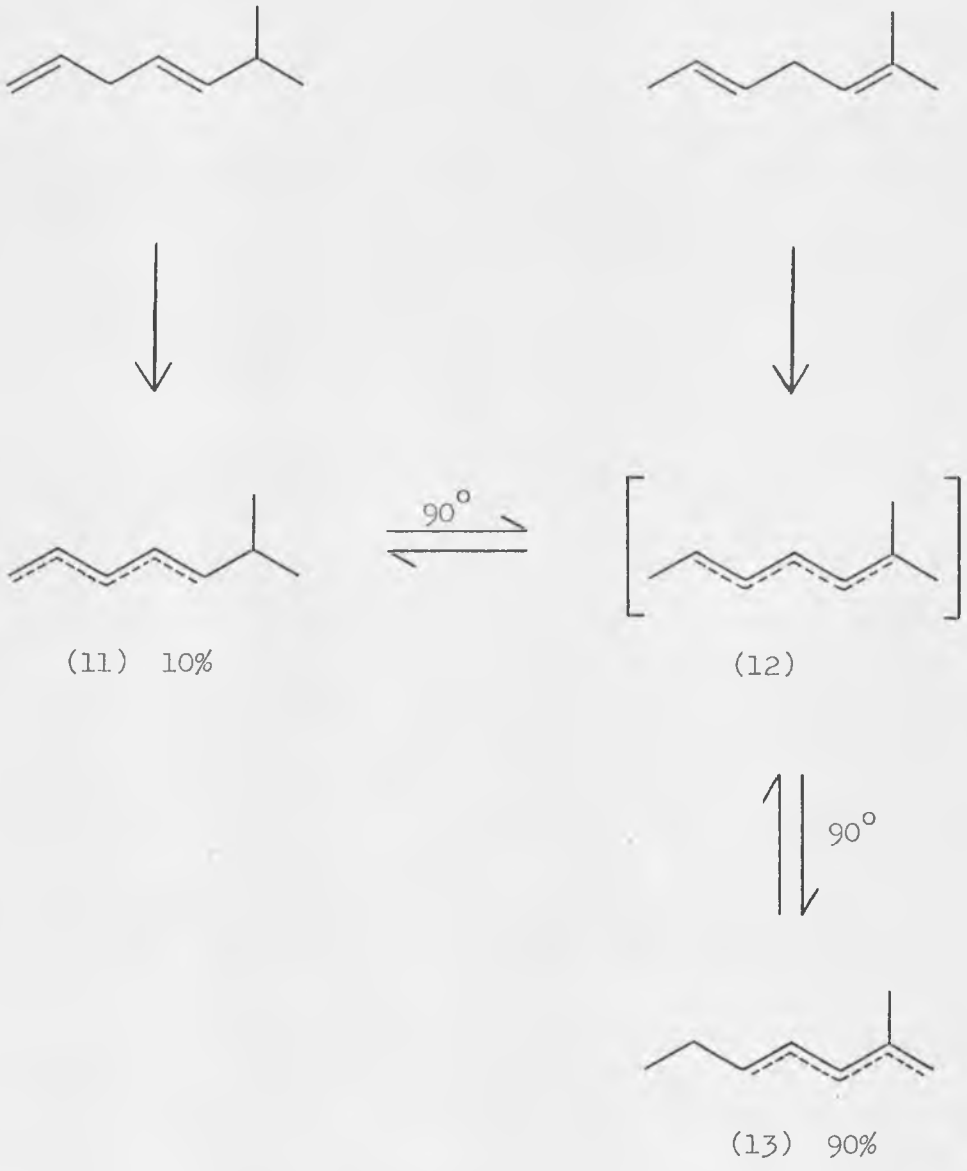


Figure 11. Equilibrium mixture of anions (11), (12), and (13).

than 12 hr at 40° and less than 5 min at 90°. Utilizing expressions (26) and (27) (Jensen et al. 1962), it is calculated that $\Delta G_1^{\ddagger}$ is be-

$$k_1 = 0.693/t_{1/2} \qquad (26)$$

$$G^{\ddagger} = -RT \ln(k_1 h/kT) \qquad (27)$$

tween 25 and 28 kcal/mol. Analysis of the NMR spectra recorded during the generation of anion (12) showed that the first order rate constant (k_1) for the rearrangement of 12 to 13 at 35° was about 2×10^{-3} sec^{-1}, and $\Delta G_3^{\ddagger}$ was calculated to be about 20 kcal/mol. Furthermore, because less than 5% of anion (12) rearranged to anion (11) under these conditions, the first order rate constant (k_1) for the reaction of 12 to 11 is less than 10^{-4} sec^{-1}. Thus $\Delta G_2^{\ddagger}$ is calculated to be greater than 23 kcal/mol. Correlation of these limiting values of ΔG and $\Delta G^{\ddagger}$ results in a $\Delta G_4^{\ddagger}$ of 21-23 kcal/mol. Although Figure 12 is an approximation of the energy curve, it does conclude that $\Delta G_2^{\ddagger}$ is indeed larger than $\Delta G_3^{\ddagger}$.

