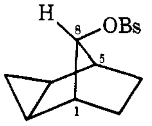
5 × 10¹² times faster. This suggests that the appropriately situated cyclopropyl group can provide anchimeric assistance in the form of a rate acceleration *much greater than 10¹³.* Presumably, this is due to the formation of an ion represented by **17**.[13]



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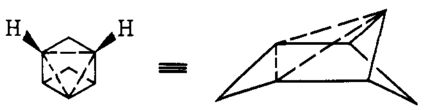
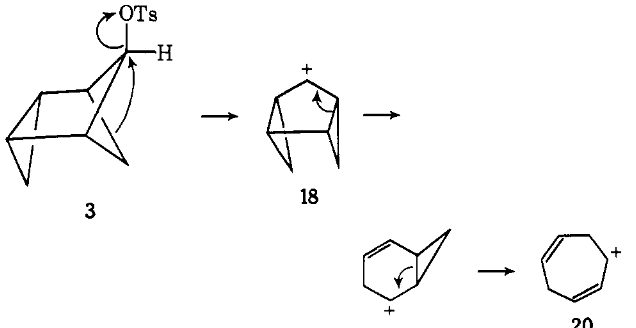


17

Comparison of the rates of solvolysis of **3** and **13** indicates that the cyclopropyl group of **3** shows only a slight rate-retarding inductive effect. Both the rate and products obtained from **3** indicate that the major influence is the rearrangement of the four-membered ring, presumably to yield **18**, followed by opening of **18** to give **19**, and partial opening of **19** to give **20**. The intermediacy of **19** would account for the formation of **10**, while **20** would serve as a precursor of **8** and **9**.



3 **18** **19** **20**

Acknowledgment. We are indebted to the National Science Foundation for a grant in partial support of this study.

(13) For a detailed discussion of this ion, generated from a different precursor see ref 5.

(14) Goodyear Research Fellow, 1971–1972.

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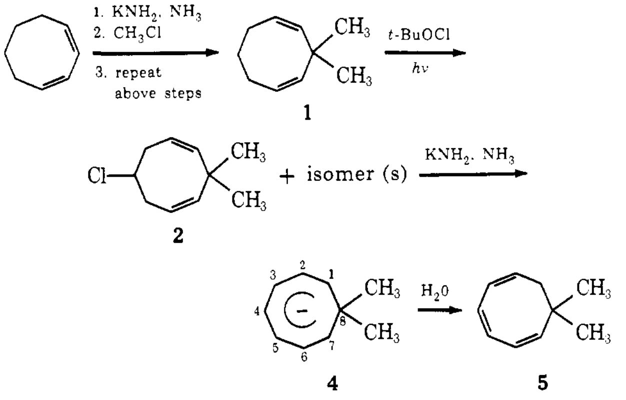
The 8,8-Dimethylcyclooctatrienyl Anion

Sir:

A great deal of progress has been made in recent years in the study of homoconjugation, and, in particular, in the preparation of homoaromatic species.[1] In contrast, only a few potentially antihomoaromatic species (all of which are carbocations) have been prepared.[2] We now report the preparation and direct observation of the title anion, a potentially antihomoaromatic 8π-electron analog of the homotropylium cation.[3]

The (potassium) cyclooctatrienyl anion cannot be observed in liquid ammonia since it is apparently thermodynamically unstable and rapidly disproportionates to 1,3,5-cyclooctatriene and the cyclooctatetraene dianion.[4] This problem is eliminated in the case of the 8,8-dimethylcyclooctatrienyl anion, the synthesis of which is given in Scheme I. The key step is the direct introduction of geminate methyl groups onto 1,3-cyclooctadiene by the methylation of cyclooctadienyl anions in a strongly basic medium. This reaction, in which 3-methyl-1,4-cyclooctadiene is an intermediate, is made possible by the fact that cyclooctadienyl anions are preferentially alkylated at C_3 rather than C_1,[5] and it occurs in 12–17% overall isolated yield.

Scheme I



Diene **1**[6] could be chlorinated with *tert*-butyl hypochlorite in 18% isolated yield (at low conversion) to afford a product mixture consisting predominantly of two monochlorides in a 55:45 ratio which could be separated by glpc only with difficulty. The major component was readily identified as 7-chloro-3,3-dimethyl-1,4-cyclooctadiene (**2**),[7] whereas the complex nmr spectrum of the minor isomer appears to be consistent with the structure of 6-chloro-3,3-dimethyl-1,4-cyclooctadiene (**3**).[8]

