Solvolysis of *cis*- and *trans*-9-Decalyl *p*-Nitrobenzoates

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ALTHOUGH many studies have been made of bridgehead carbonium ion reactivity in bridged polycyclic systems, bridgeheads in fused-ring molecules have received little attention.[1] We record data derived from such systems, which suggest the existence of diastereisomeric carbonium ions.

The *p*-nitrobenzoates of *cis*- and *trans*-9-decalol[2] were prepared by the reaction of their lithium salts with *p*-nitrobenzoyl chloride in hexane solution. Solvolysis rates for these compounds and models are given in Table 1; product analyses are in Table 2. Rate constants were determined titrimetrically.

TABLE 1

Solvolysis of the p-*nitrobenzoates in* 60% *aqueous acetone*

R	Temp.	10^{-5} *k* (sec.$^{-1}$)	Rel. rate	$\Delta H\ddagger$ (kcal.)	$\Delta S\ddagger$ (eu.)
Me_3C	100°	1·53	1·00		
Et_3C	100	8·66	5·80		
cis-9-decalyl	90	0·81			
	100	2·21	1·45	27·6	−11
	110	6·25			
trans-9-decalyl	90	0·24			
	100	0·69	0·45	28·1	−9
	110	1·96			

In the extreme that both decalyl systems solvolyze *via* a transition state resembling a single decalyl cation, then the relative rates of solvolysis are determined by the ground-state energies of the two *p*-nitrobenzoates. Since these energies differ by *ca.* 2·0 kcal.,[3] the *cis*-isomer is expected to solvolyze more rapidly than the *trans*-isomers by about two powers of ten. An alternate calculation, with the potential functions of Hendrickson,[4] and on the assumption that individual transition states resemble the respective starting materials, gave a rate difference of *ca.* 3. The latter case is clearly in accord with the experimental data, which show a rate factor of 3·3 which favours the *cis*-derivative.

Analyses of the products of solvolysis display small, but significant, differences. If the same cation were formed from both isomeric *p*-nitrobenzoates, identical product distributions would be expected. Thus both kinetic and product data suggest initial ionization to geometrically different, but interconvertable, carbonium ions. These species equilibrate to a mixture rich in the more stable *trans*-like ion at about the same rate as they suffer elimination and substitution.[5]

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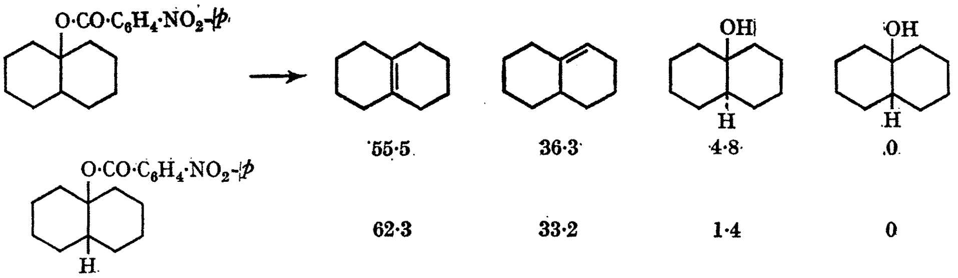
TABLE 2

Products of 9-*decalyl solvolysis* (%)



55·5	36·3	4·8	0
62·3	33·2	1·4	0

±2%; Determined gas chromatographically by comparison with authentic samples; Perkin-Elmer model 810, 150′ DC-550 silicone Golay column; remainder unidentified.

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[1] R. C. Fort, jun., and P. von R. Schleyer, *Adv. Alicyclic Chem.*, 1966, **1**, 283.

[2] H. Christol and G. Solladie, *Bull. Soc. chim. France*, 1966, 1299.

[3] This value is obtained by combining the *A* value of the hydroxyl-group with the energy difference between *cis*- and *trans*-decalin. *Cf.* E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley–Interscience, New York, 1965.

[4] J. Hendrickson, *J. Amer. Chem. Soc.*, 1961, **83**, 4537.

[5] We have recently become aware of similar conclusions reached independently by Professor C. A. Grob; these appeared in print after this note was submitted; A. F. Boschung, M. Geisel, and C. A. Grob, *Tetrahedron Letters*, 1968, 5169.