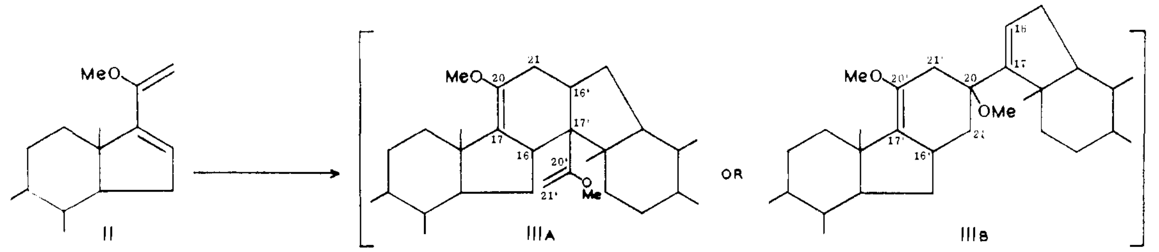
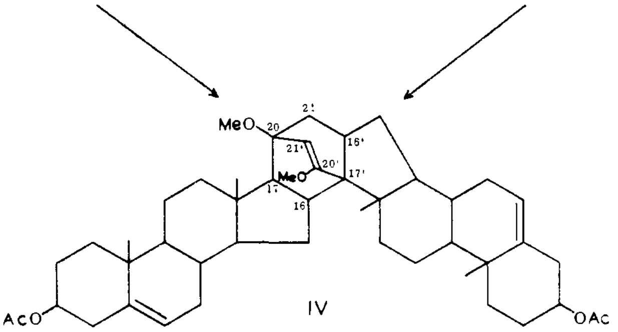
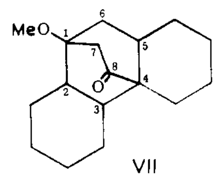


II IIIA IIIB



IV



VII

dence of: (1) analysis[3] and molecular weight (690); (2) presence of only one new double bond (n.m.r. and perbenzoic acid titration); (3) mild acid hydrolysis of the enol ether group to produce a six membered ring ketone (V, m.p. 312–313°, $\nu_{\text{KBr}}^{\text{C=O}}$ 1705 cm.$^{-1}$) possessing no new double bonds; (4) reaction with perchloryl fluoride to produce an $\alpha$-fluoroketone (VI, m.p. 291.5–292.5°, $\gamma_{\text{KBr}}^{\text{C=O}}$ 1723 cm.$^{-1}$) possessing one atom of fluorine per two steroid residues with the fluorine located on a carbon atom which also bears a hydrogen substituent but which is adjacent to carbon atoms with no hydrogen substituents (n.m.r.); and (5) studies of the model compound 1-methoxy-2,3-4,5-bis-butanobicyclo[2.2.2]octan-8-one (VII) obtained by hydrolysis of the dimeric enol ether arising from the analogous reaction of 1-acetylcyclohexene with trimethyl orthoformate in the presence of acid.

The model dimeric ketone (VII) was found to consist of a 3 to 1 mixture of two diastereoisomers (the minor one crystalline, m.p. 79–79.5°) which were separated by vapor phase chromatography and each shown to possess structure VII by n.m.r. and infrared spectra ($\nu_{\text{KBr}}^{\text{C=O}}$ 1701 cm.$^{-1}$, $\nu_{\text{liq.}}^{\text{C=O}}$ 1705 cm.$^{-1}$) and by selenium dehydrogenation to yield phenanthrene and 9-methylphenanthrene. Selenium dioxide oxidation of the unresolved ketone mixture gave no unsaturated ketone but rather a diketone, which reacted with *o*-phenylenediamine to form a quinoxaline (m.p. 186.5–187°) and was readily cleaved by alkaline hydrogen peroxide to yield a diacid (m.p. 236–240° dec.).

