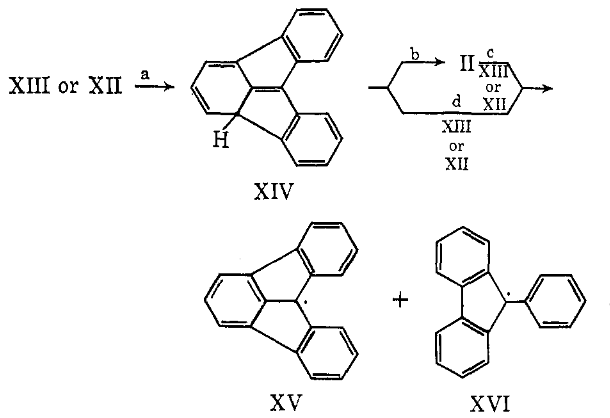
undergo diradical cyclization at the 1 position of the fluorene system to give XIV which subsequently isomerizes (eq 3). Since there is extensive formation of VII and VIII from concentrated I in decalin and related solvents, a radical-like process is implied in which hydrogen is transferred from solvent and from II to give 9-phenylfluorenyl (XVI) and fluoradenyl (XV) radicals and thence VIII and VII (eq 4 and 5). Similarly generation of a diradical from solid I in the presence of effective amounts of II or its isomeric precursor(s) such as XIV yields equivalent amounts of VIII by radical transfer and subsequent coupling of XV. Rapid heating of solid I minimizes the opportunity for partitioning of hydrogen from II and XIV.

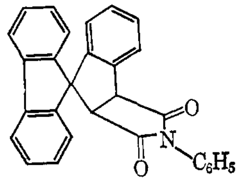


(3)

$$\text{XVI} + \text{II or XIV} \longrightarrow \text{VIII} + \text{XV} \quad (4)$$

$$2\text{XV} \longrightarrow \text{VII} \quad (5)$$

The geometric change in decomposition of I and the strain leading to XIV should provide real opportunity for spin inversion to XIII. Irradiation of I in 2-methyltetrahydrofuran at 77°K does provide evidence for a ground-state triplet, presumably XIII.[6] Photolysis of I in benzene containing N-phenylmaleimide gives the capture product XVII. In solution I photolyzes to II, VII, and VIII and products of incorporation of solvent and added oxygen. These results indicate that the photochemical and thermolysis reactions of I are generally similar and that intramolecular substitution in photolytic conversion of I to II possibly involves diradical processes; XV and XVI are generated in competitive reactions. Photolysis of I in toluene at 65° thus yields II (9%), VII (8%), and VIII (51%); in ethyl ether at −95° and subsequent exposure to air, 9-phenylfluorenyl peroxide (XVIII) forms in ∼100% yield. The conversion to 9-phenylfluorenyl rather than fluoradenyl derivatives reflects the abilities of ethyl ether and toluene to transfer hydrogen to XII and/or XIII. Trapping of XVI by oxygen results in XVIII.



XVII

I photolyzes in benzene exposed to air to give II (12%), VII (21%), XVIII (43%), 9,9-diphenylfluorene (15%), and biphenyl. Photolysis of I results in abstraction of hydrogen from benzene to give phenyl radicals; biphenyl is apparently formed from phenyl radicals by arylation of benzene and hydrogen transfer. 9,9-Diphenylfluorene presumably results from addition of XVI to benzene and hydrogen transfer.

Decompositions of I and III differ dramatically. Thermolysis or photolysis of III yields IV (>93%) and traces of diphenylacetonitrile. The processes are not effectively partitioned to diphenylacetonitrile (<1.3%) or intercepted by the chemical techniques used for I. Decomposition of III is much more caged than I; the differences can be related to the greater rotational course from I.