This is not particularly surprising if a representation of the helical all-cis transition state for the proposed thermal antarafacial [1,6] sigmatropic hydrogen shift is examined (Figure 13). In the transition state between anions (12) and (13), R_1 or R_2 will be a methyl group and the other R groups will be hydrogens. The steric hindrance will not be excessive because the methyl group can assume the position of R_2. In contrast, both R_1 and R_2 will be methyl groups in the transition state between anions (11) and (12), and this will certainly sterically hinder the formation of this entity, resulting in a higher

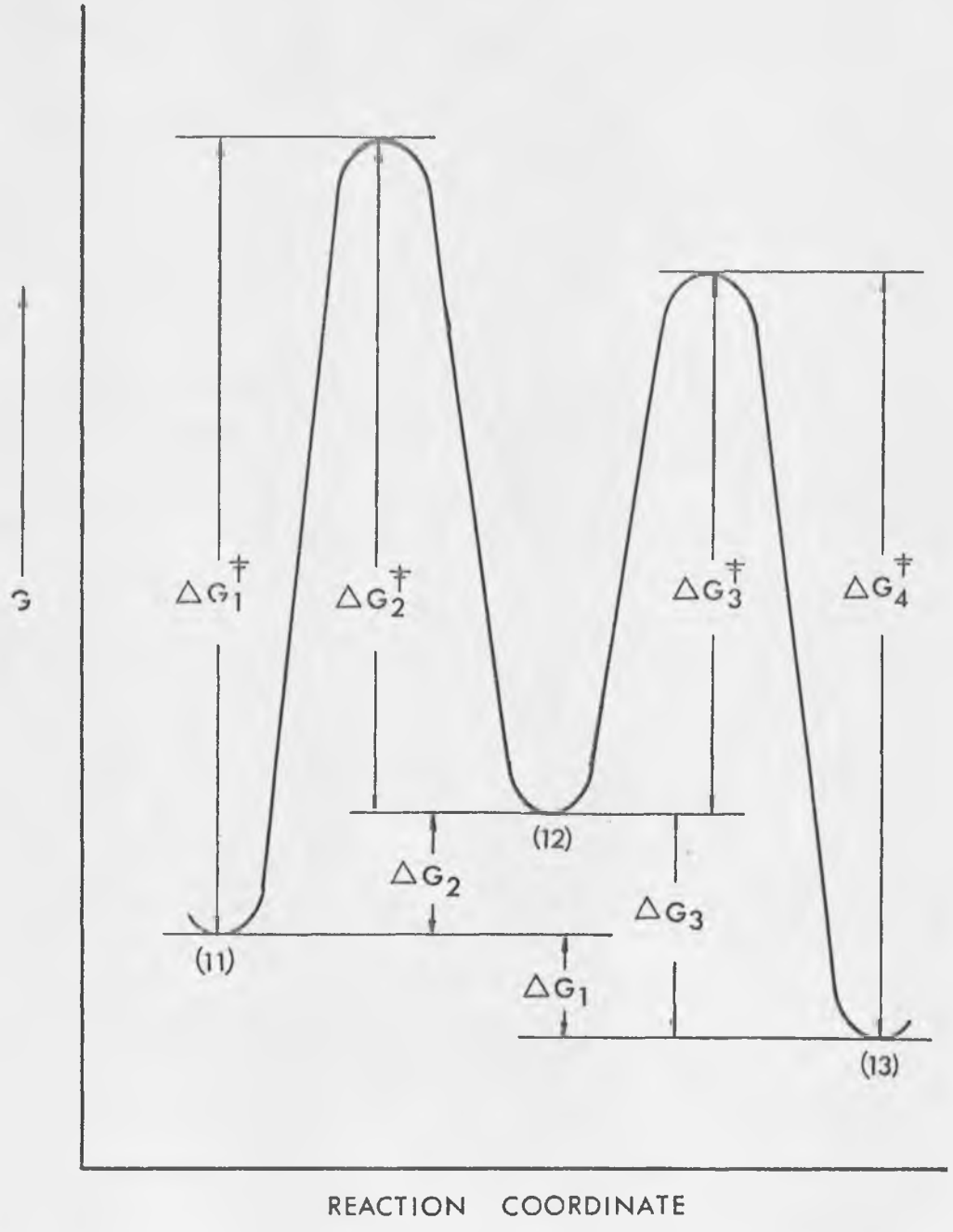


Figure 12. Potential energy curve for anions (11), (12), and (13).

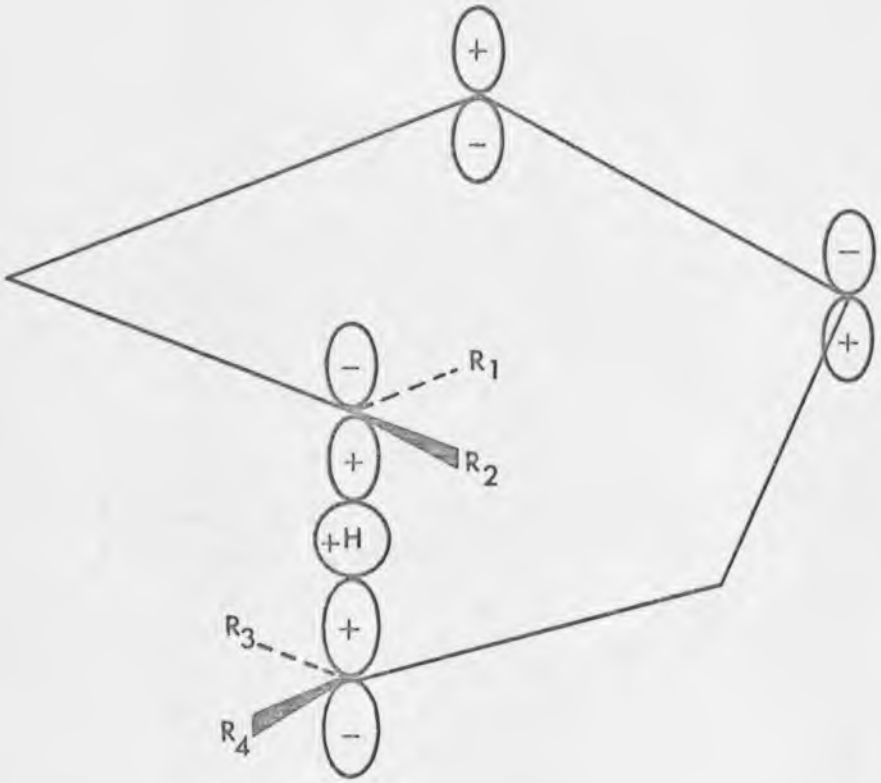


Figure 13. Helical all-cis transition state for thermal antarafacial [1,6] sigmatropic hydrogen shifts in pentadienyl anions.

energy transition state. This same line of reasoning probably accounts for the high temperature needed to equilibrate anions (7) and (8) and the relatively low temperature needed to equilibrate anions (9) and (10).