Treatment of a mixture of chlorides **2** and **3** with potassium amide in liquid ammonia produced a dark-red solution of anion **4** whose nmr spectrum (obtained at −55° with trimethylamine as internal standard) cleanly displayed a doublet of doublets at δ_{TMS} 5.43 (H_2 and H_6, J_{12} = 12.4 Hz, J_{23} = 9.0 Hz), a triplet at 5.21 (H_4, J_{34} = 11.0 Hz), an asymmetric doublet at 4.58 (H_1 and H_7, J_{12} = 12.4 Hz), a doublet of doublets at 3.56 (H_3 and H_5, J_{23} = 9.0 Hz, J_{34} = 11.0 Hz), and a sharp singlet at 1.41 (methyl protons) which remained sharp down to −77° in ammonia-d_3.[9] The nmr spectrum of the cesium salt of **4** was very similar to that of

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(1) Reviews: (a) S. Winstein, *Chem. Soc., Spec. Publ.*, **No. 21**, 5 (1967); (b) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969); (c) P. R. Story and B. C. Clark, Jr., in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1972, p 1007.

(2) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 7785 (1969), and references cited therein.

(3) (a) J. L. v. Rosenburg, Jr., J. E. Mahler, and R. Pettit, *ibid.*, **84**, 2842 (1962); (b) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970), and references cited.

(4) H. Kloosterziel and E. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **88**, 1373 (1969).

(5) F. L. Wiseman, Jr., Ph.D. Thesis, University of Maryland, 1970.

(6) Nmr (CCl_4): δ 4.64 (d, H_2 and H_4, J = 11.5 Hz), 5.10 (t of d, H_1 and H_5, $J_{1,8}$ = 8.2 Hz), 2.23 (t of d, 4 H, H_6 and H_8, J_{67} = 6.7 Hz) 1.48–1.12 (m, 2 H, H_7), and 1.08 (s, 6 H, methyl); uv (hexane) end absorption ($\epsilon_{220\ \mathrm{nm}}$ 106).

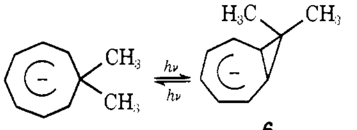
(7) Nmr (CCl_4): AB system at δ 5.67 (d, H_2 and H_4, J_{12} = 11.8 Hz) and 5.67 (t of d, H_1 and H_5, $J_{1,8a}$ = 8.6 Hz, $J_{1,8b}$ = 7.4 Hz), t of t at 3.97 (H_7, $J_{6a,7}$ = 6.5 Hz, $J_{6b,7}$ = 5.3 Hz), two d of d at 2.66 and 2.63 (H_{6a} (H_{8a}) and H_{6b} (H_{8b}), respectively), and two s at 1.14 and 1.11 (methyl).

(8) Nmr (CCl_4): multiplets at δ 4.7–5.8 (5 H) and 1.3–3.0 (4 H) and a six-proton singlet at 1.13. A mixture of **2** and **3** gave a correct analysis for $C_{10}H_{15}Cl$.

(9) I. Melczynski, *Angew. Chem.*, 74, 32 (1962). We thank Dr. John Morrison for assistance with this preparation.

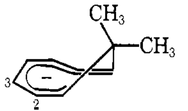
the potassium salt. Solutions of anion **4** were stable at room temperature for at least 2 hr and, when kept at low temperature and quenched into pentane–water, produced (in low yield) a mixture containing 6,6-dimethyl-1,3,5-cyclooctatriene (**5**) as the major (97%) component.[10]

Of particular interest is the observation that **4** is also produced by disrotatory opening upon photolysis[11] of the (potassium) 8,8-dimethylbicyclo[5.1.0]octadienyl anion[12] (**6**) in liquid ammonia. A photoequilibrium appeared to be established since the ratio of the nmr signals for **4** and **6** remained constant at *ca.* 1:3 on prolonged irradiation. This was confirmed by the observation that the same solution of **4** and **6** is produced by irradiation of **4** (in ammonia-d_3). This is the first example of a reversible photochemical electrocyclization of a carbanion and is also the first case in which both reactant and product have been directly observed in a photochemical electrocyclization of a carbanion.[13]

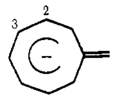


4 **6**

Whereas minimization of antibonding interactions between the π orbitals at C_1 and C_7 may be best achieved in a planar conformation of **4**,[14] this will introduce bond angle strain which might be more detrimental energetically than any increase in antihomoaromaticity expected in a folded conformation (**7**).[15] The observation of a six-proton singlet for the methyl protons at $-77°$ is compatible with either a planar conformation or a rapidly flipping folded conformation where $\Delta G^{\ddagger}$ is estimated to be <10 kcal/mol.[16] However, the fact that J_{23} in **4** (9.0 Hz) is significantly smaller than J_{23} in the methylenecyclooctatrienyl anion **8** (10.5 Hz),[17] despite the near identity of the corresponding self-consistent HMO π-bond orders (0.55 and 0.57, respectively), suggests that the former anion may be folded, as in **7**. Finally, although the signals for H_1 and H_7 appear at a lower field than usual for protons on negatively charged carbons, the question of whether **4** displays any "antihomoaromatic" behavior cannot be answered without detailed reference to appropriate model compounds.



