Anal. Calcd. for $C_{15}H_{33}B$: C, 80.4; H, 14.8. Found: C, 79.5; H, 14.5.

Hydroboration of β-Pinene.—β-Pinene, 100 mmoles, in 100 ml. of tetrahydrofuran was added slowly over 90 min. at 0° to 50 mmoles of borane in 50 ml. of the solvent. The clear solution was allowed to warm up to room temperature, then treated with methanol. There was obtained 49.8 mmoles of hydrogen. Distillation under reduced pressure yielded 6.37 mmoles of methyl borate, a yield of 12.8%.

Acknowledgment.—We are deeply indebted to Dr. Gerald J. Klender for his generous assistance with several of the experiments.

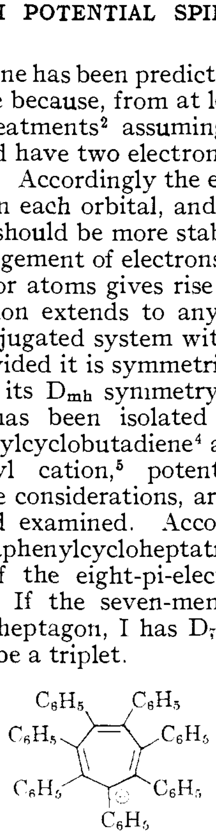
COMMUNICATIONS TO THE EDITOR

HEPTAPHENYLCYCLOHEPTATRIENYL ANION, A SINGLET WITH POTENTIAL SPIN DEGENERACY[1]

Sir:

Cyclobutadiene has been predicted to have a triplet ground state because, from at least some molecular orbital treatments[2] assuming four-fold symmetry, it should have two electrons in a degenerate pair of orbitals. Accordingly the electrons could be unpaired, one in each orbital, and the resulting diradical species should be more stable than one with any other arrangement of electrons. An equivalent consideration for atoms gives rise to Hund's rules.

This prediction extends to any derivative of a monocyclic conjugated system with 4n pi electrons in the ring provided it is symmetrically substituted so as to retain its D_{mh} symmetry, but to date no such system has been isolated and examined.[3] Both tetraphenylcyclobutadiene[4] and pentaphenylcyclopentadienyl cation,[5] potential triplets according to these considerations, are too unstable to be isolated and examined. Accordingly we have prepared heptaphenylcycloheptatrienyl anion (I), a derivative of the eight-pi-electron cycloheptatrienyl anion. If the seven-membered ring is a planar regular heptagon, I has D_{7h} symmetry[6] and is predicted to be a triplet.



I

Heptaphenylcycloheptatrienyl bromide (II), prepared by the elegant procedure of Battiste,[7] was suspended in dimethoxyethane and treated with an excess of potassium metal in a modified Schlenk tube *in vacuo*. The resulting deep purple solution (0.04 m.) of the potassium salt of I was filtered into another compartment and a portion was sealed into a tube and examined in the n.m.r. A complex multiplet for the phenyls was found at 3.25 τ, and there was no measurable broadening of the solvent line. No e.s.r. signal was detectable. The remainder of the solution was quenched with D_2O, and the organic residue isolated was found to be pure heptaphenylcycloheptatriene,[8] containing a deuteron on the seven-membered ring (the aliphatic proton of heptaphenylcycloheptatriene is found at 4.73 τ in the n.m.r.; this band is missing in our product and in authentic deuterated material prepared by $LiAlD_4$ reduction of II). The aqueous solution, by titration, contained an equivalent amount of KOD. If diethyl ether was used as solvent the potassium salt of I could be collected as a purple precipitate; this salt with D_2O also yielded the deuteriocycloheptatriene as the only organic product. The 0.04 *m* solution of I in dimethoxyethane was examined on the Gouy balance, and no net paramagnetism was detectable.

By contrast, solvent line broadening[9] was observed with a 0.004 *m* solution of di-*t*-butylnitroxide[10] in dimethoxyethane and was quite pronounced with a 0.04 *m* solution. The latter solution also gave easily detectable paramagnetism in measurements on the Gouy balance. Accordingly, it is apparent that I is not a diradical. This conclusion is confirmed by the observation that when the solution of I was added to an excess of II, the resulting russet solution now gave a strong e.s.r. signal, and paramagnetism was detected by Gouy balance measurements and from considerable solvent line broadening in the n.m.r. Spins have thus been unpaired in this reaction, most obviously by formation of heptaphenylcycloheptatrienyl radical.