The negative charge of each anion of this equilibrium system will be concentrated on carbons 1, 3, and 5 which will be 1°, 2°, and 2° in anion (11), 2°, 2°, and 3° in anion (12), and 1°, 2°, and 2° in anion (13). On this basis, one expects anion (12) to be the least favored anion in the equilibrium mixture, but it is not so obvious why anion (13) should be so favored over anion (11). The factors mentioned in connection with anions (9) and (10) will influence the relative stabilities of anions (11) and (13), but the overriding factor is probably the decrease in the angle between the gem-methyl groups from about 120° to about 109° in going from anion (13) (or 12) to anion (11).

Intramolecularity of the Positional Isomerizations of Pentadienyllithiums

The positional isomerization reactions discussed above must be intramolecular as a prerequisite to their being [1,6] sigmatropic hydrogen shifts. To test this intramolecularity, 2-methyl-5,7,7,7-tetradeutero-2,5-heptadiene (Figure 14) was prepared and then reacted in THF-d_8 with n-butyllithium in an NMR tube at 33°. An NMR spectrum recorded after 20 min (Figure 15) shows that 1,1-dimethyl-5-trideuteromethyl-4-deuteropentadienyllithium (19) is initially formed, and exists as a mixture of 40% cis-isomer (19a) and 60% trans-isomer (19b). Anion (19) was observed to rearrange rapidly to 1-ethyl-4-methylpentadienyllithium-d_4 (20) (Figure 15) which exists as a mixture of about 35%

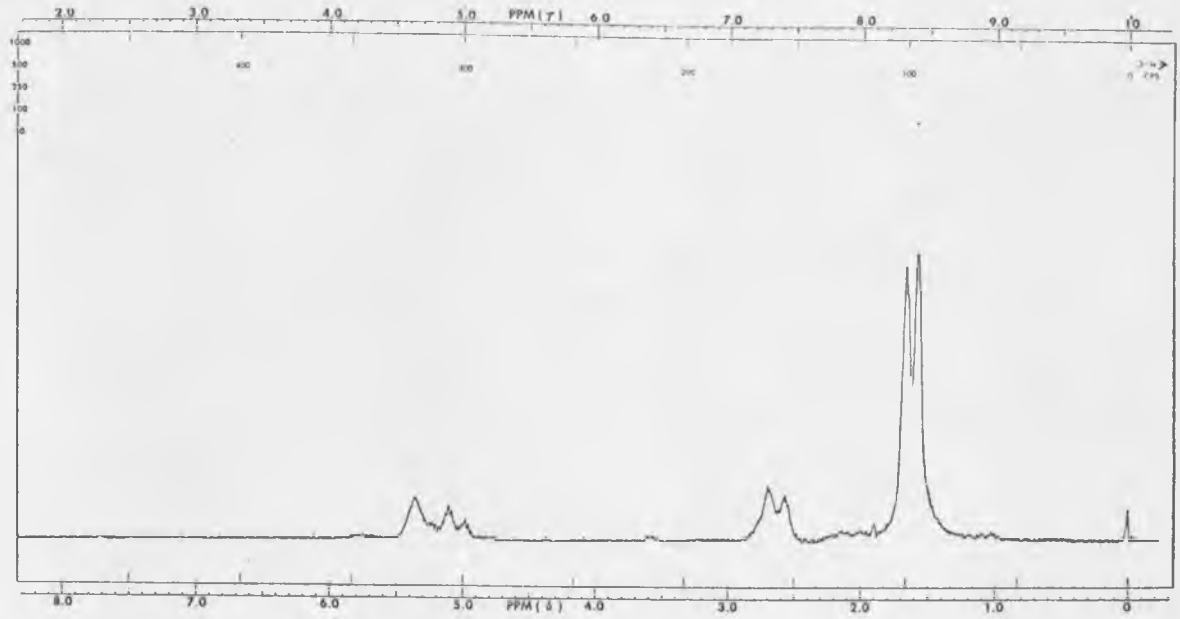


Figure 14. 60 MHz NMR spectrum of 2-methyl-5,7,7,7-tetradeutero-2,5-heptadiene.

