Monohomocyclooctatetraene Anion Radical[1]

Frank J. Smentowski, Robert M. Owens, and Billy D. Faubion

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received September 12, 1967*

Abstract: The esr spectral parameters of monohomocyclooctatetraene anion radical (II) have been found to be relatively insensitive to changes in solvent, temperature, and counterion. The similar geometry of the anion radical II and the dianion V is noted. For the systems studied, the anion radical II is favored over its valence tautomer VI.

Recently, the anion radical of monohomocyclooctatetraene (II) has been prepared and coupling constants assigned.[2] The disparity between the two sets of coupling constants is striking. It is conceivable that proposed nonclassical structures[2a,3] for II and geometrically related molecules[3] might account for the reported discrepancies, these being attributed to differences in solvent, temperature, counterion, and mode of anion radical formation.[4] The coupling constants of classical hydrocarbon anion radicals vary little with changes in temperature, solvent, and counterion.[4a,5] Our investigation shows that the anion radical II is not exceptional in this respect. The coupling constants tabulated in this study show average deviations of only 2.78% when compared to those reported by Katz and Talcott[2b] and 27.22% when compared to those reported by Rieke, *et al.*[2a]

Experimental Section

Bicyclo[6.1.0]nona-2,4,6-triene (I)[6] was prepared by the addition of cyclooctatetraene dianion to methylene chloride. I was purified by vapor phase chromatography, mp 18°. After purification, the samples used for extensive investigation were shown to be greater than 99.9% pure by vpc analysis. Comparison of esr spectra obtained by reduction of both 99.9% pure and less highly purified substrate showed no spectral differences for the systems studied.

The anion radicals were prepared *in vacuo* by reduction of I with potassium or sodium metal mirrors or lithium metal in 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF) at −78°.[7]

The spectra were recorded using the X band of a Varian V-4502-15 esr spectrometer with a 12-in. magnet. Temperature was controlled within ±1° by a Varian V-4557 variable-temperature controller. A copper–constantan thermocouple was used to calibrate the variable-temperature controller.

The calculated spectra were obtained with a Cal. Comp. adaption to the IBM 7094 computer.

All spectra were simulated by a systematic variation of the coupling constants and line widths. The line width (of the individual hfs) was varied over a range of 100 mG by 10-mG increments around the experimental hfs line width.

The accuracy of our experimentally determined total line width for all systems was verified by enlarging the spectral wings.

That no significant error is imposed on our simulated spectra by assuming Gaussian rather than Lorentzian line shapes was shown in a control experiment by comparing spectra simulated under conditions which were identical except for the line shape. The hfs line width used in this control experiment was 130 mG (maximum hfs line width reported in this paper). These spectra were essentially identical.


I


II

Results and Discussion

Table I gives the sets of coupling constants assigned to II under various experimental conditions. The anion radical is assigned the structure II on the basis of HMO and SCF calculations[8] and by the experimental observation of large differences in the coupling constants at the 9 and 9′ positions, respectively (Table I). Figures 1a–f show the experimental and calculated spectra of the various monohomocyclooctatetraenide salts in DME. The calculated spectra utilizing these sets of coupling constants (columns 3, 4, and 5 of Table I) for the lithium and sodium salts of II reproduce the experimental spectra, giving excellent agreement regarding peak positions and line intensities. Similar results were obtained for the potassium salt of II at −30°. The less than exact fit for the potassium salt of II at −96° is due to line-width phenomena[9,10] arising from differences in the individual hyperfine line widths which are observable experimentally.

Confirmation of the assignment of the coupling constants of II was assured by a determination of the coupling constants of the dideuterio analog of II (IV). Alkali metal reduction (lithium, sodium, or potassium)

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[1] Temperature-Dependent Electron Spin Resonance Studies. III.

[2] (a) R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 4729 (1966); (b) T. J. Katz and C. Talcott, *ibid.*, **88**, 4732 (1966).

[3] (a) S. Winstein, E. C. Friedrich, R. Baker, and Y.-I. Lin, *Tetrahedron*, **22**, S621 (1966), and references therein; (b) M. Ogliaruso, R. Rieke, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 4731 (1966); (c) C. E. Keller and R. Pettit, *ibid.*, **88**, 604, 606 (1966).