Several special explanations are available for our finding that I is a singlet. It may be that there is unsymmetrical coördination of I with a potassium ion, although the crowding predicted from models because of the extreme non-planarity of the phenyls should make specific interaction difficult.[11] Alternatively, the central ring may be non-planar, although models show that any distortion tends im-

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(1) This work was supported by grants from the Sloan Foundation and the Petroleum Research Fund.

(2) For a review, *cf.* A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 261–262.

(3) Cycloöctatetraene would be such a system if it were planar.

(4) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2195 (1961).

(5) R. Breslow and H. W. Chang, *ibid.*, **83**, 3727 (1961).

(6) This refers only to symmetry with respect to chemical interactions. The seven phenyls are undoubtedly out of the plane, and unless they are 90° out of plane the geometric space-group is no longer D_{7h}, but this could only affect the calculations if direct electronic interactions between phenyl groups were taken into account.

(7) M. A. Battiste, *J. Am. Chem. Soc.*, **83**, 4101 (1961); we wish to thank Dr. Battiste for making his results available to us before publication.

(8) M. A. Battiste, *Chem. & Ind.*, 550 (1961).

(9) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 207 ff.

(10) A. K. Hoffmann and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4672 (1961).

(11) The absence of vinyl hydrogens in the n.m.r. spectrum of I excludes the possibility of ring-chain tautomerism involving the phenyls.[5]

mediately to localize the negative charge. It may also be that in our particular system the lowering of the singlet state energy which accompanies Jahn–Teller distortion is greater than the singlet-triplet energy difference. Thus our evidence does not conclusively demonstrate that cyclobutadiene and other members of this class of compounds will not have triplet ground states, but it is suggestive.

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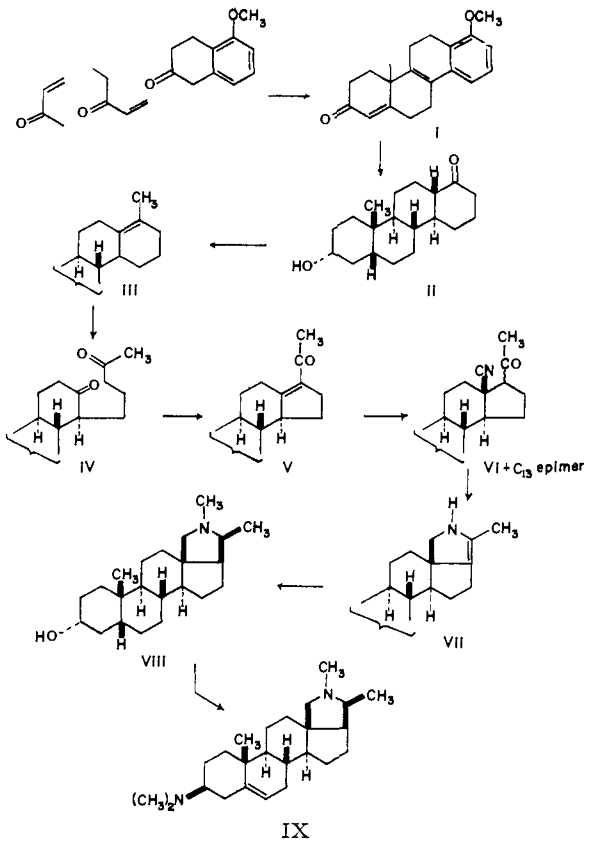
TOTAL SYNTHESIS OF RACEMIC CONESSINE

Sir:

Barton and Morgan[1] recently have described an ingenious synthesis of conessine from Δ^5-pregnene-3β,20β-diol. In the present communication we wish to disclose a synthesis of the racemic form of the alkaloid starting from coal tar intermediates.

The tetracyclic ketone I, which is readily available from 5-methoxy-2-tetralone by successive (*in situ*) condensation with ethyl vinyl ketone followed by methyl vinyl ketone, has been stereoselectively converted into the hydroxy ketone II.[2] The present report discloses the transformation of this latter substance into racemic conessine.