Although the same decacyclic structure (IV) can arise from either IIIa or IIIb, the more probable intermediate is IIIa, since its formation by an acid-catalyzed Diels–Alder reaction and its further cyclization both can take place by reaction sequences in which an electrophilic species interacts with the strongly nucleophilic center in an enol ether group. Compound IV and the ketone (V) derived from it appear to consist predominantly of one stereochemical modification, the nature of which will be discussed in a subsequent paper.

The formation of a bicyclooctane system by further cyclization of a Diels–Alder type adduct bears a formal relation to the Woodward–Katz rearrangement[4] of the Diels–Alder adducts of cyclopentadiene derivatives, a process which recently has been shown to be strongly catalyzed by acid.[5] The carbon–carbon bond formed in the final step of the present reaction corresponds to the new bond produced in the Woodward–Katz rearrangement. In the cyclopentadiene case, formation of this bond is accompanied by cleavage of one of the original carbon–carbon bonds of the Diels–Alder adduct, whereas, in the present reaction, both original carbon–carbon bonds are retained, and a carbon–hydrogen bond is broken instead.

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[3] All novel compounds here described gave satisfactory analyses.

[4] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959). The authors are indebted to Prof. Woodward for his helpful comments.

[5] P. Yates and P. Eaton, *Tetrahedron Letters*, no. 11, 5 (1960); R. C. Cookson, J. Hudec and R. O. Williams, *ibid.*, no. 22, 29 (1960).

BEN MAY LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO 37, ILLINOIS
THE UPJOHN COMPANY
KALAMAZOO, MICHIGAN

KEN-ICHI MORITA
GEORGE SLOMP, JR.
ELWOOD V. JENSEN

RECEIVED AUGUST 6, 1962

## THE HEPTAPHENYLTROPYLIUM (HEPTAPHENYLCYCLOHEPTATRIENYL) RADICAL IN SOLUTION[1]

*Sir:*

On the basis of some simple molecular orbital treatments the odd electron of the tropylium radical is predicted to be in an anti-bonding orbital which is, furthermore, doubly degenerate and subject to Jahn–Teller distortions.[2] In apparent accord with this predicted instability, no simple derivative of the seven-pi-electron tropylium radical has been prepared previously or observed unambiguously in

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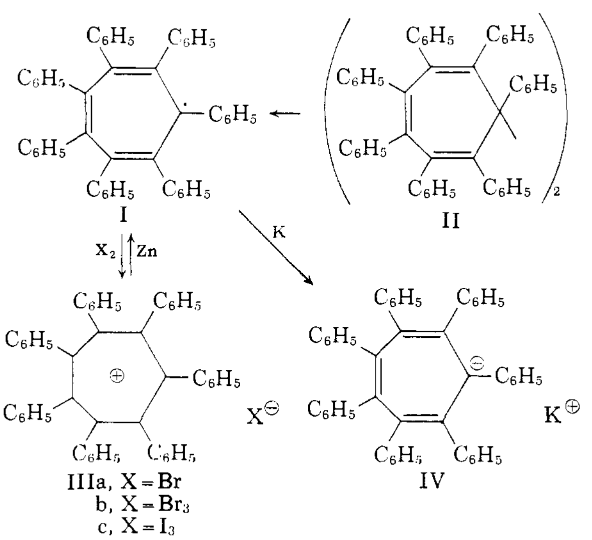
[1] Polyarylcycloheptatrienes, III; previous papers in this series (a) Part II, M. A. Battiste, *J. Am. Chem. Soc.*, **83**, 4101 (1961); (b) Part I, M. A. Battiste, *Chem. and Ind.*, 550 (1961).

[2] *Cf.* A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 260 and 279.

olution,[3] although the parent radical is presumed to be an intermediate in the formation of ditropyl from the zinc dust reduction of tropylium bromide in aqueous solution.[4] The tropylium radical has, however, been detected in the vapor state and its ionization potential determined by the electron impact method.[5] We now wish to report the preparation and some observations on the reactions of a moderately stable tropylium radical, heptaphenyltropylium (heptaphenylcycloheptatrienyl) (I), in dimethoxyethane and benzene solutions.[7] In this system the large steric requirements of the phenyl rings should accordingly render the dimer, bis-heptaphenylcycloheptatrienyl (II), relatively less stable compared to dissociated radicals (I).