[4] (a) A. H. Reddoch, *J. Chem. Phys.*, **43**, 225 (1965); (b) E. W. Stone and A. H. Maki, *ibid.*, **36**, 1944 (1962); (c) J. Q. Chambers and R. N. Adams, *Mol. Phys.*, **9**, 413 (1965); (d) N. Hirota, *J. Chem. Phys.*, **37**, 1884 (1962); (e) F. M. Millett and J. Harriman, *ibid.*, **44**, 1945 (1966).

[5] (a) H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi, and H. Takaki, *Mol. Phys.*, **9**, 153 (1965); (b) E. deBoer and C. MacLean, *J. Chem. Phys.*, **44**, 1334 (1966); (c) N. M. Atherton and S. I. Weissman, *J. Amer. Chem. Soc.*, **83**, 1330 (1961); (d) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964); (e) A. H. Reddoch, *ibid.*, **41**, 444 (1964).

[6] (a) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 5194 (1964); (b) E. Vogel, *Angew. Chem.*, **74**, 829 (1962); (c) E. Vogel, W. Widemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, 673 (1963).

[7] The over-all visual features of the spectra of the various systems studied in this paper indicate that the esr spectral parameters of the anion radical II produced from the reduction of I with lithium, sodium, or potassium are quite similar in nature under variations of temperature and/or solvent. Identical reasoning holds for the anion radical IV produced from III. The excellent agreement between the simulated and experimental spectra of Li^+II, Na^+II, Li^+IV, Na^+IV for the temperature range studied and K^+II at −30° using nearly identical coupling constants substantiates our belief that the esr spectral parameters of K^+II and K^+IV in the temperature range from −96 to −84° are not characterized by coupling constants differing significantly from those of the other systems studied. Simulated spectra using the coupling constants reported by Rieke, *et al.*,[2a] and an hfs line width near 0.12 G gave spectra in poor agreement with Figure 1c.

[8] F. J. Smentowski, B. D. Faubion, R. M. Owens, and L. R. Lizardi, to be published separately.

[9] G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967).

[10] A similar explanation is used for the inexact fit of the coupling constants of the analogous alkylcyclooctatetraene anion radicals (A. Carrington and P. F. Todd, *Mol. Phys.*, **7**, 533 (1964)).

