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An Octahydrodimethanonaphthyl Non-Classical Homocyclopropenyl Cation[1]

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In connection with non-classical carbonium ions, system II was of interest for comparison with the anti-7-norbornenyl[2] analog I and the unsaturated endo-endo system[3] III. One could anticipate great anchimeric acceleration of ionization of suitable II-derivatives, with formation of a relatively unique homocyclopropenyl variety of carbonium ion IV.

Alcohol II-OH has now been prepared through the Diels-Alder condensation of cyclopentadiene with anti-7-norbornenol[2] tetrahydropyranyl ether[4], b.p. 89-93° (2.5 mm.), $n^{25}D$ 1.4865, under nitrogen at 215° in the presence of diphenyl amine. Careful hydrolysis of the fraction of the product with b.p. 105-130° (2.5 mm.), followed by recrystallization and sublimation, leads to alcohol[4] II-OH, m.p. 108-109°; p-nitrobenzoate[4], m.p. 131-132°; p-toluenesulfonate[4], m.p. 102.5-103°; p-bromobenzenesulfonate[4] II-OBs, m.p. 96-97° (dec.).

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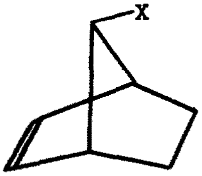
[1] Research sponsored by the Office of Ordnance Research, U.S. Army.

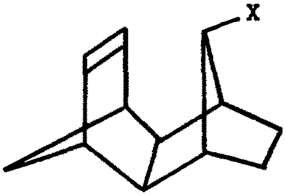
[2] (a) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, J. Am. Chem. Soc. **77**, 4183 (1955); (b) S. Winstein and M. Shatavsky, ibid. **78**, 592 (1956).

[3] P. Bruck, D. Thompson and S. Winstein, Chemistry and Industry 590 (1960).

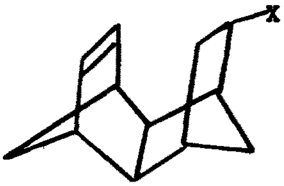
[4] A satisfactory C,H-analysis was obtained for this and the other indicated new compounds here reported.



I



II



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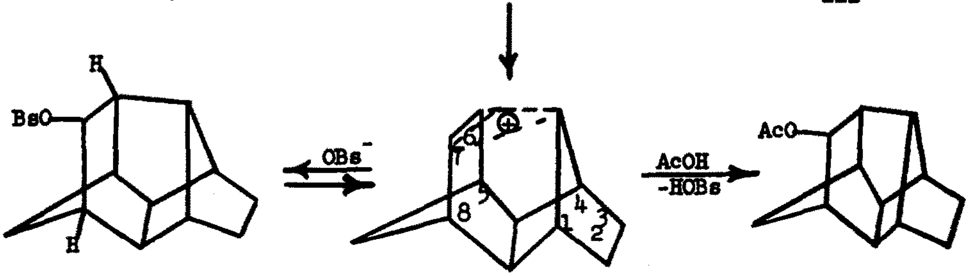
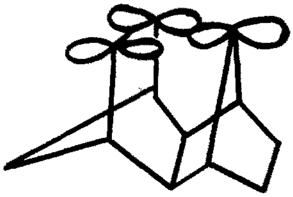
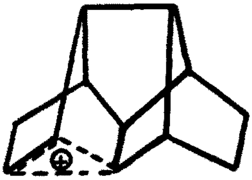


V-OBs IV V-OAc



IVa



IVb

Bromobenzenesulfonate II-OBs is very reactive in acetolysis, the first order rate constant being (2.38 ± 0.02) x 10^{-4} $sec.^{-1}$ at 25.0°. Ion pair return accompanies the acetolysis, 12% of a less reactive bromobenzenesulfonate being formed. The acetolysis rate constant of this latter isomer, measured after the solvolysis of II-OBs was complete, was (8.9 ± 0.3) x 10^{-5} $sec.^{-1}$ at 75.0°.

The solvolysis product from II-OBs is saturated and consists of a single compound as indicated by vapor phase chromatographic examination of the acetate (A-OAc) and the derived alcohol[4] (A-OH), m.p. 80.0-81.5°. The acetolysis rate constant of the bromobenzenesulfonate[4] (A-OBs) of this latter alcohol, m.p. 112.5-113.8°, is identical with that of the isomer formed from II-OBs during its acetolysis, being $(9.12 \pm 0.08) \times 10^{-5}$ sec.^{-5} at 75.0° and $(3.85 \pm 0.04) \times 10^{-6}$ sec.^{-1} at 50.4°. Further, no visible rearrangement occurs in acetolysis of A-OBs, only A-OAc being regenerated.

