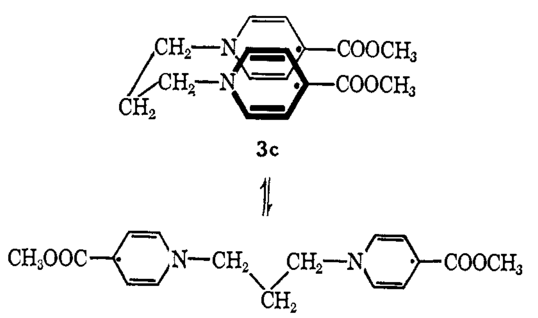

3c

30

These findings extend our knowledge of the behavior of diradicals and of the phenomenon of radical–radical association to diradical dimers.[3-10]

Acknowledgment. The authors are grateful to Dr. P. C. Huang for the preparation of the pyridinium diiodides and to the National Institutes of Health, the National Science Foundation, the Army Research Office (Durham), and the Research Laboratories, Edgewood Arsenal (through Contract DA 18-035-AMC-138(A)), for support.

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(7) K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

(8) E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, **86**, 5524 (1964).

(9) N. Hirota and S. I. Weissman, *ibid.*, **86**, 2538 (1964).

(10) R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965).

(11) On leave from the Faculty of Pharmaceutical Sciences, The University of Tokyo, Hongo, Tokyo, Japan.

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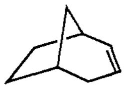
Direct Observation of a Homoaromatic Bishomocyclopentadienide Anion[1]

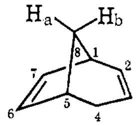
Sir:

Bicyclooctadiene II has been reported by Brown and Occolowitz[2] to be more reactive than monoene I in allylic proton–deuterium exchange by a factor of $10^{4.5}$ in DMSO-KOBu-*t* at 50°. This increased reactivity of the diene was ascribed to the presence of the additional olefinic group in II, and the possible formulation of the intermediate anion as a bishomocyclopentadienide species III was suggested. The reported exchange involved only allylic protons, and no formation of isomeric tricyclic and tetracyclic hydrocarbons IV and V from the diene II was observed.

HMO calculations do in fact predict a bonding interaction between allylic anion and olefinic systems in a carbanion such as IIIa. Such interaction is predicted to be quite appreciable[3] even for (β_{27}/β_0) equal to 0.3, and it is specifically allowed for by the 1,3-bishomocyclopentadienide[4] description III. The charge distribution in such an ion depends, of course, on the molecular geometry and the relative importance of the different atomic orbital overlaps.[3] One may visualize protonation at the different carbanionic centers of III, C_2 or C_4 to yield bicyclic diene II, C_6 or C_7 to yield tricyclic IV, and C_8 to give tetracyclic V. One may in fact anticipate the possibility of base-catalyzed equilibration of II, IV, and V, and such is indeed observed[4c,5a] in Streitwieser's catalyst–solvent system,[5b] $CsNHC_6H_{11}$ in $C_6H_{11}NH_2$, which gives much greater equilibration (and exchange) rates than does the KOBu-*t*–DMSO system. We are now able to report the direct observation of anion III and its behavior in protonation since relatively stable solutions of anion III in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) may be prepared by the classical ether cleavage method[6a] using the reaction between Na–K alloy and *exo*-4-methoxybicyclo[3.2.1]octadiene-2,6 (VII-OMe).[7]



I



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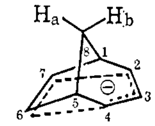

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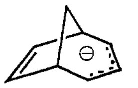
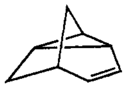
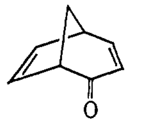


IIIa

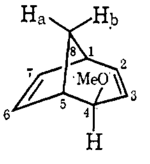


IV

V



VI



VII·MeO

Ether VII-OMe was prepared by methylation of the corresponding *exo* alcohol[7] VII-OH, mp 45–48°, *p*-nitrobenzoate[7] mp 79–81°. Alcohol VII-OH was obtained along with its *endo* epimer,[7] *p*-nitrobenzoate[7] mp 72–72.5°, by various reductions of the corresponding ketone[8a] VI; it was also obtained by saponification of the benzoate ester from *t*-butyl perbenzoate oxidation of diene II. The nmr spectrum of VII-OMe as well as that of diene[8b] is summarized in Table I.