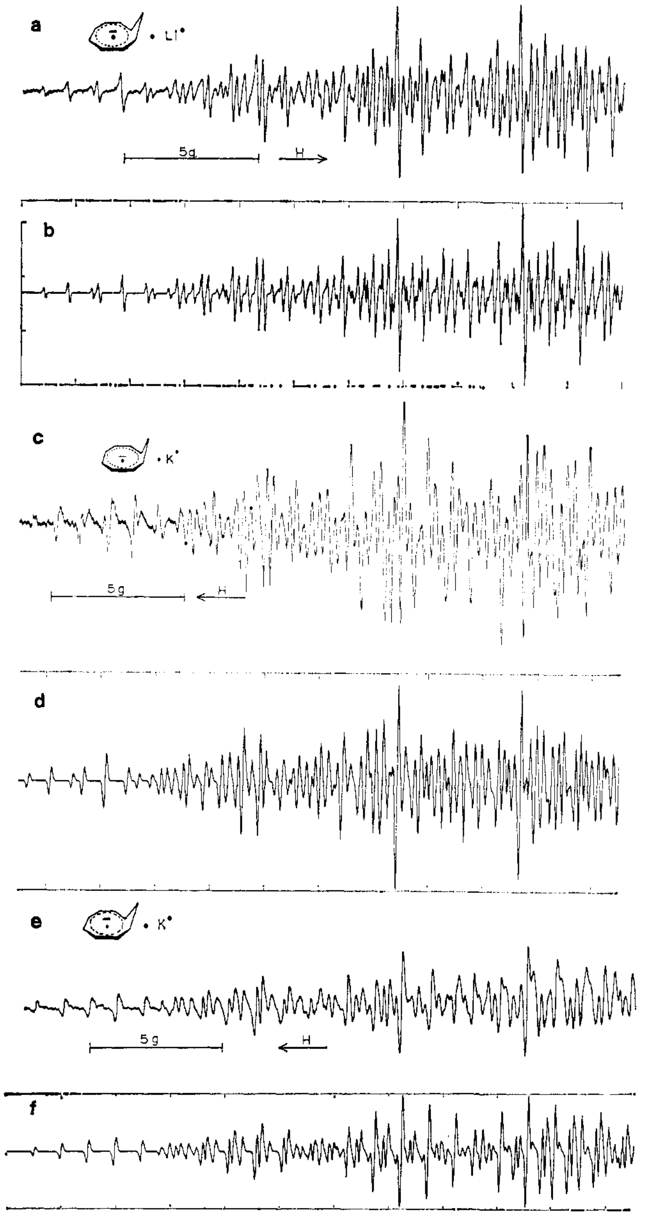


Figure 1. (a) Electron spin resonance spectrum of lithium monohomocyclooctatetraene anion radical in dimethoxyethane at −90°. (b) Computer-simulated spectrum of lithium monohomocyclooctatetraene anion radical utilizing the coupling constants found in column 3 of Table I, a 0.09-G line width, and a gaussian line shape. (c) Electron spin resonance spectrum of potassium monohomocyclooctatetraene anion radical in dimethoxyethane at −96°. (d) Computer-simulated spectrum of potassium monohomocyclooctatetraene anion radical utilizing the coupling constants found in column 4 of Table I, a 0.12-G line width, and a gaussian line shape. (e) Electron spin resonance spectrum of potassium monohomocyclooctatetraene anion radical in dimethoxyethane at −30°. (f) Computer-simulated spectrum of potassium monohomocyclooctatetraene anion radical utilizing the coupling constants found in column 5 of Table I, a 0.13-G line width, and a gaussian line shape. (In all cases, only one-half of the spectrum is shown.)

Table I. Esr Spectral Parameters of II

Position assignment[a]	No. of protons	Li^+II, Na^+II coupling constants a_i, G,[b,d,e] −90°	K^+II coupling constants a_i, G,[c,d,e] −96°	K^+II coupling constants a_i, G,[d,e] −30°
1,8	2	5.36 ± 0.05	5.87 ± 0.10	5.53 ± 0.05
2,7	2	0.92 ± 0.05	0.84 ± 0.10	1.02 ± 0.05
3,6	2	5.13 ± 0.05	5.26 ± 0.10	5.11 ± 0.05
4,5	2	2.08 ± 0.05	2.11 ± 0.10	2.04 ± 0.05
9	1	4.78 ± 0.05	4.71 ± 0.10	4.81 ± 0.05
9	1	12.24 ± 0.05	12.22 ± 0.10	12.93 ± 0.05

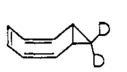
[a] Based on HMO and SCF calculations. [b] The coupling constants for the lithium and sodium salts are identical; *i.e.*: the coupling constants for these salts are within the ranges reported and remain so from −130 to −30° for Li^+II and Na^+II, and from −130 to −60° for Li^+IV and Na^+IV. [c] The coupling constants for the potassium salts are within the ranges reported from −130 to −85° for K^+II and K^+IV. [d] The coupling constants are within the ranges reported in tetrahydrofuran, dimethoxyethane, or mixtures of these two solvents. [e] No metal splitting is observed for the three counterions in the temperature ranges studied from −130 to −30° for Li^+II and Na^+II, from −130 to −60° for Li^+IV and Na^+IV, from −130 to +40° for K^+II, and from −130 to −85° for K^+IV.

Table II. Esr Spectral Parameters of IV

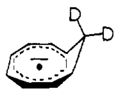
Position assignment[a]	No. of protons	Li^+IV, Na^+IV coupling constants a_i, G,[b,d,e] −90°	K^+IV coupling constants a_i, G,[c,d,e] −96°
1,8	2	5.37 ± 0.05	5.89 ± 0.10
2,7	2	0.92 ± 0.05	0.85 ± 0.10
3,6	2	5.13 ± 0.05	5.26 ± 0.10
4,5	2	2.08 ± 0.05	2.11 ± 0.10
9	1	0.74 ± 0.05	0.73 ± 0.10
9	1	1.92 ± 0.05	1.88 ± 0.10

[a–e] See corresponding footnotes in Table I.

of bicyclo[6.1.0]nona-2,4,6-triene-9,9′-d_2 (III)[11] in DME and THF at −78° gave the anion radical IV. Figures 2–5 show the experimental and calculated spectra of the various salts of IV in DME utilizing the coupling constants in columns 3 and 4 of Table II. The values for the coupling constants of the 9 and 9′ positions were determined from the relation $a_D = 2a_H/13$ and adjustment of these values to give the best spectral fit. The experimental and calculated spectra for the lithium and sodium salts of IV show excellent agreement regarding line positions and intensities. The less than exact fit of the calculated and experimental spectra for the potassium salt of IV at −96° is due to line width phenomena, as noted above for the potassium salt of II.[9,10]