Treatment of a stirred suspension of heptaphenyltropylium bromide (IIIa)[1a] in dimethoxyethane with an excess of zinc dust under a dry, inert atmosphere at room temperature resulted in complete disappearance of the reddish-orange organic solid within two hours.[9] The resulting deep reddish-brown (russet) solution (0.04–0.05 *M*) gave a strong singlet e.s.r. signal and also showed considerable solvent line broadening in the n.m.r., confirming a high radical concentration. Aliquots of the above solution were treated with excess bromine or iodine in dimethoxyethane solution at sample times from 2–7 hr., giving in each case immediate and quantitative precipitation of the tribromide IIIb[1a] or triiodide IIIc, respectively. The triiodide was characterized by its infrared and ultraviolet spectra and by its identity with an authentic sample of IIIc prepared by treating heptaphenyltropyl alcohol[1a] with hydroiodic acid in the presence of excess iodine.



Reductions in benzene followed a similar course, although much longer reduction periods, *ca.* 15 hr., were required for the complete reduction of IIIa. The effect of solvent here is apparently due to a lower solubility of IIIa in benzene. Net paramagnetism was observed for a benzene solution of I on the Gouy balance, and from the determined magnetic moment (1.7–1.8 B.M.) it was concluded that relatively little, if any, of the dimer II was present.[10]

Solutions of I may be stored in sealed ampoules under an argon atmosphere for several weeks with no apparent decomposition or rearrangement. On exposure to oxygen, however, the color of these solutions was changed rapidly from deep reddish-brown to light orange. Similarly, nitric oxide completely discharged the color from a benzene solution of I, imparting a bluish-green tinge toward the end, which later changed to bright yellow on exposure of the solution to the atmosphere. Solid products have been isolated from both reactions; however, their structures have not as yet been established.

Further reduction of I with an excess of potassium metal in dimethoxyethane produced the characteristic deep purple solution of the recently reported[8] potassium salt of the heptaphenyltropylium anion (IV). Conversely, the addition of a solution of IV to an excess of IIIa gave the russet-colored solution previously noted by Breslow and Chang[7] to be strongly paramagnetic. This solution gave all the reactions of I, although the yields of tribromide IIIb and triiodide IIIc were substantially below theoretical. Nevertheless, it seems clear that I has been obtained via an electron transfer between IIIa and IV, and further, that I is the initial product of potassium metal reduction of IIIa, but undergoes further reduction by the excess potassium. The latter conclusion is supported by the observation of transient reddish-brown colors during the initial phase of the potassium metal reductions.

The singlet e.s.r. signal for I[13] (line width 2.2 gauss at maximum slope) at $g = 2.008$ suggests that the unpaired spin density is localized on the carbon atoms of the tropylium ring. This is consistent with the structure for I in which the seven phenyls are twisted appreciably out of the plane of the central ring. Comparison with the similar pentaphenylcyclopentadienyl system suggests, however, that

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(3) Wittig, Hahn and Tochtermann [*Ber.*, **95**, 431 (1962)] recently have prepared bis-(1-phenyltribenzocycloheptatrienyl) and bis-(1-phenyl-2,3;6,7-dibenzocycloheptatrienyl) and have shown that these hydrocarbons dissociate respectively to the 1-phenyltribenzocycloheptatrienyl and the 1-phenyl-2,3;6,7-dibenzocycloheptatrienyl radicals on heating. Benzene ring fusion in these radicals, however, complicates their $\pi$-electronic makeup and hinders effective comparison to non ring-fused tropylium radicals.

(4) W. v. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

(5) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *ibid.*, **82**, 5593 (1960); the extremely low experimental value of 6.60 e.v. is in good agreement with the calculated value[6] and apparently reflects the greater electronic stability of the cation over the radical.

(6) A. Streitwieser, *ibid.*, **82**, 4123 (1960).