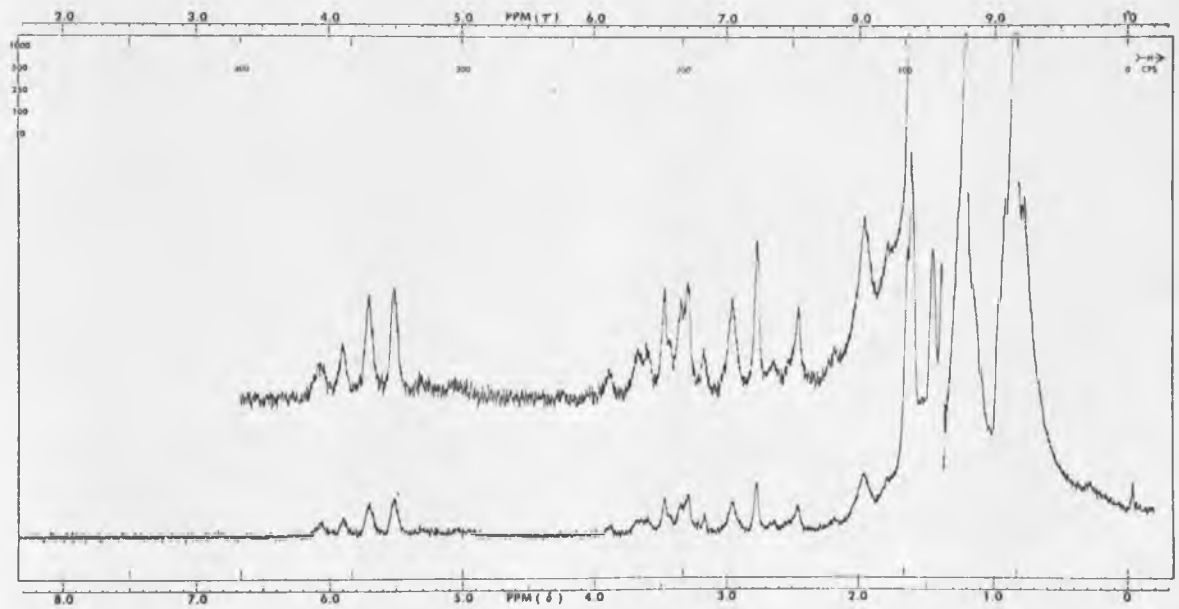


Figure 15. 60 MHz NMR spectrum of 2-methyl-5,7,7,7-tetradeutero-2,5-heptadiene and anions (19) and (20).

cis-isomer (20a) and 65% trans-isomer (20b). The NMR parameters for anions (19a), (19b), (20a), and (20b) are presented in Figures 17-20. The sample was then warmed at 90° for 30 min and a NMR spectrum (Figure 16, 82 Hz offset) was recorded which showed the presence of anion (20) and 1-isopropylpentadienyllithium-d_4 (21) (C_2 hydrogen at τ 3.88) in the ratio of about 9:1. It was concluded that equilibrium had been reached. The anion mixture was then protonated, and a mass spectrum was taken of the organic layer. The ratios of peak heights from m/e 112 to 116 matched those of the mass spectrum of the starting diene. It was concluded, therefore, that no detectable intermolecular scrambling of deuterium label had occurred, because such scrambling would have statistically enriched m/e values above and below 114, the parent peak of the d_4-dienes in the protonation mixture.

A second test for intramolecularity was conducted by preparing a 1:1 mixture of anions (12) and (19), warming the mixture at 90° for 30 min, protonating the mixture of anions, and recording the mass spectrum of the organic layer. The ratios of peak heights from m/e 109 to 115 matched those of the mass spectrum of a 1:1 mixture of the starting dienes. Again it was concluded that no detectable intermolecular scrambling of deuterium label had occurred. Therefore, the intramolecularity of the thermal positional isomerizations of pentadienyllithiums has been demonstrated.

Stereochemical Studies of the Positional Isomerizations of Pentadienyllithiums

The Woodward-Hoffmann selection rules (Woodward and Hoffman 1965, 1970) for [1,6] sigmatropic hydrogen shifts predict that the

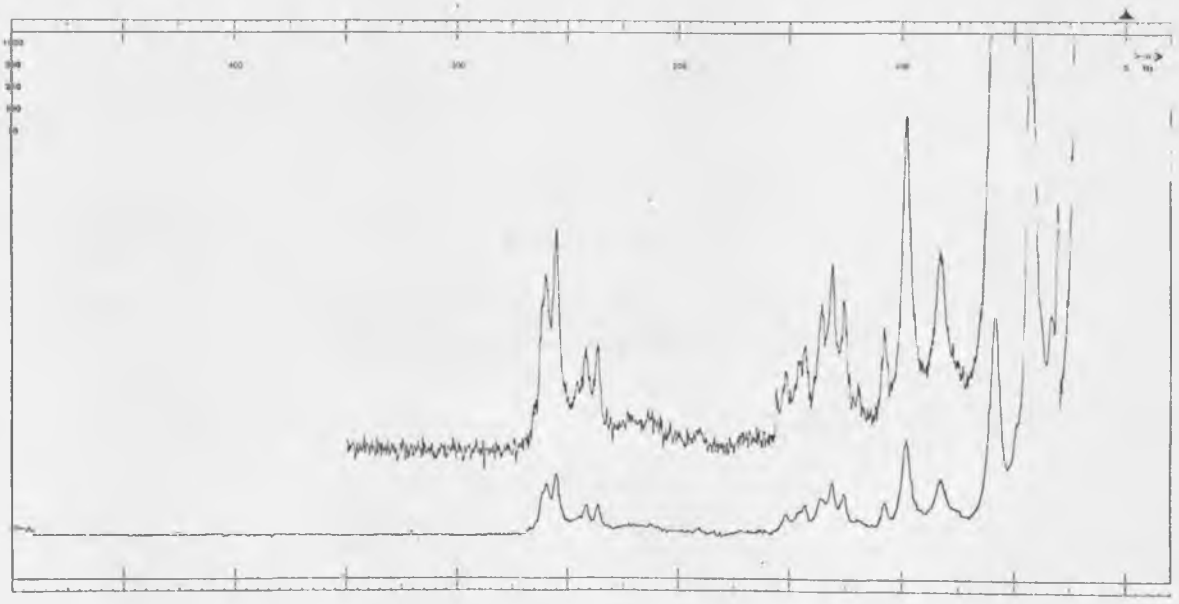
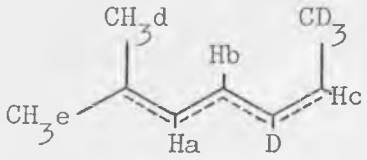
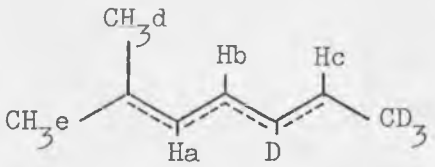


Figure 16. 100 MHz NMR spectrum of anions (20) and (21).