III



IV

A measure of the constancy of the tabulated coupling constants for the parameters studied is obtained by examination of the experimental ratio, $a_9/a_{9'}$, for the various systems studied. The experimental $a_9/a_{9'}$ ratios are: 2.56 for the lithium and sodium salts of II, 2.59 for the lithium and sodium salts of IV, 2.59 for the potassium salt of II at −96°, 2.59 for the potassium salt of IV at −96°, and 2.69 for the potassium salt of II at −30°. These ratios show excellent agreement with the $a_9/a_{9'}$ ratio of 2.50 for II generated electrolytically in liquid ammonia.[2b]

Temperature-dependent studies of II in either THF or DME showed no dramatic changes in spectral parameters for the systems studied. The coupling constants for the lithium and sodium salts of II remained well

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[11] We gratefully acknowledge the receipt of the samples of III from Professor S. Winstein.

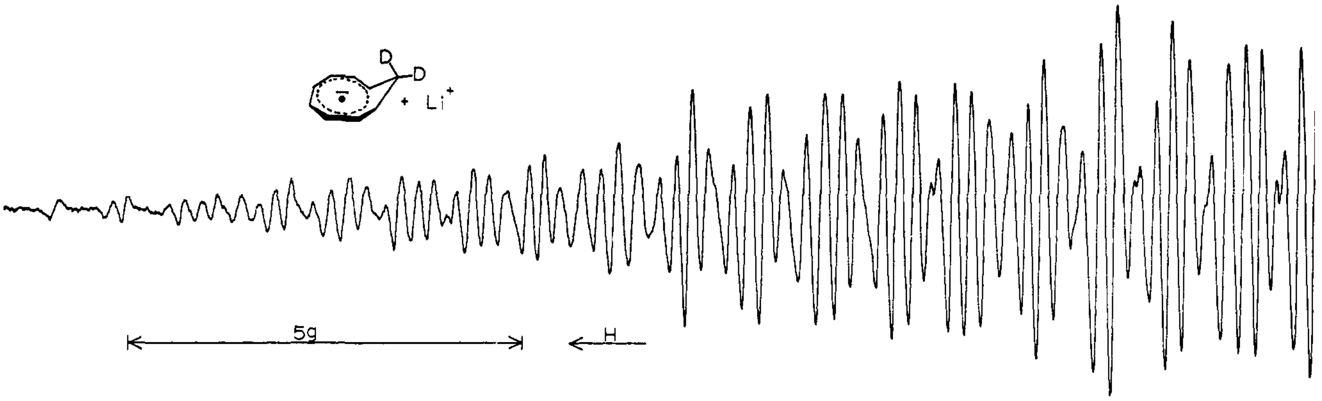

Figure 2. Electron spin resonance spectrum of lithium monohomocyclooctatetraene-9,9′-d_2 anion radical in dimethoxyethane at −90°. (Only one-half of the spectrum is shown.)