(7) While this work was in progress Breslow and Chang communicated to this journal[8] their preparation of the potassium salt of the heptaphenyltropylium anion (IV) and its reaction with excess heptaphenyltropylium bromide (IIIa). In the latter reaction a strongly paramagnetic solution was obtained leading these authors to correctly infer the formation of the heptaphenyltropylium radical.

(8) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 1484 (1962); we wish to thank Dr. Breslow for notification of these results prior to publication.

(9) Under the same conditions, but without added zinc dust, the salt IIIa was recovered unchanged after simple filtration.

(10) Compare this result with the earlier observations on bis-pentaphenylcyclopentadienyl[11] and, also, bis-triphenylcyclopropenyl.[12]

(11) (a) K. Ziegler and B. Schnell, *Ann.*, **446**, 266 (1925); (b) E. Muller and I. Muller-Rodloff, *Ber.*, **69B**, 665 (1936).

(12) R. Breslow and P. Gal, *J. Am. Chem. Soc.*, **81**, 4747 (1959).

(13) The author is indebted to Mr. S. Milligan of Florida State University for the measurement of this spectrum.

some hyperfine splitting by the phenyl hydrogens may be uncovered with further resolution.[14] In support of this, possible side band structure was noted in the spectrum of I from the present work. Further investigation of this point is planned.

Helpful discussions with Dr. W. M. Jones and Dr. W. S. Brey, Jr., of this department, are gratefully acknowledged.

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[14] Reitz recently has resolved the e.s.r. spectrum of pentaphenylcyclopentadienyl into at least 33 lines separated by 0.3 gauss. The pattern observed is that expected for the ratios of spin densities in an odd-alternant radical such as the triphenylmethyl radical, but the magnitude of the splitting is best accounted for by twisted phenyl rings [D. C. Reitz, *J. Chem. Phys.*, **34**, 701 (1961)].

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA
MERLE A. BATTISTE

RECEIVED AUGUST 3, 1962

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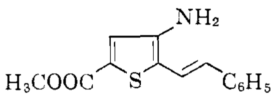
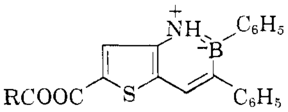
## A DERIVATIVE OF BORAZARENE[1]

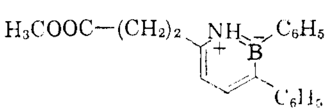
*Sir:*

We wish to report the first synthesis of a derivative of borazarene.[2] Reduction of methyl 2-styryl-3-nitrothiophene-5-carboxylate[3] with tin and hydrochloric acid gave methyl 2-styryl-3-aminothiophene-5-carboxylate (I), isolated as its acetyl derivative, m.p. 203–203.5°. *Anal.* Calcd. for $C_{16}H_{15}NO_3S$: C, 63.8; H, 4.98; N, 4.65. Found: C, 63.7; H, 4.9; N, 4.75. Condensation of (I) with phenyl dichlorobornite gave 2-carbomethoxy-5,6-diphenyl-5,4-borazarobenzothiophene (IIa). The product crystallized as pale yellow needles from a solution of benzene and methylene chloride, m.p. 200–201°, $\lambda_{\max}^{\text{EtOH}}$ 222 mμ (ε 20,100), 240 mμ (ε 17,1780), 286 mμ (ε 14,930), 310 mμ (ε 10,310), 355 mμ (ε 25,500). *Anal.* Calcd. for $C_{20}H_{16}NO_2BS$: C, 69.6; H, 4.69; N, 4.1. Found: C, 69.7; H, 4.69; N, 4.2.

This is the first sulfur-containing heteroaromatic boron compound of this type to be reported. Hydrolysis of (IIa) with methanolic sodium hydroxide gave the corresponding acid (IIb), m.p. 205°. *Anal.* Calcd. for $C_{19}H_{14}NO_2BS$: C, 68.9; H, 4.23; N, 4.23. Found: C, 68.9; H, 4.15; N, 4.15.