On shaking in THF or DME with Na–K alloy at *ca.* 0°, VII-OMe reacts quite rapidly to generate the bicyclooctadienide salt.[6b,c] This reaction was carried out in an evacuated apparatus which permitted filtration to remove excess alloy and methoxide salt and collection and concentration of the carbanion solution in an nmr tube. The resulting orange carbanion solutions are only very faintly contaminated, *e.g.*, with diene II, and are stable for many hours. One of the signals in the nmr spectrum of III is obscured by a solvent

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(1) (a) Research supported in part by the U. S. Army Research Office (Durham); (b) research supported in part by the National Science Foundation; (c) acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 376 (1965).

(3) Simple HMO calculations give values of $E_\pi - 6\alpha$ of $4.828\beta_0$, $5.032\beta_0$, $5.346\beta_0$, and $5.862\beta_0$ for β_{27}/β_0 values of 0, 0.3, 0.5, and 0.75, respectively. The corresponding negative charges at $C_{2,4}$:$C_{6,7}$:C_8 are 0.426:0.064:0.021, 0.346:0.126:0.056, and 0.263:0.177:0.120 for β_{27}/β_0 values of 0.3, 0.5, and 0.75, respectively.

(4) (a) S. Winstein, *J. Am. Chem. Soc.*, **81**, 6524 (1959); S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3244 (1961); (c) S. Winstein, Chemical Society International Symposium on Aromaticity, Sheffield, England, July 6–8, 1966; Special Publication No. 21, The Chemical Society, London, 1967.

(5) (a) J. M. Nicholson, unpublished work; (b) A. Streitwieser, Jr., and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963).

(6) (a) K. Ziegler and B. Schnell, *Ann.*, **437**, 227 (1924). (b) Attempts to generate anion III by reaction of Na or Na-K alloy with diene II or tricyclic bromide[4c] in THF were not very successful. (c) J. M. Brown (private communication) has also employed this method to generate III.

(7) New compounds gave satisfactory carbon and hydrogen analyses. Configurations assigned on the basis of the usual nmr and chemical criteria.

(8) (a) P. K. Freeman and D. G. Kuper, *Chem. Ind.* (London), 424 (1965); (b) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).

Table I. Summary of Nmr Data

Proton	Chemical shifts,[a] τ II[b,e] in THF	VII-OMe in DME	III[f] in THF-d_8	III in DME
$H_{1,5}$	7.43	7.26	7.55	7.51
H_2	4.08	3.90	7.16	7.18
H_4	7.83[c] 8.21[d]	~6.7	7.16	7.18
H_3	4.85	4.72	4.61	4.65
H_6	4.35	4.18	6.33	
H_7	3.82	3.57	6.33	
H_{8a}	8.10	8.2	9.13	9.16
H_{8b}	8.34		9.58	9.58

[a] Relative to τ 6.40 and 8.25 signals for THF or τ 6.58 and 6.75 signals for DME. [b] Based partly on 60- and 100-Mc spectra of neat II and II-2,4,4-d_3. [c] *exo*. [d] *endo*. [e] $J_{2,3} = 10$ cps; $J_{8a,8b} = 9$ cps; $J_{6,7} = 5.6$ cps; $J_{1,8a} = J_{5,8a} = 4$ cps; $J_{1,7} = 2.8$ cps; $J_{5,6} = 2.6$ cps; $J_{3,4}$-*exo*, $J_{3,4}$-*endo*, $J_{1,8b}$, $J_{5,8b}$ all <2 cps. [f] $J_{8a,8b} = 8$ cps; $J_{2,3} = 6.7$ cps; $J_{1,2} = 5.3$ cps; $J_{1,8a} = 4$ cps; $J_{1,7}$, $J_{1,8b}$ both <2 cps.

signal in ordinary THF or DME, but this difficulty is largely avoided in THF-d_8 (Table I and Figure 1).

In the nmr spectrum of the anion III the signal for vinylic protons $H_{2,4}$ appears as a triplet at τ 7.16, shifted upfield by 3.1 ppm relative to H_2 in diene II. The signal for $H_{6,7}$ appears as a singlet at τ 6.33, upfield by an average of 2.3 ppm relative to H_6 and H_7 in II. On the other hand, the signal for H_3 appears as a triplet at τ 4.62, actually slightly downfield (*ca.* 0.2 ppm) from H_3 in II. For the bridgehead protons $H_{1,5}$ in the anion, the signal appears as a skewed triplet at τ 7.55, nearly the same position as in II (τ 7.43). The signals for the H_8 protons appear as a multiplet at τ 9.12 for H_{8a} and a doublet at τ 9.58 for H_{8b}, an average of 1.1 ppm upfield relative to the values for $H_{8a,b}$ in II.