Reaction of the hydroxy ketone II with excess methyllithium afforded a dihydroxy compound, m.p. 155–156°, which on treatment with acetic anhydride and pyridine was selectively acetylated to give the 3-acetate, m.p. 166–167°. Treatment of this hydroxy ester with phosphorus oxychloride and pyridine effected dehydration to yield a mixture of olefins which was rich in the desired 13,17a-dehydro isomer III (acetoxy group at C_3) as shown by ozonolysis and subsequent work-up with formaldehyde to give the diketo 3-acetate IV, m.p. 79.5–80.5°. This last substance was cyclized smoothly with dilute alcoholic potassium hydroxide to the unsaturated ketone V, m.p. 72–74°, $\lambda_{\max}^{\mathrm{EtOH}}$ 257 mμ (ϵ 14,200) which on treatment with potassium cyanide and ammonium chloride in dimethylformamide[3] was converted, in excellent yield, into a mixture of epimeric 13-cyano-3-hydroxy compounds, m.p. 144–145° and 169–171°, formed in approximately equal amounts. The cyano ketones were easily separated by chromatography, and the 171° compound proved to be the 13β isomer VI as shown by its conversion to conessine as described below.[3a]



Preliminary attempts to effect direct conversion of the cyano ketone VI into N-desmethyl VIII by catalytic hydrogenation were unpromising; therefore the cyano ketone was converted to the ethylene ketal which, without purification, was treated in turn with lithium aluminum hydride to reduce the cyano group, then with dilute acid to hydrolyze the ketal, and finally with hydrogen in the presence of platinum oxide in order to reduce the enamine VII ($\lambda_{\max}^{\mathrm{film}}$ 6.03 μ). The crude basic material was treated with formaldehyde and formic acid[4] to effect N-methylation, and the product, m.p. 168.5–170°, was shown to be the racemic form of the hydroxy compound VIII by virtue of the complete identity of the infrared and high temperature mass spectra with those of D-VIII derived from natural conessine.[5] Oxidation of racemic VIII with chromium trioxide and perchloric acid in acetic acid afforded the corresponding 3-keto compound, m.p. 147–149°, having an infrared spectrum indistinguishable from that of naturally derived D-material.[5] Bromination followed by dehydrobromination gave the racemic 3-keto-Δ^4-unsaturated derivative which was transformed into the N,N-dimethylenamine and reduced with sodium borohydride and acetic acid.[5b,6] The product melted at 127–128.5° and was shown to be racemic conessine by the complete identity of

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[1] D. H. R. Barton and L. R. Morgan, *Proc. Chem. Soc.*, 206 (1961).

[2] W. S. Johnson, W. A. Vredenburgh and J. E. Pike, *J. Am. Chem. Soc.*, **82**, 3409 (1960).

[3] *Cf.* the work of W. Nagata, I. Kikkawa and K. Takeda, *Chem. and Pharm. Bull.* (*Japan*), **9**, 79 (1961), on the cyanation of the corresponding unsaturated ketone in the estratriene series. It also is to be noted that W. L. Meyer and I. F. Wolfe are studying the reaction in the model two-ring system, and we wish to thank Professor Meyer for advising us of his unpublished work.

[3a] ADDED IN PROOF.—On April 2, 1962, we discovered that the 13a-cyano ketone, on heating at 350°, rapidly loses hydrogen cyanide and is smoothly reconverted to unsaturated ketone in excellent yield. Through this recycling process, the synthesis of conessine reported here is thus rendered stereoselective at every stage.

[4] R. Tschesche and A. C. Roy, *Ber.*, **89**, 1288 (1956).

[5] *Cf.* (a) R. Pappo, U. S. Patent No. 2,913,455, Nov. 17, 1959 [*Chem. Abst.*, **54**, 3527 (1960)]; (b) W. S. Johnson, V. J. Bauer and R. W. Franck, *Tetrahedron Letters*, No. 2, 72 (1961).

[6] Since our previous work (ref. 5b), we have found that reaction occurs only *after* acetic acid is added to the mixture of borohydride and enamine in dioxane. Since better yields are obtained after refluxing the acidified mixture (a treatment originally done in order to hydrolyze any unreacted enamine), we suspect that the reduction process may involve hydroboration followed by hydrolysis, as suggested by G. Stork and G. Birnbaum, *Tetrahedron Letters*, No. 10, 313 (1961).