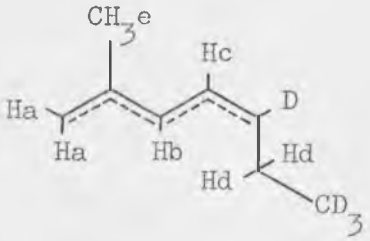
Chemical Shifts (τ)		Coupling Constants (Hz)
Ha ~4.3	He ~8.5	Jab 11.0
Hb 6.46		
Hc ~6.9		
Hd ~8.4		

Figure 17. NMR parameters for anion (19a).



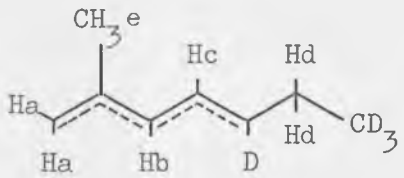
Chemical Shifts (τ)		Coupling Constants (Hz)
Ha ~4.3	He ~8.5	Jab 11.0
Hb 6.74		
Hc ~6.6		
Hd ~8.4		

Figure 18. NMR parameters for anion (19b).



Chemical Shifts (τ)				Coupling Constants (Hz)	
Ha	7.52	He	8.32	Jbc	10.0
Hb	6.51				
Hc	4.03				
Hd	8.01				

Figure 19. NMR parameters for anion (20a).



Chemical Shifts (τ)				Coupling Constants (Hz)	
Ha	7.22	He	8.30	Jbc	10.0
Hb	6.62				
Hc	4.05				
Hd	8.01				

Figure 20. NMR parameters for anion (20b).

thermal reaction in pentadienyllithiums will proceed antarafacially, necessitating a helical all-cis transition state for the transformation (Figure 13). This will cause some strain in the acyclic pentadienyl anion system. The sp^2 carbons will deviate from coplanarity, resulting in less than maximum overlap of their p-orbitals. However, it has been demonstrated that a distorted pentadienyl anion system can exist in cyclooctadienyllithium (Bates and McCombs 1969) and cycloheptadienyllithiums (Bates et al. 1969). It was decided to utilize several cycloheptadienyllithiums in determining whether the observed isomerizations in acyclic pentadienyllithiums were stereochemically consistent with the Woodward-Hoffmann rules.

The highest occupied molecular orbital (17) of cycloheptadienyllithiums possesses the same symmetry as the acyclic counterparts, so a thermal antarafacial shift is predicted. However, the rigid geometry of the seven-membered ring should prohibit antarafacial rearrangement. For this reason, three cycloheptadienyllithiums were prepared and subjected to high temperatures.

In THF-d_8, 3-methyl-1,4-cycloheptadiene (Figure 21) was reacted with n-butyllithium to give the first anion, 3-methylcycloheptadienyllithium (22), in quantitative yield. The NMR spectrum of 22 is presented in Figure 22, and the NMR parameters of the anion appear in Figure 25. The second anion, 6-methylcycloheptadienyllithium (23), was prepared quantitatively by reacting purified 1,3,6-octatriene (Figure 23) in THF-d_8 with n-butyllithium. The partial NMR spectrum and approximate NMR parameters for this anion have been reported by McCombs

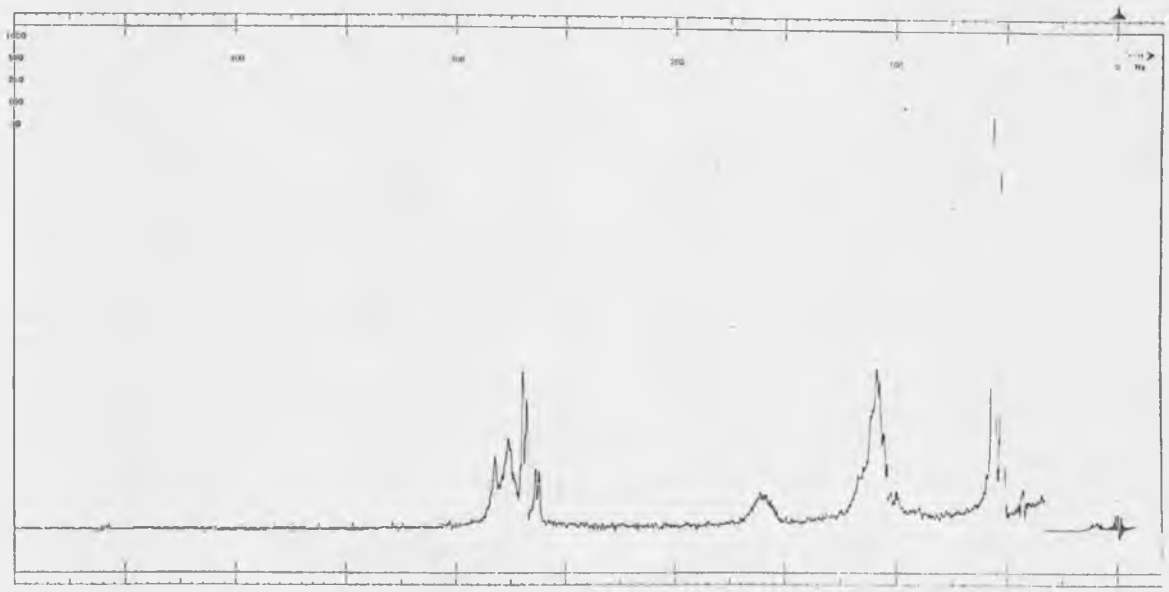


Figure 21. 100 MHz NMR spectrum of 3-methyl-1,4-cycloheptadiene.

