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Solvolysis of 2-Oxiryl-2-propyl *p*-Nitrobenzoate. Evidence on the Mode of Stabilization of the Oxirylcarbinyl Cation

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The effect of a neighboring oxiryl group on the stability of an adjacent developing cationic center is minor in comparison to a cyclopropyl group. Thus, a neighboring oxiryl group increases the rate of solvolysis by a factor of 10 over an acyclic analogue. By comparison, a neighboring cyclopropyl provides a rate enhancement of 10^5 over an acyclic control.

There has been considerable interest in the solvolytic behavior of heterocyclic analogues of cyclopropylcarbinyl systems. The effect of a neighboring oxirane has been studied by several workers.[1-6] The oxirane ring can theoretically stabilize an adjacent cationic center by conjugative stabilization through its strained bonds and/or by participation of the nonbonded electrons on oxygen.[1-6]

However, the degree to which a neighboring oxirane group stabilizes an adjacent cationic center is in doubt. Reports have varied from a lack of significant participation to an oxirane group being almost as effective as a cyclopropyl group in stabilizing a cationic center.[1,5,6] Therefore, a comparison of the rates of solvolysis of the 2-oxiryl-2-propyl system with a suitable reference system, 2-methyl-3-methoxy-2-butyl, which allows for the estimation of inductive effects and the participation by lone pair electrons on a β oxygen, and the 2-cyclopropyl-2-propyl system with the 2,3-dimethyl-2-butyl system was undertaken.

Results

Synthesis. 2-Oxiryl-2-propyl *p*-nitrobenzoate (1) was prepared by the epoxidation of 2-methyl-3-buten-2-yl *p*-nitrobenzoate with *m*-chloroperbenzoic acid at 0 °C in methylene chloride. At higher temperatures the oxiryl ring is opened by the *m*-chlorobenzoic acid which is formed in the reaction.

Rates. Rates of solvolysis were determined titrimetrically in 80:20 acetone–water (v/v) by the procedure previously reported.[7] The compounds followed first-order kinetics except for 2-oxiryl-2-propyl *p*-nitrobenzoate (1) which exhibited a decrease in rate after 20% reaction. Therefore, the initial rate constant was determined during the first 20% of the reaction. This deviation was due to side reactions as described below in the product study. The rate data appear in Table I.

Products of Solvolysis. Oxiranes undergo facile reactions with both electrophilic and nucleophilic reagents. As noted in the synthesis of 1, the presence of benzoic acid derivatives leads to opening of the oxiryl ring. Thus, during solvolysis of 1, ≥50% rearranges to a secondary *p*-nitrobenzoate (via NMR). The formation of relatively unreactive secondary esters results in a decrease in rate.

Kinsman has reported that solvolysis of 2-oxiryl-2-propyl dinitrobenzoate gives a complex mixture of products.[9] Between 65 and 80% rearranges to 2,2-dimethyl-3-oxetanyl dinitrobenzoate. The products arising from solvolysis are 2,2-dimethyl-3-oxetanol and polymer (polyether). 2-Oxiryl-2-propanol rearranges to triols under solvolytic conditions; however, none was reported in the reaction products.[9]

These results suggest that 2-oxiryl-2-propyl derivatives react via ring expansion to give secondary esters (ion pair return) and oxetanols (hydrolysis by an ionizing mechanism in which the dinitrobenzoate acts as a leaving group).[3,9]

Discussion

The strained bonds in an oxiryl group have been reported to be almost as effective as the strained bonds of the cyclopropyl group in stabilizing a cationic center.[1,5] However, the strain energy in the oxiryl group is substantially less than in a cyclopropyl group.[10]

If neighboring group stabilization is important in a system, the rate of solvolysis must be greater than the unassisted rate of solvolysis estimated from reference compounds.[11] Clearly the choice of a reference system which reacts without stabilization is critical.[7,12] The isopropyl group is a suitable model system for the cyclopropyl group because of similar steric requirements.[13] On the other hand, the isopropyl group is a

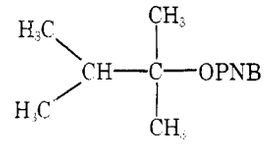
Table I. Rate Constants in 80% Acetone

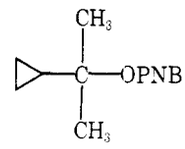
p-nitrobenzoate	temp, °C	k_1, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
2,3-dimethyl-2-butyl[a] (3)	25.0	2.15×10^{-10}[b]	28.5	−7.3
2-cyclopropyl-2-propyl[a] (2)	25.0	3.75×10^{-5}	20.8	−9.0
2-methyl-3-methoxy-2-butyl (4)	150.0	1.97×10^{-5}		
	125.0	1.66×10^{-6}		
	25.0	1.32×10^{-12}[b]	32.5	−3.8
2-oxiryl-2-propyl (1)	150.0	1.49×10^{-4}[c]		
	125.0	1.31×10^{-5}[c]		
	25.0	1.33×10^{-11}[b]	(32)	(−1)

