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BRIDGED POLYCYCLIC COMPOUNDS. XX. THE *cis*-STEREOCHEMISTRY OF THE ADDITION OF METHANOL AND WATER TO ENDO-TRIMETHYLENENORBORNENE.[1]

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IT was recently shown that sulfuric acid-catalyzed additions of methanol (or of water in methanol) to *endo*-trimethylenenorbornene (1,2-dihydrodicyclopentadiene, I), and to the *exo* isomer (II) give differing ratios of *endo* (III) and *exo* (IV) ring skeleton ethers (or alcohols). Thus, for example, I and methanol was reported to give a mixture containing 14.5% of IIIa and 85.5% of IVa, while II gave 3.5% of IIIa and 96.5% of IVa. We now wish to report that the reactions with I are, within the limits of our experimental procedures, entirely *cis*-*exo* additions.

The previous data made it clear that at least two paths are available for such additions, as it is obvious that such data cannot be accommodated by a single path or by a single product-determining intermediate. As addition to II gave results similar to those obtained in the solvolysis of the p-toluenesulfonates IIIc and IVc, these might be considered "normal" results and could be accommodated by a single intermediate such as the non-classical ion V.[1] Among the other product-determining intermediates that were considered earlier were the classical ions VI and VII (or unsymmetrically solvated species equivalent to them) and the *endo*

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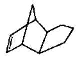
[1] Previous paper in series: S. J. Cristol, W. K. Seifert, D. W. Johnson and J. B. Jurale, *J. Am. Chem. Soc.* **84**, 3918 (1962)

protonated π complex VIII. The exo protonated π complex IX was rejected as one leading directly to products, as it was assumed that trans ring opening by solvent of such an intermediate would occur,[2] and this would lead to products with endo configurations of the Y group. These were not observed, and thus IX apparently does not react directly with solvent molecules in a pseudo-displacement mechanism.


I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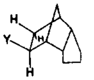

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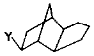

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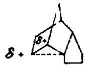
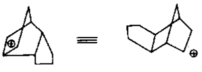


V


VI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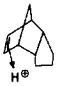

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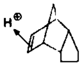

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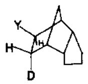
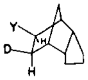
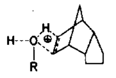


X



XI



R = H or CH_3

XII

(a) Y = OCH_3
(b) Y = OH
(c) Y = OTs
(d) Y = $OCOC_6H_4NO_2$

If the endo protonated π complex VIII (or an equivalent "hydrogen-bridged" ion) reacted directly with a solvent molecule by the equivalent of trans ring opening,[2] addition of CH_3OD and D_2O to I would lead to Xa and Xb. As indicated earlier,[1] I and II lead to III and IV in such amounts that at least 80% of the III from I arises via a path different from that utilized in the addition to II. If the alternative path then involved VIII,

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[2] (a) S. Winstein and N. J. Holness, ibid. 77, 5562 (1955); (b) G. S. Hammond and T. D. Nevitt, ibid. 76, 4121 (1954); (c) C. H. Collins and G. S. Hammond, J. Org. Chem. 25, 911 (1960).

at least 80% of the III isomer isolated in the deuterated series would be labeled as in X. This in fact would also be true if VIII were formed and ultimately gave III by isomerization to a carbonium ion such as VI or V. On the other hand, if VIII is not involved in the reaction sequence, product III might be expected to be labeled as in XI, assuming *exo* protonation as in IX followed by transformation to carbonium-ion intermediates, which then coordinate with solvent from the *exo* side.