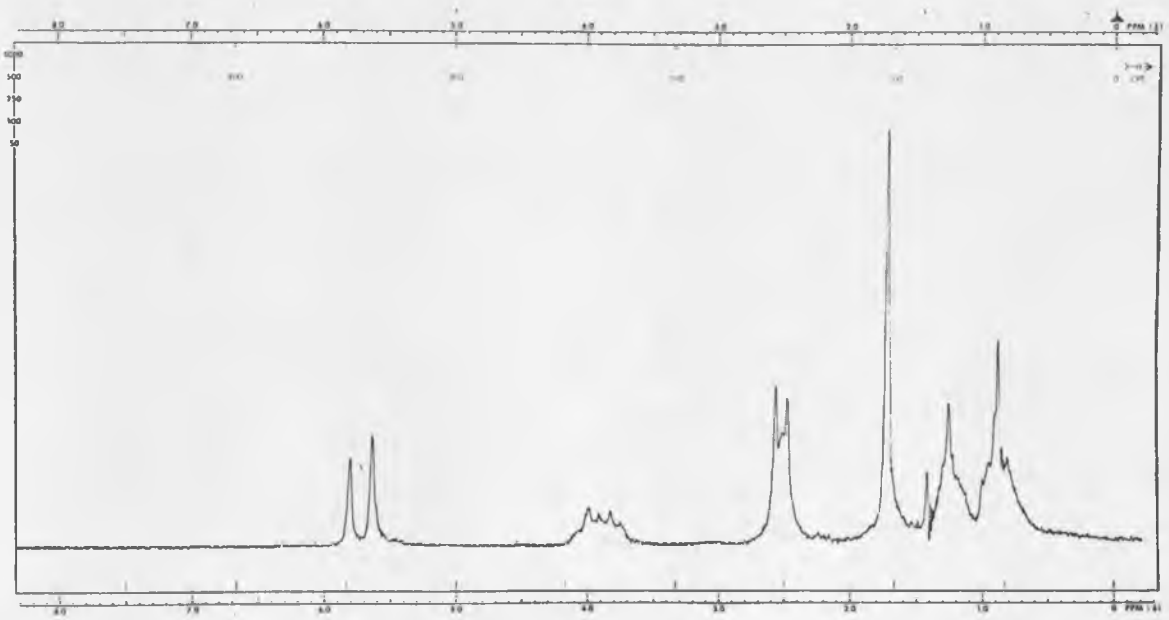


Figure 22. 60 MHz NMR spectrum of anion (22).

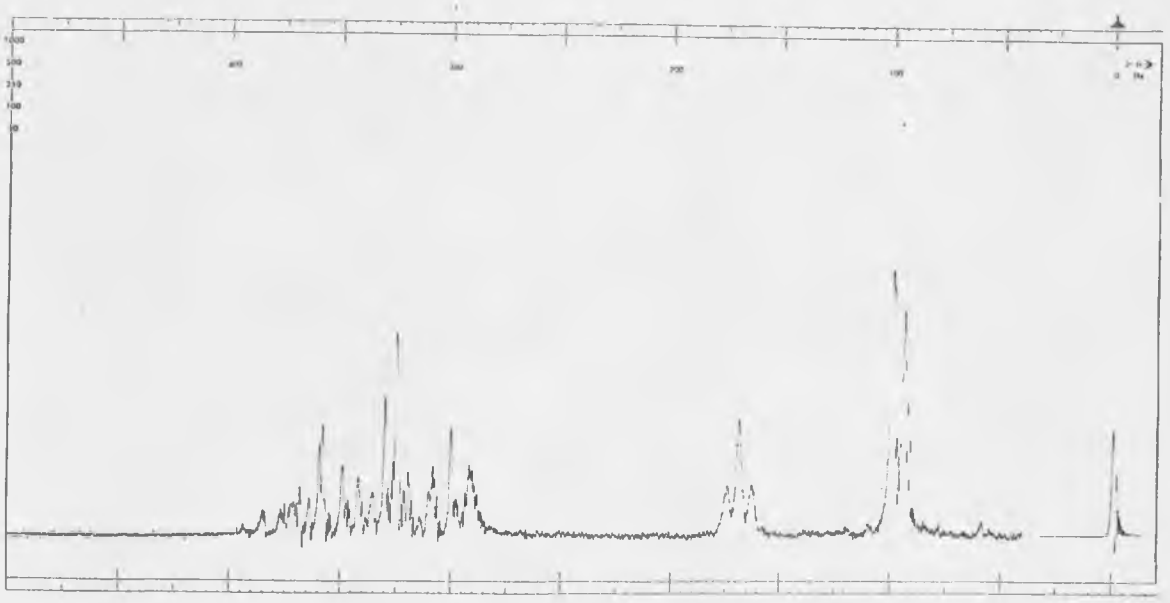


Figure 23. 60 MHz NMR spectrum of 1,3,6-octatriene.

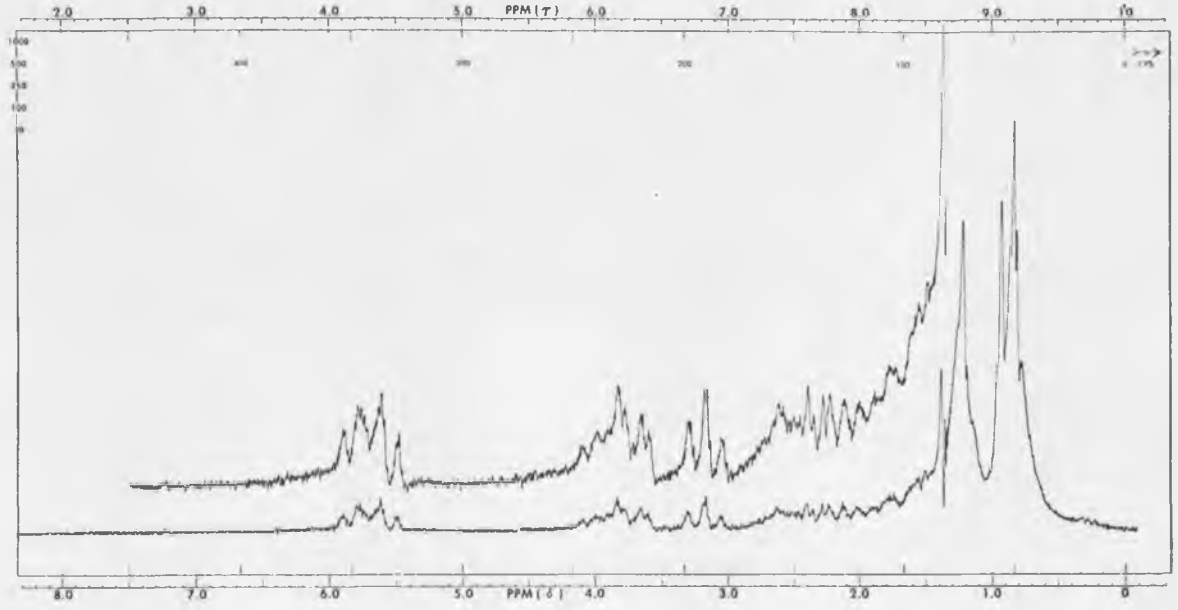
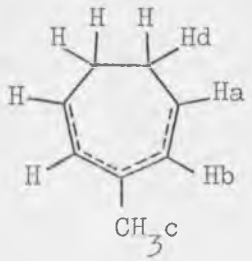