All the features of the nmr spectrum of the anion are very much in accord with a delocalized bishomocyclopentadienide structure III with an appreciable aromatic ring current. Very striking is the relatively large upfield shift of the $H_{6,7}$ signal on going from II to III, in contrast with the negligible effect on the bridgehead 1,5 protons. The upfield shift of the $H_{6,7}$ signal by an amount *ca.* two-thirds as large as that for $H_{2,4}$ indicates the substantial delocalization of negative charge to C_6 and C_7. The chemical shifts of the $H_{2,4}$, $H_{6,7}$, and H_3 protons relative to the values in II, namely 3.1, 2.3, and −0.2 ppm, respectively, are in just the $C_{2,4} > C_{6,7} > C_3$ order for the predicted[3] charge distribution in anion III. The slight negative shift for H_3 relative to H_3 in II can be ascribed to the fact that the appreciable deshielding due to the aromatic ring current more than offsets the shielding effect of the negative charge at C_3, the very atom expected[3] to bear the least negative charge. The substantial shielding of the H_8 protons in III relative to II by 1.1 ppm may also be ascribed at least partly to a ring-current effect.[9]

Quenching of the carbanion III solutions in CH_3OH or CH_3OD produces essentially quantitatively the diene II containing <0.5% of tricyclic hydrocarbon IV or tetracyclic V. The identity of the diene from the CH_3OH quench was confirmed by vpc and by the nmr spectrum of the recovered material. The data show that kinetic control in the protonation of III favors $C_{2,4}$ very strongly.[10] As regards possible stereospecificity of the protonation, the nmr spectrum of the diene II recovered from the CH_3OD quench shows the presence of both *exo*- and *endo*-4-D in comparable amounts. Thus, no appreciable stereospecificity is evident in protonation of III, as was also indicated by the behavior of diene II in the deuterium exchange study.[5a]

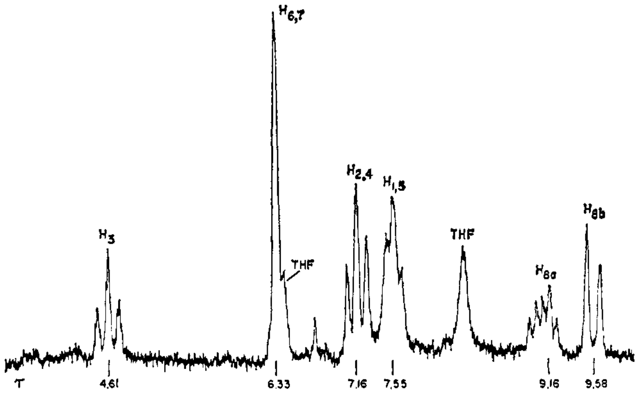

Figure 1. Nmr spectrum of bicyclooctadienide anion III in THF-d_8 (Varian A-60 spectrometer).

We are now employing carbanion III in the synthesis of homocounterparts of cyclopentadienyl complexes.

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(9) *E.g.*, S. Winstein, C. G. Kreiter, and J. I. Brauman, *J. Am. Chem. Soc.*, **88**, 2047 (1966).

(10) Appreciable amounts of tricyclic IV and tetracyclic V are detected in the products from Na-NH_3(l) reduction of tricyclic or tetracyclic halides or from preparation and hydrolysis of the corresponding Grignard reagents.[4c,5a] Thus, as we already surmised,[4c] these latter conversions do not proceed entirely *via* carbanion III.

(11) National Science Foundation Postdoctoral Fellow, 1965–1966.

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Alkyladamantanes by Rearrangement from Diverse Starting Materials

Sir:

When Nujol (refined petroleum oil) is heated with aluminum halide catalysts, a mixture of polysubstituted alkyladamantanes is formed in yields of up to 11%. A variety of other substances, including cholesterol, cholestane, abietic acid, cedrene, caryophyllene, camphene, cyclohexene, cyclohexanol, cyclohexane, squallene, squallane, and dodecane, also give similar alkyladamantane mixtures (Table I).

These reactions were most successfully carried out in pressure bottles agitated by a wrist-action shaker at 110–130° for 2–5-day periods. Various catalysts were effective. The best were $AlBr_3$[1,2] and $AlCl_3$[3] "sludge" catalysts which facilitated contact when used in excess. To a lesser degree, $AlBr_3$ and $AlCl_3$ also worked. Solvents were not needed, but CS_2 could be

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(1) (a) V. Z. Williams, Jr., A.B. Thesis, Princeton University, 1965; (b) V. Z. Williams, Jr., P. von R. Schleyer, G. J. Gleicher, and L. B. Rodewald, *J. Am. Chem. Soc.*, **88**, 3862 (1966).

(2) A. Schneider, R. W. Warren, and E. J. Janoski, *J. Org. Chem.*, **31**, 1617 (1966).

(3) Prepared from $AlCl_3$ and *t*-BuBr following Williams[1] by M. Nomura.