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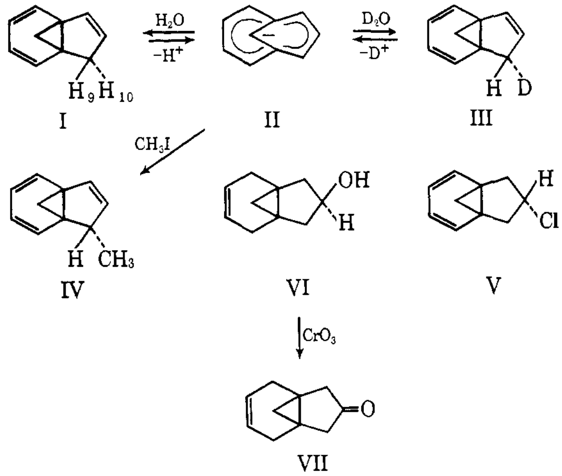
A Stereospecific Base-Catalyzed Deuterium Exchange of Tricyclo[4.3.1.0]deca-2,4,7-triene

Sir:

We have recently shown that the hydrocarbon tricyclo[4.3.1.0]deca-2,4,7-triene (I) gives rise to a ten-π-electron aromatic anion (II) when treated with sodium dimethylsulfinyl anion.[1] In this communication we report that base-catalyzed exchange of I leads to a remarkable stereospecific abstraction of proton and stereospecific incorporation of deuterium.



When a solution of II in dimethyl-d_6 sulfoxide was quenched with D_2O, the hydrocarbon isolated contained one deuterium atom at C_9. That the incorporation of the deuterium atom was stereospecific was evident from a comparison of the nmr spectrum of the deuterated hydrocarbon III at 100 MHz with that of the undeuterated I. The protons of interest in I are H_8 at τ 4.68 (double triplet, $J_{7,8} = 6$ Hz, $J_{8,9} = J_{8,10} = 2$ Hz), H_9 at τ 7.35 (double triplet, $J_{9,10} = 17$ Hz, $J_{8,9} = J_{7,9} = 2$ Hz), and H_{10} at τ 7.65 (double triplet, $J_{8,10} = J_{7,10} = 2$ Hz).[2] The nmr spectrum of III had H_8 at τ 4.68

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(6) The esr spectrum consists of an intense band at 3210.8 gauss (g = 2.0022), a weaker band at half-field (1618.4 gauss, A_m = 2), and poorly resolved satellite bands.

(1) P. Radlick and W. Rosen, *J. Am. Chem. Soc.*, **88**, 3461 (1966).

(2) The assignment of H_9 and H_{10} as *cis* and *trans*, respectively, to the cyclopropane ring was made on the basis that in compounds where the methylene protons on carbon adjacent to a cyclopropane ring are not

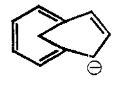
(double doublet) and H_9 at τ 7.65 (pentuplet), and integration of the spectrum indicated that the band at τ 7.65 represented 1.0 proton. The change in H_8 from a double triplet in I to a double doublet in III plus the appearance of only one proton at C_9 in III and the absence of any signal at τ 7.35 in III is uniquely consistent with stereospecific deuterium incorporation at C_9 as depicted at III.

In addition, when III was treated with sodium dimethyl-d_5-sulfinyl anion in dimethyl-d_6 sulfoxide the anion II which resulted had an nmr spectrum identical with that of the anion produced from I and no bands were observed for dimethyl-d_5 sulfoxide, monoprotiodimethyl sulfoxide. Therefore, the deuterium atom at C_9 in III must have been removed stereospecifically by the base when II was generated.

The results prompted an investigation of the base-catalyzed exchange of I. The hydrocarbon was allowed to react with a saturated solution of NaOD in dimethyl-d_6 sulfoxide at 30° and the reaction was followed by nmr. By this technique a value of *ca.* 240 sec was calculated for the half-life of exchange of one proton. The reaction was followed for the equivalent of 20,000 half-lives and no exchange of H_9 for deuterium could be detected. Upon quenching the reaction mixture after 20,000 half-lives and isolating the product, it was found that it was identical with III, obtained from the quenching of the anion II with D_2O. These results indicate that there is a difference of at least 10^4 in kinetic acidity between H_9 and H_{10} in I.[4]

We have also prepared 9-methyltricyclo[4.3.1.0]deca-2,4,7-triene (IV)[6] by allowing II in dimethyl sulfoxide to react with methyl iodide and subjected it to an exchange experiment. When treated with NaOD in dimethyl-d_6 sulfoxide even after 3 months at 30°, IV was not observed to undergo any proton exchange for deuterium. Furthermore, it was found that allowing IV to react with sodium dimethylsulfinyl anion did not give rise to an aromatic ten-π-electron anion.