Figure 24. 60 MHz NMR spectrum of anion (23).

(1969). In the present discussion the complete NMR spectrum of anion (23) is shown in Figure 24 and a corrected and more complete list of NMR parameters appear in Figure 26. The third anion, 1,3,5-trimethylcycloheptadienyllithium, was prepared in greater than 50% yield according to the general procedure of McCombs (1969) by reacting 2,4,6-trimethyl-1,3,5-heptatriene in THF-d_8 with n-butyllithium. The NMR spectra of the starting triene and the anion and the NMR parameters of the anion have been reported by the above investigator.

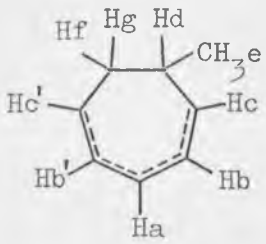
The three cycloheptadienyllithiums were warmed together in sealed NMR tubes at 10° intervals from 35° to 145° for 30 min at each temperature. The NMR spectra of each sample were recorded at 33° after heating at a given temperature, and the anions remained virtually unchanged. These results provide further supporting evidence that the thermal positional isomerizations of pentadienyllithiums are consistent with the Woodward-Hoffmann rules since no rearrangements were observed. This experiment is particularly significant in that 1,3,5-trimethylcycloheptadienyllithium is a 3°, 3°, 3° anion and would be expected to rearrange preferentially to the more stable 2°, 2°, 2° anion, 2,4,6-trimethylcycloheptadienyllithium if such a transformation were allowed. Finally, it was observed that warming the three cycloheptadienyllithiums to 175° resulted in apparent sample decomposition in all three cases.

The orbital symmetry of the first excited state (18) leads to the prediction that a <u>suprafacial</u> [1,6] sigmatropic hydrogen shift could be photochemically induced in pentadienyl anion systems, and such



Chemical Shifts (τ)		Coupling Constants (Hz)	
Ha	6.15	Jab	10.0
Hb	4.27	Jad	5.5
Hc	8.28		
Hd	7.47		

Figure 25. NMR parameters for anion (22).



Chemical Shifts (τ)				Coupling Constants (Hz)			
Ha	6.78	Hd	~7.4	Jab	7.5	Jbc	10.5
Hb	4.43	He	9.09	Jab'	7.5	Jb'c'	10.0
Hb'	4.50	Hf	~7.7	Jac	1.5	Jcd	3.5
Hc	6.23	Hg	~7.7	Jac'	1.5	Jde	7.0
Hc'	6.12						

Figure 26. NMR parameters for anion (23).

a transformation is geometrically allowable in cycloheptadienyllithiums. Anions (22) and (23), prepared in quartz NMR tubes, were used in the subsequent irradiation study. Attempts to obtain the UV spectra of these anions were unsuccessful, because the solvent system absorbed off-scale up to about 300 nm. It has been reported (Brenner 1970, Brenner and Klein 1969) that 1,5-diphenylpentadienyllithium absorbs at 503 nm, and it is expected that the aromatic substitution in this system produces a large bathochromic shift in the λ_{max} of the pentadienyl anion. Thus, it was concluded that the cycloheptadienyllithium absorptions were at lower λ_{max} values and were hidden by solvent absorptions. For this reason, a high-pressure mercury lamp was used in the irradiation study, so as to provide a broad spectrum of incident light.

After 580 hr of irradiation at 0°, anion (23) showed no change except some line broadening in the NMR spectrum. Anion (22), however, rearranged nearly quantitatively to a new anion, 2-methylcycloheptadienyllithium (24), after 280 hr of irradiation. The NMR spectrum of anion (24) after 160 hr is presented in Figure 27; some line broadening is evident, and anion (22) is still present in the mixture. The NMR parameters for anion (24) are presented in Figure 28.

The two irradiated anions were protonated and analyzed by VPC. Anion (23) gave the three expected protonation products, identified by their NMR spectra and by comparison of VPC data with authentic samples to be 6-methyl-1,4-cycloheptadiene, 6-methyl-1,3-cycloheptadiene, and 5-methyl-1,3-cycloheptadiene. Anion (24) also gave three protonation products. The first and third VPC components were not identified, but

