Transannular Cyclopropyl Participation

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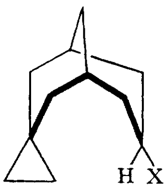
ALTHOUGH cyclopropylcarbinyl[1] and homocyclopropylcarbinyl[2] cationic systems have been examined in considerable detail, the possible interaction of a cyclopropyl group and developing carbonium ion which are separated by more than one carbon atom has received scant attention.[3] In this context, we chose to examine the solvolysis of (I; X = OTs).

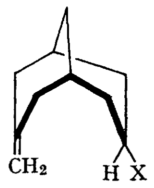
The alcohol, (I; X = OH) (m.p. 90—90·5°), obtained in 40% yield from (II; X = OH)[4] by treatment with CH_2I_2 and a zinc–copper couple,[5] exhibited a mass-spectral parent ion at 166 and maxima at 3627, 3063, 1176, 1036 and 1012 cm.$^{-1}$ in the infrared spectrum. The ^1H n.m.r. spectrum (100 Mc./sec., $CDCl_3$ solution) showed a nine-line multiplet at τ 5·2 (1H), two overlapping broad peaks at τ 7·9 and 7·98 (6H), a broad singlet at τ 8·5 (4H) with a sharp singlet superimposed at τ 8·63 (1H, hydroxylic), a doublet centred at τ 9·06 (2H, *J* 12 c./sec.) and a centrosymmetric A_2B_2 signal centred at τ 9·6 (4H, baseline width 45 c./sec.). The corresponding toluene-*p*-sulphonate (m.p. 68·5—70·5°) was solvolysed in sodium acetate–acetic acid, and gave as the sole product 3-homoadamantyl acetate (III; X = OAc) identified by lithium aluminium hydride reduction to an alcohol identical with an authentic sample of (III; X = OH) kindly supplied by Professor P. von R. Schleyer.

Acetolysis of (II; X = OTs)[4] gave 1-adamantyl acetate as the sole product, whereas corresponding treatment of (IV; X = OTs) gave 1-adamantyl acetate (82%), (II; X = OAc) (3%), and 7-exomethylenebicyclo[3,3,1]non-2-ene (15%). In an attempt to prepare the epimer of (I; X = OH), a Simmons–Smith reaction was carried out on (IV; X = OH), but the sole product proved to be identical with that obtained from mineral acid treatment of (IV; X = OH) and is formulated as the cyclic



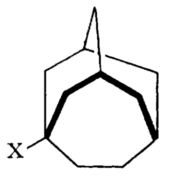
(I)

$k(25°)$ 2·14 × 10^{-4}



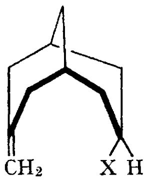
(II)

$k(25°)$ 6·56 × 10^{-4}

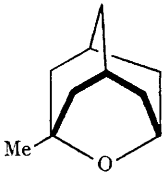


(III)

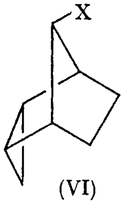
ether (V).[6] Preliminary results suggest that the conversion (IV; X = OH) → (V) can be a purely thermal rearrangement.



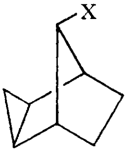
(IV)



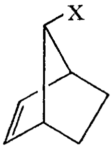
(V)



(VI)



(VII)



(VIII)

The striking difference in solvolysis rates[7,8] of (VI) and (VII) ($k_{\text{VI}}/k_{\text{VII}} = 10^{15}$) indicates that cyclopropyl participation is dependent on its orientation[9] with respect to the developing carbonium ion. In addition the relative reactivity of (VI) and (VIII) ($k_{\text{VI}}/k_{\text{VIII}} = 10^{3}$) has been taken[8] to indicate that, in general, a cyclopropyl group provides *better* anchimeric assistance than a double bond (in these cases *via* the tris- and bis-homocyclopropenyl cations respectively).

An examination of models of (I; X = OTs) and (II; X = OTs) shows that one lobe of the developing *p*-orbital at C-3 is *in the plane of* and directed toward the cyclopropane ring and π-orbitals respectively, yet *there is little difference* in the anchimeric assistance afforded by the transannular groups $k_{\text{II}}/k_{\text{cyclohexyl}} = 13{,}500$; $k_{\text{I}}/k_{\text{cyclohexyl}} = 4500$ at 25°). The difference in these two sets of data may be a reflection of the uniquely stabilised *symmetrical* nonclassical intermediates involved in the solvolysis of (VI) and (VIII) as compared with *unsymmetrical* nonclassical or probably preferred classical tertiary 1-adamantyl and 3-homoadamantyl[10] cations in the case of (II) and (I).

(*Received, July 27th,* 1967; *Com.* 782.)

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[1] C. G. Bergstrom and S. Siegel, *J. Amer. Chem. Soc.*, 1952, **74**, 145; H. Hart and P. A. Law, *ibid.*, 1959, **81**, 320; 1962, **84**, 2462; J. D. Roberts *et al.*, *ibid.*, 1959, **81**, 4390; 1961, **83**, 2719, 3671; *Tetrahedron*, 1960, **11**, 171; C. U. Pittman, jun., and G. A. Olah, *J. Amer. Chem. Soc.*, 1965, **87**, 2998, 5123.

[2] (a) S. Winstein, J. Sonnenberg, and L. De Vries, *J. Amer. Chem. Soc.*, 1953, **81**, 6523; (b) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, 1961, **83**, 3235, 3244; (c) T. Norin, *Tetrahedron Letters*, 1964, 37; (d) S. Winstein, P. Bruck, P. Radlick, and R. Baker, *J. Amer. Chem. Soc.*, 1964, **86**, 1867; (e) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, 1965, **30**, 2278; (f) A. K. Colter and R. C. Musso, *J. Org. Chem.*, 1965, **30**, 2462.

[3] A. C. Cope, S. Moon, and C. H. Park, *J. Amer. Chem. Soc.*, 1962, **84**, 4850.

[4] M. A. Eakin, J. Martin, and W. Parker, *Chem. Comm.*, 1965, 206.

[5] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 1958, **80**, 5323; 1959, **81**, 4256 and ref. 2 (b).

[6] W. A. Ayers and K. Piers, *Chem. Comm.*, 1965, 541.

[7] H. Tanida, T. Tsuji and T. Irie, *J. Amer. Chem. Soc.*, 1967, **89**, 1953.

[8] M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Heywood-Farmer, *J. Amer. Chem. Soc.*, 1967, **89**, 1954.

[9] C. F. Wilcox, jun., and R. G. Jesaitis, *Tetrahedron Letters*, 1967, 2567 and references cited therein.

[10] G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 582.