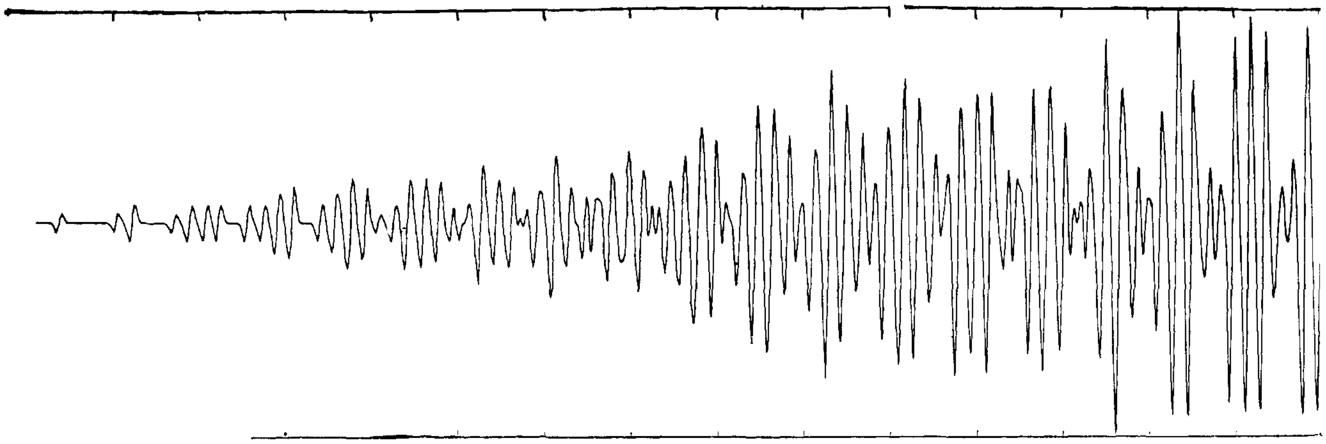

Figure 3. Computer-simulated spectrum of lithium monohomocyclooctatetraene-9,9′-d_2 anion radical utilizing the coupling constants found in column 3 of Table II, a 0.08-G line width, and a gaussian line shape. (Only one-half of the spectrum is shown.)

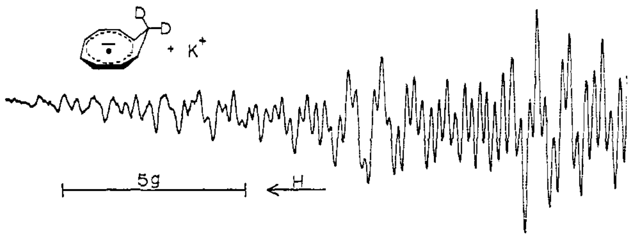

Figure 4. Electron spin resonance spectrum of potassium monohomocyclooctatetraene-9,9′-d_2 anion radical in dimethoxyethane at −96°. (Only one-half of the spectrum is shown.)

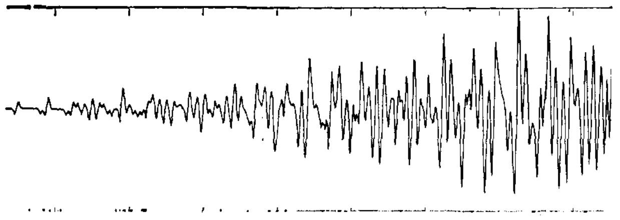

Figure 5. Computer-simulated spectrum of potassium monohomocyclooctatetraene-9,9-d_2 anion radical utilizing the coupling constants found in column 4 of Table II, a 0.12-G line width, and a gaussian line shape. (Only one-half of the spectrum is shown.)

within the limits reported in Table I over a temperature range from −130 to −30°. However, for the potassium salt of II, there is some variation of the coupling constants with temperature, particularly at 9,9′ and 1 and 8 positions (Table I). Above −30°, the lithium and sodium salts of II undergo rapid decomposition to diamagnetic products. The potassium salt of II shows somewhat greater thermal stability and its spectrum can be recorded up to +40° before appreciable decomposition occurs.

For anion radicals having metal splitting due to an associated metal cation, this a_M is usually linear and/or strongly dependent upon the temperature.[5b,12] The absence of this temperature-dependent behavior for the coupling constants of II argues against any form of metal splitting in the systems studied.

A final experiment, paralleling an analogous experiment with cyclooctatetraene,[13] demonstrates the similar geometry of II and the monohomocyclooctatetraene dianion, V.[3b] Upon treatment of a 0.1 *M* sample of I in DME with successive amounts of potassium metal at −78° and recording the spectrum of II after each successive addition, the line widths of all the individual hyperfine splittings were seen to broaden from an initial value of 0.120 G. This phenomena continued until precipitation of the dianion V was visually evident. Further addition of potassium to the system failed to increase the hyperfine line widths and the sample slowly

[12] (a) N. Hirota, *J. Phys. Chem.*, 71, 127 (1967); (b) J. dos Santos-Veiga and A. F. Neiva-Correia, *Mol. Phys.*, 9, 395 (1965); (c) N. M. Atherton and A. E. Goggins, *Trans. Faraday Soc.*, 62, 1702 (1966).

[13] T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, 32, 1873 (1960).

became diamagnetic as 2 mol of potassium was added. Similar results were obtained in samples of 0.01 and 0.005 *M* in I without concomitant precipitation of V. The lithium and sodium reductions of I behaved similarly.


V


VI

Alkali metal reduction of I gives the anion radical II whose esr spectral parameters are relatively insensitive to changes in experimental conditions. Likewise, no appearance of new lines or disappearance of old lines is noted for II for the systems studied. Thus, the presence of a valence tautomer anion radical such as VI cannot be detected, and the anion radical II having more extensive delocalization is favored.[14]

Acknowledgments. The authors are indebted to Professors S. Winstein and R. M. Hedges for helpful discussion. We are indebted to Mr. T. Atkinson for calibration spectra. The esr spectrometer was made available by National Science Foundation Grant GP-3767. Support from the Robert A. Welch Foundation and The Research Council of Texas A&M University are gratefully acknowledged. We also acknowledge the computer facilities made available by the Data Processing Center of Texas A&M University.