It is quite clear that A-OAc and A-OBs, the saturated isomers of II-OAc and II-OBs formed during acetolysis of II-OBs, have the V-structure. Thus, bromobenzenesulfonate A-OBs is recovered unchanged from an 18 hour treatment with potassium t-butoxide in refluxing benzene, no elimination being observed. Under these conditions, the olefinic group is introduced smoothly into other bicycloheptyl derivatives[5]. Further, the A-ketone from oxidation of A-OH showed no detectable deuterium exchange on treatment with 0.05 M sodium methoxide in 95% tetrahydrofuran-deuterium oxide for 51 hours at 50°. Under these conditions, ketone VI, obtained by oxidation of the corresponding alcohol[6], exchanges rapidly. The behavior of A-OBs and A-ketone is in accord with the position of the OBs and ketone groups in structures V-OBs and VII, since these would require a double bond or the enolate ion to be formed at a bridgehead. Finally, the carbon skeleton of V is confirmed by conversion of ketone VII to hydrocarbon VIII. Treatment of ketone VII with ethylene dithiol under forcing conditions converts it to an ethylene dithioketal. By Raney nickel desulfurization the latter is reduced to a saturated hydrocarbon whose infrared spectrum and vapor phase chromatographic behavior are

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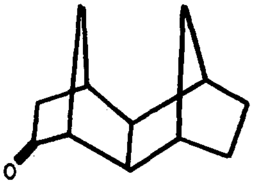
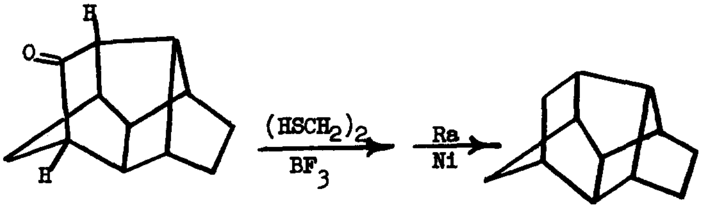
[5] (a) S. Winstein and E. T. Stafford, J. Am. Chem. Soc. **79**, 505 (1957); (b) S. Winstein and C. Ordronneau, ibid. **82**, 2084 (1960); (c) E. T. Stafford, F. Gadient and R. Hansen, unpublished work.

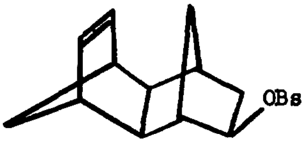
[6] S. B. Soloway, J. Am. Chem. Soc. **74**, 1027 (1952).



VI



VII VIII



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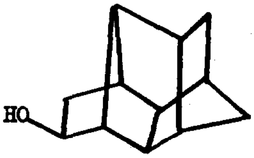
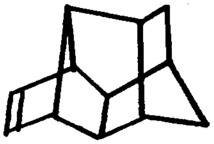


X



XI

identical with those of hydrocarbon[4] VIII obtained by hydrogenation of olefin[7] XI. The latter olefin is the one related to the "twisted" alcohol[3,7] X, one of the important rearranged saturated products of solvolysis of system[3] III or bromobenzenesulfonate[7] IX.

While rate of ionization in the II-system is not up to that observed[3] with III, it is nearly the same as that for anti-7-norbornenyl[2] (I). The rate constants observed with II-OTs or II-OBs are lower than those for the anti-7-norbornenyl analogs by a factor of only ca. 4. Thus, II-OBs ionizes more rapidly than 7-norbornyl[2,5c] bromobenzenesulfonate by the very large factor of 10^{11}.

The anchimerically accelerated ionization of II-OBs presumably leads to the non-classical cationic structure IV, which may be regarded as a cyclopropenyl cation in which 3-carbon segments have been inserted in each of two sides. The homoconjugation in ion IV, involving electron delocali-

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[7] L. de Vries and S. Winstein, ibid. in press.

zation across intervening carbon atoms[8], is wave-mechanically analogous to that in cyclopropenyl[9], except that 1,3- as well as 1,2-overlap and exchange integrals are involved. As illustrated in IVa, the axes of the p-orbitals on the three cationic carbon atoms are each turned ca. 90° from their orientation in cyclopropenyl. The situation is quite analogous in the non-classical cation described by Leal and Pettit[10].

The simplest mechanism of formation of the single solvolysis product from II-OBs and V-OBs involves solvent attack on carbon atoms C-6 and C-7 of ion IV, rather than on a further rearranged species such as IVb. This point is subject to stereochemical check, so the stereochemistry of solvolysis of V-OBs is being examined.

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[8] (a) M. Simonetta and S. Winstein, ibid. 76, 18 (1954); (b) S. Winstein, ibid. 81, 6524 (1959).

[9] (a) E. Hückel, Z. Physik 70, 204 (1931); (b) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, J. Am. Chem. Soc. 74, 4579 (1952); (c) W. G. Woods, R. A. Carboni and J. D. Roberts, ibid. 78, 5653 (1956).

[10] G. Leal and R. Pettit, ibid. 81, 3160 (1959).