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RACEMIZATION AND RADIO-CHLORIDE EXCHANGE OF P-CHLOROBENZHYDRYL CHLORIDE IN ACETONE[1]

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In rearrangement, exchange and solvolysis reactions of neutral organic substrates proceeding by way of carbonium ions, it is important to distinguish between ionization and dissociation and to consider explicitly the role of different ionic intermediates representing various stages of ionization-dissociation[2,3]. In fact, a considerable body of information is now available on the intimate course of carbonium ion reactions of allylic, homoallylic and various other rearranging systems[2,3]. We have now compared the rates of racemization and radio-chloride exchange of p-chlorobenzhydryl chloride in acetone solvent. These differ by a substantial factor and therefore give considerable insight into the behavior of the ionic intermediates involved.

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[1] Research supported by the National Science Foundation.

[2] (a) W. G. Young, S. Winstein and H. L. Goering, *J. Am. Chem. Soc.* **73**, 1958 (1951); (b) S. Winstein, *et.al.*, *ibid.* **74**, 1154, 2165, 2171 (1952); (c) C. A. Grob and S. Winstein, *Helv. Chim. Acta* **35**, 782 (1952).

[3] (a) S. Winstein, *et.al.*, *J. Am. Chem. Soc.* **76**, 2597 (1954); *Chemistry and Industry*, 664 (1954); *J. Am. Chem. Soc.* **78**, 328, 2763, 2767, 2784 (1956); **80**, 169, 459 (1958); (b) S. Winstein, *Experientia Supplementum II* 137 (1955); (c) E. F. Jenny and S. Winstein, *Helv. Chim. Acta* **41**, 807 (1958).

Treatment of optically active p-chlorobenzhydrol[4], m.p. 53-55°, $[\alpha]_D^{25}$ +18.2° (Me_2CO,C=13), with thionyl chloride in benzene gives rise to p-chlorobenzhydryl chloride, $[\alpha]_D^{25}$ -3.4° (Me_2CO,C=10), with a low rotation which is sufficiently high, however, to permit measurement of first order racemization rates with an accuracy of ca. 5 percent.

As summarized in Table I, p-chlorobenzhydryl chloride racemizes with first order kinetics at a convenient rate in acetone at 75°C. The first order racemization rate constant, k_α, is increased slightly by added lithium chloride or perchlorate and enormously by tetrabutylammonium chloride or perchlorate. The first order rate constants[5] for exchange with lithium or tetrabutylammonium radio-chloride, symbolized by k_e, are considerably smaller than the polarimetric rate constants. The k_e and k_α values show a roughly linear[3a] pattern of increase with salt concentration, (MY), and they may be fit quite well by equations (1) and (2), respectively, as summarized in Table II.

$$k_e = b_e \text{ (MCl)} \qquad (1)$$

$$k_\alpha = k_\alpha^\circ [1 + b_\alpha \text{ (MY)}] \qquad (2)$$

The relative efficiency of perchlorate salts compared to the corresponding chlorides in promoting racemization and the observed (k_α/k_e) ratios of ca. 15 in the presence of chloride salts show that ionization is the main cause of racemization. More direct so-called S_N2 displacement by added chloride is relatively unimportant, as can be shown analytically with

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[4] J. Kenyon and G. H. Green, J. Chem. Soc. 751 (1950).

[5] e.g., L. J. leRoux and E. R. Swart, ibid. 1475 (1955).

Table I

Summary of Racemization and Radio-Chloride Exchange Rates in Acetone at 75.0°C

[RCl] 10^2M	Added Salt	10^2 M	10^5k Values (sec $^{-1}$)		
			10^5k_α	10^5k_e	(k_α/k_e)
17.2[a]			1.29		
16.0[a]	LiCl	0.55[b]	1.74	0.101	17
16.4[a]	LiCl	1.10[b]	2.16	.169	13
12.1[a]	$LiClO_4$	4.00	7.37		
16.9[a]	Bu_4NClO_4	4.00	54.4		
1.07	Bu_4NCl	0.623[b]		1.05	
12.1[a]	Bu_4NCl	.900	22.6		16
1.04	Bu_4NCl	1.71[b]		2.75	
1.10	Bu_4NCl	1.79[b]		2.83	
1.16	Bu_4NCl	2.60[b]		4.11	
19.1[a]	Bu_4NCl	2.70	65.4		15
20.0[a]	Bu_4NCl	4.65[b]	107.0	7.39	15
1.07	Bu_4NCl	4.84[b]		7.45	

[a] Optically active chloride

[b] Radio-chloride

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the aid of equations (3), (4) and (5). In these equations, k_1 and k_2 are

$$k_e = k_1E + k_2 \qquad (3)$$

$$k_\alpha = k_1R + 2\,k_2 \qquad (4)$$

Table II

Fit of k_e and k_α Values to Equations (1) and (2)

Salt	10^5k° (sec^{-1})	b	Ave. Fit % of k
Racemization			
LiCl	1.29	62	0.6
$LiClO_4$	1.29	118[a]	-
Bu_4NClO_4	1.29	1030[a]	-
Bu_4NCl	1.29	1780	2.2
Exchange			
LiCl	0	1.6×10^{-4}	8.5
Bu_4NCl	0	1.6×10^{-3}	2.7

[a] Based on only one salt concentration

$$\frac{k_e}{k_\alpha} = \frac{(E/R) + (k_2/k_1R)}{1 + 2\,(k_2/k_1R)} \qquad (5)$$

first order rate constants for ionization and S_N2 displacement, respectively, R is the fraction of all the ionic intermediates from ionization of chlorobenzhydryl chloride which lose stereochemical configuration and become racemic, and E is the fraction of all such ionic intermediates which lead to chloride exchange. By setting (E/R) equal to zero an upper limit to the ratio $[k_2/(k_1R)]$ of $[(k_e/k_\alpha) / (1 - 2\,k_e/k_\alpha)]$ may be set. On this basis, no more than ca. 13 percent of the racemization of p-chlorobenzhydryl chloride in the presence of chloride salt can be due to direct chloride displacement.

The b_α values in Table II reflect considerable specificity as regards the nature of the added salt, and they become very large for tetrabutylammonium chloride and perchlorate. Since racemization proceeds largely through ionization, the b_α values show that salt effects on ionization of chlorobenzhydryl chloride can be very large in acetone[6].

Setting (k_2/k_1R) equal to zero in equation (5) gives an upper limit of (k_e/k_α) or 1/15 for the ratio (E/R). Therefore, less than one-fifteenth as big a fraction of ionic intermediates from ionization of chlorobenzhydryl chloride lead to exchange as become racemic. Since the maximum value of R is unity, the maximum value of E is 0.07. Chloride exchange is inevitable if dissociated carbonium ions are formed and returned to covalent chloride[3a]; therefore, the maximum fraction of ionic intermediates which become dissociated before return to the covalent condition is also 0.07.

The above analysis shows that at least 93 percent of carbonium ion intermediates from ionization of chlorobenzhydryl chloride return to the covalent condition before dissociating. Since at least some of the ionic intermediates may be expected to maintain configuration and make R less than unity, the fraction of intermediates which become covalent before dissociating may be even greater.

In acetic acid solvent[2,3], rate of solvolysis (k_t), as well as racemization and radio-chloride exchange, can be measured. In this solvent, k_α exceeds both k_e and k_t by factors[7] considerably larger than the (k_α/k_e) ratios observed in acetone.

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[6] S. Winstein, S. Smith and D. Darwish, J. Am. Chem. Soc. **81**, 5511 (1959); Tetrahedron Letters **16**, 24 (1959).

[7] J. S. Gall, unpublished work.