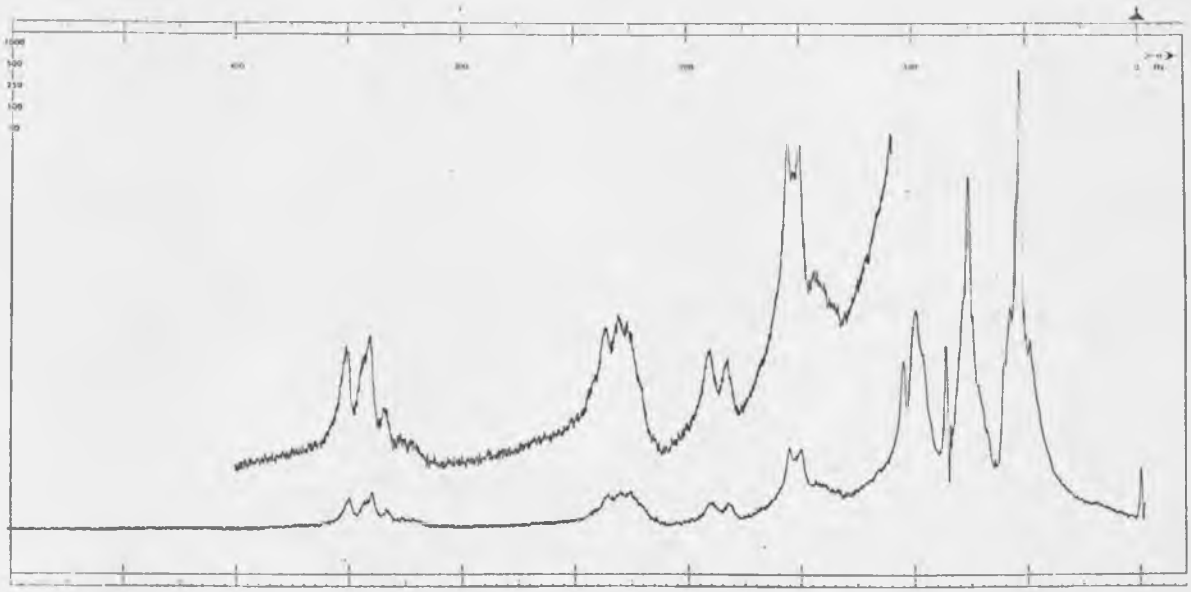
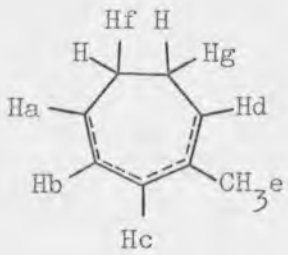


Figure 27. 60 MHz NMR spectrum of anions (22) and (24).

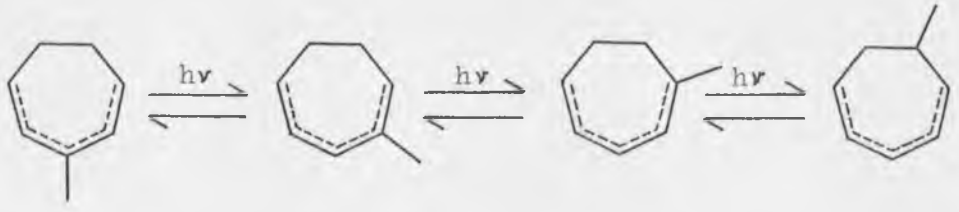


Chemical Shifts (τ)				Coupling Constants (Hz)			
Ha	6.22	He	8.35	Jab	10.0	Jdg	~6
Hb	4.32	Hf	~7.7	Jbc	7.5		
Hc	6.90	Hg	~7.7	Jce	<1.0		
Hd	6.15			Jde	<1.0		

Figure 28. NMR parameters for anion (24).

comparison of VPC data with an authentic sample demonstrated that neither was 3-methyl-1,4-cycloheptadiene. The second VPC component was identified as 2-methyl-1,3-cycloheptadiene by comparison of VPC retention times with an authentic sample. This diene is an expected protonation product of both anions (22) and (24). However, it was demonstrated that protonation of anion (22) reproducibly gives 2-methyl-1,3-cycloheptadiene and 3-methyl-1,4-cycloheptadiene in a 2:1 ratio; the observed absence of 2-methyl-1,3-cycloheptadiene in the mixture of protonation products of anion (24) is strong supporting evidence that anion (24) is indeed the rearrangement product, 2-methylcycloheptadienyllithium. This rearrangement provides supporting evidence that the observed positional isomerizations of pentadienyllithiums result from [1,6] sigmatropic hydrogen shifts.

Anions (22) and (23) were used in the irradiation study because of the possibility that both might rearrange to give the same equilibrium mixture of anions (22)-(25). Instead, anion (23) did not detectably



(22) (24) (25) (23)

react and anion (24), once formed, reacted no further. One possible conclusion is that anions (23) and (24) do not absorb enough at any of the incident wavelengths. A second possibility is that the activation energies for reaction of excited anions (23) and (24) are greater than

those for reaction of excited anions (22) and (25). Assuming anions (22)-(25) have about the same λ_{max} and assuming the energies of all the transition states involved in the proposed equilibrium are comparable, one might conclude that the apparent differences in activation energies are due to differences in the relative stabilities of the anions. Thus, the more stable anions would require more activation energy to undergo reaction, and this reasoning predicts that anions (23) and (24) are more stable than anions (22) and (25). This conclusion can be supported by noting that anions (23) and (24) are 2^{o}, 2^{o}, 2^{o}, whereas anion (22) is 2^{o}, 3^{o}, 2^{o} and anion (25) is 2^{o}, 2^{o}, 3^{o}.

Conclusions

Equilibrium has been demonstrated in two acyclic pentadienyllithium systems. Evidence has been presented which demonstrates that positional isomerizations of several pentadienyllithiums involve [1,6] sigmatropic hydrogen shifts. Consistent with Woodward-Hoffmann selection rules for such transformations, these hydrogen shifts have been shown to be intramolecular, to proceed thermally in an antarafacial manner, and, observed for the first time, to proceed photochemically in a suprafacial manner. Contrary to the statement by Klein et al. (1970), it has been demonstrated that a minimum number of 14 carbons in the pentadienyl anion chain is not necessary to observe these transformations.

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