[a] Reference 8. [b] Calculated from data at other temperatures. [c] Initial (20%) rate constants.

poor reference system for the oxiryl group because of the greater electronegativity of the oxygen which can decrease the rate as well as any participation by the nonbonded electrons on oxygen. Although neighboring alkoxy participation has been reported to be unimportant, it can decrease the rate of solvolysis.[14] Therefore, the 1-methoxy-1-ethyl group was used as a reference system for the oxiryl group.

2-Cyclopropyl-2-propyl p-nitrobenzoate (2) solvolyzes 175 000 times faster than 2,3-dimethyl-2-butyl p-nitrobenzoate (3). Thus, the strained carbon–carbon bonds in cyclo-



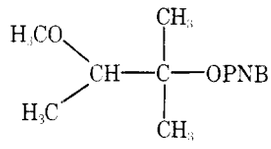


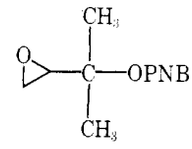
3 2

relative rate	1.0	175 000

propyl are playing a substantial role in the stabilization of the developing cationic center.

2-Oxiryl-2-propyl p-nitrobenzoate (1) reacts 10 times faster than 2-methyl-3-methoxy-2-butyl p-nitrobenzoate (4).





4 1

relative rate	1.0	10.1

Clearly the strained bonds in the oxiryl group are only contributing a minor amount of stabilization to the developing cationic center.

Conclusions

Using 4 as a model system for an indication of the inductive effect of the oxygen and any participation by the nonbonded electrons of oxygen[14] on the rate, the strained oxirane bonds in 1 increase the rate of solvolysis by a factor of 10. Thus, these results indicate that the oxiryl group is substantially less effective than a cyclopropyl group in stabilizing an adjacent cationic center. Indeed, the rate of solvolysis of 1 is 10^5 times slower than the rate of solvolysis of 2 under similar conditions.

Experimental Section

2-Methyl-3-buten-2-yl p-nitrobenzoate was prepared from 2-methyl-3-buten-2-ol (Aldrich Chemical Co.) via the lithium alkoxide method[7] (89% yield), mp 115.5–116.5 °C.

Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.38; H, 5.62; N, 6.05.

2-Oxiryl-2-propyl p-Nitrobenzoate. A 1-g (4.25 mmol) amount of 2-methyl-3-buten-2-yl p-nitrobenzoate in 50 mL of methylene chloride was reacted with 7.42 mmol of m-chloroperbenzoic acid at 0 °C for 41 days. The precipitated m-chlorobenzoic acid was filtered, and the residue from the methylene chloride was recrystallized from hexane to a constant melting point: mp 62–63 °C; NMR ($CDCl_3$) δ 1.63 (s, 6 H, CH_3), 2.86 (d, J = 2 Hz, 1 H, epoxy CH), 3.43 (t, J = 2 Hz, 2 H, epoxy CH_2), 8.27 (d, 4 H, OPNB).

Anal. Calcd for $C_{12}H_{13}NO_5$: C, 57.37; H, 5.21; N, 5.58. Found: C, 57.43; H, 5.30; N, 5.47.

2-Methyl-3-methoxy-2-butyl p-nitrobenzoate was prepared from 2-methyl-3-methoxy-2-butanol[15] via the lithium alkoxide method (85% yield): mp 90.0–91.0 °C; NMR ($CDCl_3$) δ 1.23 (d, J = 7 Hz, 3 H, CH_3), 1.60 (s, 6 H, CH_3), 3.43 (s, 3 H, OCH_3), 3.80 (q, J = 7 Hz, 1 H, CH), 8.23 (d, 4 H, OPNB).

Anal. Calcd for $C_{13}H_{17}NO_5$: C, 58.41; N, 6.41; N. 5.24. Found: C, 58.36; H, 6.37; N, 5.21.

Registry No.—1, 67382-29-0; 2, 23437-9902; 3, 55705-64-1; 4, 67382-28-9; 2-methyl-3-buten-2-yl p-nitrobenzoate, 35945-67-6; 2-methyl-3-buten-2-ol, 115-18-4; 2-methyl-3-methoxy-2-butanol, 67382-30-3.

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