It seemed unlikely that a steric effect accounted for the difference in kinetic acidity of the two protons at C_9 in I since this hydrocarbon had been so readily generated by the elimination of HCl from V with potassium hydroxide in methanol.[1] Since this elimination was probably *trans* in nature, the proton *cis* to the cyclopropane ring was removed and could therefore not be hindered from attack by hydroxide ion. We have confirmed that a steric effect is not responsible for the stereospecificity of the exchange reaction with I by conducting the same exchange experiment on VII. This ketone (VII) was prepared by chromic acid oxidation of the alcohol[1] VI and was subjected to an exchange experiment using NaOD in dimethyl-d_6 sulfoxide. The exchange was followed by nmr, and the band at τ 7.78, which had all eight of the methylene protons which are on the five- and six-membered rings, was observed to rapidly and smoothly decrease in area until it contained only the four methylene protons adjacent to the double bond in the six-membered ring, after which no more deuterium atoms were incorporated.[7] This result demonstrates that the protons *cis* to the cyclopropane ring in I are not sterically prevented from undergoing base-catalyzed exchange with NaOD in dimethyl-d_6 sulfoxide.



IX

We contend that the stereospecificity of the exchange of hydrogen for deuterium in I is due to the rigid stereoelectronic requirement that the cyclopropane ring places upon the molecule. H_{10} is more readily abstracted by the base than H_9 because the electron pair in the orbital between C_9 and H_{10} can overlap much more effectively in the transition state with the electron pair in the zero-bridge bond (C_1–C_6) of the cyclopropane ring than can the electron pair between C_9 and H_9. Furthermore, in the anion II we suggest that the orbitals at C_1 and C_6 are not of the p–π type, as valence bond resonance structures for II, *e.g.*, IX, imply, but are directed anisotropically so that the face of the molecule opposite the methylene bridge has a higher electron density. This effect renders the face opposite to the methylene bridge to be the preferential one for attack of an electrophile, *e.g.*, proton or deuteron.

Acknowledgment. The authors gratefully acknowledge support from the Petroleum Research Fund of the American Chemical Society and partial support from the Intramural Research Fund of the University of California.

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equivalent it is the proton which is *cis* to the cyclopropane ring which appears at higher field.[3]

[3] Unpublished work: S. Winstein, P. Radlick, R. Boikess, and J. Brauman.

[4] Exchange experiments conducted on indene under identical conditions resulted in complete exchange of all three protons on carbons 1 and 3. For an excellent discussion of the exchange of indene see ref 5.

[5] G. Bergson, *Acta Chem. Scand.*, **17**, 2691 (1963).

[6] The stereochemistry of the methyl group could not be rigorously determined. However, we believe that, in analogy to the attack of II by D_2O, attack by methyl iodide must occur from the side opposite the methylene bridge.

[7] The protons adjacent to the carbonyl group stood out clearly from the others and despite our efforts it was not possible to determine any kinetic acidity difference between the *cis* and *trans* protons.

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Received July 31, 1967

Ionic Organoboranes. III.
The 1-Methyl-2-tropenyliumyl-1,2-dicarbaclovododecaborane(12) Cation[1,2]

Sir:

The 1,2-dicarbaclovododecaborane(12) (*o*-carborane) cage has been shown to be electron attracting.[6] In a

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[1] Work supported by the National Science Foundation, Grant GP-5554, and the Petroleum Research Fund, Grant 443-A4.

[2] We have used the name "tropenylium"[3,4] for the $C_7H_6^+$– substituent obtained by hydride removal from a C_7H_7– tropenyl group. In a new system for naming cycloheptatriene derivatives,[5] the name "tropenylium" is assigned to the $C_7H_7^+$ ion, and the $C_7H_6^+$– substituent becomes "tropenyliumyl."

[3] K. M. Harmon, A. B. Harmon, and A. A. MacDonald, *J. Am. Chem. Soc.*, **86**, 5036 (1964).

[4] A. B. Harmon and K. M. Harmon, *ibid.*, **88**, 4093 (1966).

[5] H. J. Dauben, Jr., and D. F. Rhoades, *ibid.*, in press.

[6] (a) T. L. Heying, J. W. Ager, S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963); (b) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1105 (1963); (c) D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963); (d)