It seemed likely that X and XI could be distinguished by nuclear magnetic resonance spectral studies. An n. m. r. spectrum (Varian A-60 spectrometer) of the alcohol IIIb in chloroform showed a distinctive doublet centering at 6.07 τ with a coupling constant J = 6.6 c.p.s. ascribable to the hydrogen on the carbinol carbon atom, as well as complicated absorption in the 7.6-9.2 τ region, which was not readily resolved. The doublet at 6.07 τ consisted of two broad halves with some subsidiary approximately 1 cycle splitting. Similar doublets were observed for IIIc (5.46 τ, J = 6.6) in carbon tetrachloride and for IIId (4.90 τ, J = 6.6) for the appropriate hydrogen atom. It appeared likely that the principal coupling (J∼7 cycles) was due to interaction between that hydrogen and the hydrogen on C_3 eclipsed with it,[3,4] and that this coupling would be observed in XI and would not appear in X. In order to check this, Xb was prepared by treatment of 5,6-*endo*-trimethylene-2,3-*exo*-epoxynorbornane with lithium aluminum deuteride and gave a broad singlet centering at 6.02 τ. Its *p*-nitrobenzoate, m.p. 123-126°, also had a broad singlet (4.89 τ). XIb was prepared by addition of hexadeuterodiborane to I followed by oxidation.[5] It showed a

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[3] M. Karplus, *J. Chem. Phys.* **30**, 11 (1959).

[4] F. A. L. Anet, *Can. J. Chem.* **39**, 789 (1961).

[5] (a) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.* **78**, 5694 (1956); (b) S. Wolfe, M. Nussim, Y. Mazur and F. Sondheimer, *J. Org. Chem.* **24**, 1034 (1959).

doublet of two relatively sharp bands at 6.09 τ, with J = 6.9 c.p.s. and its *p*-nitrobenzoate (XId), m.p. 128-129°, had a similar doublet, (4.99 τ, J = 7.0 cycles).

A mixture of 8.04 g. (0.060 moles) of I (containing 9.7% of II and 1.5% of dicyclopentadiene), 5.5 ml. of deuterosulfuric acid, 2.2 ml. of deuterium oxide and 46 ml. of O-deuteromethanol was stirred and heated at reflux for 10 hours. Sodium carbonate (10 g.) was added and the mixture was poured into water and extracted with ether. Removal of the ether gave a residue that analyzed (v.p.c.) as 5.2% I, 10.3% IIIa, 68.7% IVa, 2.6% IIIb and 13.2% IVb. The mixture was chromatographed on neutral alumina, the ether mixture was eluted with pentane and the alcohol mixture with ether. The ether mixture was separated on a 3/8 in. x 2 m. 30% Carbowax 1540 on Chromosorb column at 123° and 88 ml. of helium/min. The olefin I appeared at 26 min., *exo* ether IVa at 106 min. and *endo* ether IIIa at 136 min. The n. m. r. spectrum of IIIa had a fairly sharp doublet (J = 6.7) at 6.74 τ. The region between the peaks of the doublet returned almost to baseline, indicating that less than 10% of Xa could be present as a contaminant in XIa. The alcohol fractions were converted to *p*-nitrobenzoates, but could not be separated into isomers. The esters were reduced with lithium aluminum hydride, chromatographed on alumina and separated on a 1/4 in. x 1 m. 30% Carbowax 1540 column at 130° with 88 ml. of helium/min. The *exo* alcohol IVb appeared at 66 min. and the *endo* alcohol IIIb at 86 min. The n. m. r. spectrum of IIIb showed a doublet (J = 6.6) at 6.08 τ. Again less than 10% of Xb could be present in the XIb produced.

These results show clearly that *cis*-*exo* addition of both the H and Y portions of the addenda occurs, and exclude the *endo*-protonated π complex VIII as a significant intermediate in the addition reaction leading to III from I. These results combined with the earlier ones[1] suggest that at least one of the intermediates involved in this addition reaction is a classical ion such as VI (or an equivalent non-symmetrical "non-classical" ion) or that a *cis* addition four-center transition state such as XII is involved, in which a carbonium ion is not developed. The data force the requirement of two alternative paths or intermediates for the addition reaction. It is of interest that such alternatives are required even in solvents as polar as methanol.[6]

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[6] M. J. S. Dewar and R. C. Fahey, *ibid.* **84**, 2012 (1962) report that polar addition of hydrogen bromide to acenaphthylene goes by *cis* addition and prove that π complexes are therefore not product-determining intermediates in that case as well.