(14) NOTE ADDED IN PROOF. Methylcyclooctatetraene anion radical (VII) is observed during the electrolytic reduction of I in liquid ammonia[2b] and during the alkali metal reduction of I in liquid ammonia (R. M. Owens, unpublished results). For the systems I-DME-M and I-THF-M for M = Li, Na, K over the temperature range −130 to +30°, VII is not observed, either alone or concurrently with anion radical II.

Photolyses of Trienes. II. Selective Photoreactions of 2,7,7-Trimethylcycloheptatriene[1]

Lee B. Jones and Vera K. Jones

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721. *Received September 18, 1967*

Abstract: Irradiation of a benzene or cyclohexane solution of 2,7,7-trimethylcycloheptatriene (**1**) in a Pyrex tube with a Hanovia medium-pressure mercury arc lamp yields a mixture containing 2,2,4-trimethylbicyclo[3.2.0]hepta-3,6-diene (**5**), 1,3,7-trimethylcycloheptatriene (**4**), 1,5,7-trimethylcycloheptatriene (**3**), and recovered starting material. Compounds **4** and **5** are primary photoproducts while **3** arises from further irradiation of **4**. The new trienes arise from highly selective [1,7] sigmatropic methyl and hydrogen migrations, and the bicyclic product arises from a selective electrocyclization reaction. The origin of these highly selective transformations and sensitization studies of these reactions are discussed.

Photoisomerization reactions of a number of cycloheptatrienes have been investigated. Irradiation of cycloheptatriene in solution[2] gives bicyclo[3.2.0]-hepta-2,6-diene as the major product, while the gas phase reaction[3] yields predominantly toluene. Photochemical studies of certain substituted cycloheptatrienes have shown highly selective [1,7] sigmatropic hydrogen migrations.[4–6] Examples of methyl migrations have also been reported[1,7] in studies involving methyl-substituted cycloheptatrienes.

As a continuation of our study of the photoisomerization reactions of cyclic conjugated trienes,[1] we now wish to report the results of a study of the photolysis of 2,7,7-trimethylcycloheptatriene (**1**). As was demonstrated by the photolysis of 3,7,7-trimethylcycloheptatriene (**2**),[1] the methyl group situated at carbon atom 3 in **2** exerts a strong directive influence on the course of both the methyl migration and electrocyclization reactions. It seemed of interest to determine the effect of a methyl group at position 2 on the course of reaction under photolytic conditions and to compare the results with those previously observed[1] for the photolysis of **2**.

2,7,7-Trimethylcycloheptatriene (**1**) has been identified as one of the products of the gas phase pyrolysis of 3,7,7-trimethylcycloheptatriene (**2**).[8] Because of the complexity of this reaction, the pyrolysis did not appear to be a convenient method for the synthesis of **1**. We therefore prepared 2,7,7-trimethylcycloheptatriene (**1**) by the lithium aluminum hydride reduction of 3,3,5-trimethylcycloheptadien-1-one, prepared as described by Büchi and Burgess,[9] followed by acid-catalyzed dehydration.

Our investigation[1] of the photolysis of **2** demonstrated that a new triene, 1,5,7-trimethylcycloheptatriene (**3**), arose from a selective [1,7] sigmatropic methyl migration, and that a second triene, 1,3,7-trimethylcycloheptatriene (**4**), arose from a selective [1,7] sigmatropic hydrogen migration. In addition, 2,2,6-trimethylbicyclo[3.2.0]hepta-3,6-diene was formed as a result of a selective electrocyclization reaction.

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(1) For Part I see: L. B. Jones and V. K. Jones, *J. Am. Chem. Soc.*, **89**, 1880 (1967).

(2) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

(3) R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 3432 (1962).

(4) A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 241 (1965).

(5) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **88**, 3527 (1966).

(6) G. W. Borden, O. L. Chapman, R. Swindell, and T. Tezuka, *ibid.*, **89**, 2979 (1967).

(7) O. L. Chapman and S. L. Smith, *J. Org. Chem.*, **27**, 2291 (1962).

(8) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **88**, 2494 (1966).

(9) G. Büchi and E. M. Burgess, *ibid.*, **82**, 433 (1960).