7



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Acknowledgment. We are pleased to acknowledge the support of this work by the National Science Foundation.

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[10] Nmr (CCl_4): three two-proton multiplets centered at δ 6.02, 5.72, and 5.45 (olefinic), a multiplet at 2.23 (2 H, methylene), and a singlet at 1.05 (6 H, methyl); uv (hexane) λ_{max} 261 nm (ϵ 3850).

[11] A 0.1 *M* solution of **6** was irradiated through Pyrex with a 275-W GE sunlamp.

[12] Anion **6** was prepared by reaction of potassium amide in liquid ammonia with 8,8-dimethylbicyclo[5.1.0]octa-2,4-diene. The latter was prepared from 8,8-dibromobicyclo[5.1.0]octa-2,4-diene (from an extension of the procedure of A. P. ter Borg and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **80**, 1217 (1961)) by methylation with lithium dimethylcopper (E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967)).

[13] H. Kloosterziel and G. M. Gorter-la Roy (*J. Chem. Soc., Chem. Commun.*, 352 (1972)) have postulated the intermediacy of the cyclooctatrienyl anion in the photochemical conversion of the (potassium) bicyclo[5.1.0]octadienyl anion to the cyclooctatetraene dianion in liquid ammonia.

[14] M. Feldman and W. C. Flythe, *J. Amer. Chem. Soc.*, **93**, 1547 (1971).

[15] Cyclononatrienyl anions have recently been shown to be significantly bent; S. W. Staley and N. J. Pearl, manuscript submitted for publication.

[16] This value of $\Delta G^{\ddagger}$ was calculated by assuming a difference of 0.65 ppm in the chemical shifts of the methyl groups in the hypothetical conformation **7**. This is the chemical-shift difference for the methyl protons in **6** and is probably a high estimate. (See F. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, Chapter VII.)

[17] S. W. Staley and G. M. Cramer, manuscript submitted for publication.

Structural Study of a Ruthenium Hydride Cluster by Nematic-Phase Proton Magnetic Resonance

Sir:

The difficulties in establishing hydride proton positions in transition metal hydrides are well known.[1] We wish to report the structural information obtained from a study of the proton magnetic resonance of the recently synthesized[2] compound $H_3Ru_3(CO)_9CCH_3$ (I) dissolved in the nematic phase of a liquid crystal.

Several spectra of width 5000 Hz were obtained on a Varian XL-100-15 spectrometer in Fourier-transform mode at probe temperature (37°) using a saturated solution of I in the Vari-Light liquid crystal VL-3268-N (less than 10 mg of solute/0.5 ml of solvent). The 5-mm sample tube was placed coaxially inside a 12-mm tube (nonspinning) containing D_2O as a heteronuclear lock. Resultant line widths at half-height were approximately 10 Hz.

Assuming I has C_{3v} symmetry (Figure 1), as deduced by Canty, *et al.*,[2] only one orientation parameter S_{zz} is required to characterize its orientation.[3] The nearly first-order spectra display the expected two groups of triplets of quartets (Figure 2). The dipolar couplings T_{ij}, defined by

$$T_{ij} = -\frac{\hbar\gamma_i\gamma_j}{2\pi r_{ij}^3}(3\cos^2\beta_{ij} - 1)S_{zz} \qquad (1)$$

where r_{ij} is the distance between nuclei i and j, γ_i and γ_j are magnetogyric ratios, and β_{ij} is the angle between the internuclear vector and the z axis (the symmetry axis), were obtained from a modified version of the LAOCOON2 nmr program.[4] This program iterates on dipolar couplings and chemical shifts to give the best agreement with weighted experimental frequencies and calculates the corresponding uncertainties in the computed dipolar couplings. The best fit values are given in Table I. Indirect couplings between methyl protons and hydride protons were taken to be zero,[2] and the indirect couplings between fully equivalent nuclei

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[1] B. A. Frenz and J. A. Ibers, "The Hydrogen Series," Vol. 1, "Transition Metal Hydrides," Marcel Dekker, New York, N. Y., 1971, p 33.

[2] A. J. Canty, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 1331 (1972).

[3] A. D. Buckingham and K. A. McLauchlan, *Progr. Nucl. Magn. Res. Spectrosc.*, **2**, 63 (1967).

[4] D. Bailey, A. D. Buckingham, M. C. McIvor, and A. J. Rest, *Mol. Phys.*, **25**, 479 (1973).