I


IIa, R = CH₃
b, R = H


III

Attempts to desulfurize (II) with freshly prepared active Raney nickel[4] by the method of Blicke and Sheets[5] failed to give any new compound; however, reactions of (II) with samples of Raney nickel that had been prepared some months earlier gave excellent yields (80–85%) of 2,3-diphenyl-6-(2-carbomethoxy-ethyl)-2,1-borazarene (III), m.p. 110–110.5°, $\lambda_{\max}^{\text{EtOH}}$ 220 mμ (ε 18,450), 275 mμ (ε 10,970), 306 mμ (ε 15,850). *Anal.* Calcd. for $C_{20}H_{20}NO_2B$: C, 75.7; H, 6.39; N, 4.42. Found: C, 75.52; H, 6.39; N, 4.55. No change was observed in the ultraviolet spectrum of (III) in absolute ethanol in the presence of acid or alkali over a period of a week. The latter evidence, and the fact that the double bonds in the borazarene ring remained intact during the desulfurization of (II), indicate that (III) is an aromatic compound of considerable stability.

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[1] This work has been supported by the Atomic Energy Commission under Contract No. A.E.C. 889.

[2] M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 2728 (1959), suggested that borazarobenzene should be given the trivial name borazarene. Since 2,1-borazarobenzene is expected on theoretical grounds to be much more stable than the 3,1- or 4,1-isomers, we suggest that the name "borazarene" apply only to the 2,1-isomer. The other isomers could be called β-borazarene and γ-borazarene (*cf.* tropolone, β-tropolone and γ-tropolone).

[3] I. J. Rinkes, *Rec. Trav. Chim.*, [4] **52**, 538 (1933).

[4] R. Mozingo, D. E. Wolfe, S. A. Harris and K. Folkers, *J. Am. Chem. Soc.*, **65**, 1013 (1943).

[5] F. F. Blicke and D. G. Sheets, *ibid.*, **71**, 4010 (1949).

GEORGE HERBERT JONES LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO 37, ILLINOIS
MICHAEL J. S. DEWAR
PETER A. MARR

RECEIVED JULY 27, 1962

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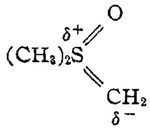
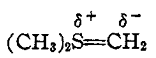
## DIMETHYLSULFONIUM METHYLIDE, A REAGENT FOR SELECTIVE OXIRANE SYNTHESIS FROM ALDEHYDES AND KETONES

*Sir:*

As a result of the general synthetic utility of dimethyloxosulfonium methylide (alternatively dimethylsulfoxonium methylide) (I) as a reagent for the addition of methylene to double bonds which are receptive to nucleophiles,[1] a study of the related dimethylsulfonium methylide (II) seemed appropriate despite indications that sulfonium ylides derived from non-stabilized carbanions are subject to rapid spontaneous decomposition[2] while those in a highly stabilized condition, *e.g.*, 9-fluorenyl derivatives,[3] are of very limited synthetic import. This report summarizes the first returns of such an investigation including a practical method for the generation of the ylide II in a reasonably stable condition and the application of this substance as a reactive but *exceedingly selective* methylene transfer agent.


I


$$\overset{\delta+}{(CH_3)_2S}{=}\overset{\delta-}{CH_2}$$
II

Solutions of dimethylsulfonium methylide were prepared successfully by addition of a solution of trimethylsulfonium iodide with stirring to a solution of methylsulfinylcarbanion[4] in equivalent amount under nitrogen, as was the case with the oxosulfonium ylide I[1] except that it was necessary to conduct the reaction at lower temperatures (0 to −10° in dimethyl sulfoxide containing enough tetrahydrofuran to prevent freezing) be-

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[1] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962).

[2] *Cf.* V. Franzen, H.-J. Schmidt and C. Mertz, *Ber.*, **94**, 2942 (1961).

[3] A. W. Johnson and R. B. LaCount, *J. Am. Chem. Soc.*, **83**, 417 (1961).

[4] E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962).