Double-bond Participation and Conformational Effects in the Acetolysis of 1-Methylcyclohept-4-enylmethyl p-Bromobenzenesulphonate and 2-(1-Methylcyclohex-3-enyl)ethyl p-Bromobenzenesulphonate

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THE unsaturated cyclic p-bromobenzenesulphonates (brosylates) (I, R = H)[1] and (III, R = H)[2] have been shown to undergo acetolysis with double-bond participation: the rate factors are about 60 and 4, respectively, with respect to the corresponding saturated brosylates, and the major products are bicyclic, as formulated.

Double-bond participation in these systems can only involve conformers such as (Ib) and (IIIb), in which the CH_2OBs group is "axial" and, in the

case of (IIIb), oriented so as to be situated over the ring. When R = H, these conformers (and the corresponding transition states) embody more "skew-butane" interactions (two and three, respectively) than, e.g., the conformers (Ia) and (IIIa); when R = Me, however, the number of such interactions is the same in (Ia) and (Ib), and in (IIIa) and (IIIb), and the equilibrium concentrations of the "axial" conformers (Ib) and (IIIb) must therefore be greater when R = Me than when

R = H. These differences in ground-state "skew-butane" interactions were expected to lead to enhanced double-bond participation in the case of the methylated brosylates (I, R = Me) and (III, R = Me).

however, prediction (based upon ground-state "skew-butane" interactions) and experiment differ by a factor of about 250, corresponding to a free-energy difference of 3·9 kcal.mole⁻¹.

This difference can only be ascribed to eclipsing

$$\text{CH}_2\text{OBs}$$

(Ia)   (Ib)   (II)

(IIIa)   (IIIb)   (IV)   +   (V)
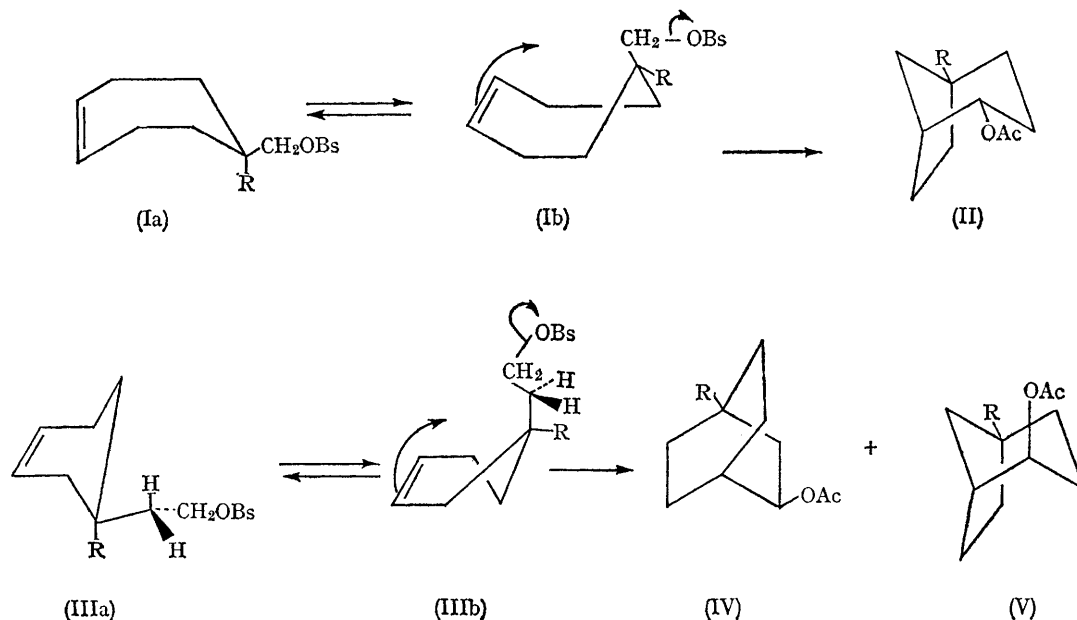
In fact, we have found that, whereas the acetolysis of the cyclohexenyl compound (III, R = Me)[3] is indeed faster than that of (III, R = H)[2] by a factor of about 25, the acetolysis of the cycloheptenyl compound (I, R = Me)[3] is slower than that of (I, R = H)[1] by a factor of at least 50. In both cases, the major products are bicyclic (II, and IV and V, R = Me).[4]

Considering the approximations involved, the agreement between prediction (a rate factor of 16)[5] and experiment in the case of the cyclohexenyl compound (III, R = Me) is quite good. In the case of the cycloheptenyl compound (I, R = Me),

interactions, in the transition state (cf., Ib), between the departing OBs anion and the neighbouring R group; such interactions are certainly larger when R = Me than when R = H. That they are so much larger is, however, unexpected; it emphasises the collinearity requirements of the incoming and outgoing groups in the transition state, and the importance of eclipsing interactions,[6] even when one of the eclipsed groups is in the process of undergoing intramolecular nucleophilic displacement.

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[1] G. Le Ny, Compt. rend., 1960, 251, 1526; H. Felkin, G. Le Ny, C. Lion, W. F. K. Macrosson, J. Martin, and W. Parker, Tetrahedron Letters, 1966, 157.

[2] S. Winstein and P. Carter, J. Amer. Chem. Soc., 1961, 83, 4484.

[3] The brosylates (I, R = Me) and (III, R = Me) were prepared by unambiguous routes and had spectral properties (i.r. and n.m.r.) consistent with the structures assigned to them. The acetolysis rates were measured at 79·9° in 0·01M-AcOH–AcO⁻.

[4] Detailed product analyses will be reported later. We are indebted to Prof. J. Klein for help with the preparation of 4-methyl 2-bicyclo[2,2,2]octanol, and to Dr. H. J. E. Loewenthal for advice on the first stages of the preparation of the 5-methylbicyclo[3,2,1]octan-2-ols.

[5] Calculated on the basis of an enthalpy difference of 0·85 kcal.mole⁻¹ per "skew-butane" interaction, non-chair conformations being neglected. See: E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, 1965, p. 23.

[6] Cf. P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon, and G. H. Schmid, J. Amer. Chem. Soc., 1965, 87, 1314.