

lated presence of nonclassical resonance in the norbornyl cation or transition state.⁷

It has been suggested that the failure to observe any decreased contribution of the 2-methyl and 2-phenyl substituents in the norbornyl derivatives may be due to the fortuitous cancellation of opposing factors. On the one hand, carbon participation might decrease from norbornyl to 2-methylnorbornyl to 2-phenylnorbornyl, with steric acceleration of the solvolysis providing a compensating rate-enhancing factor.⁸ However, this possible interpretation is rendered untenable by the observation that carbon participation is not a significant factor in the solvolysis of 1,2-dimethylnorbornyl derivatives.¹¹

Another possible interpretation would postulate that the relief of steric strain in the essentially classical tertiary norbornyl derivatives counterbalances precisely the nonclassical resonance energy in the *exo*-norbornyl transition state. However, this requires the highly improbable assumptions that the steric requirements of *endo*-2-methyl and *endo*-2-phenyl are equal and that the decrease in steric strain between the initial and the transition states in these tertiary derivatives will amount to 6.0 kcal./mole.

Consequently, it does not appear possible to escape the conclusion that the norbornyl cation fails to exhibit the delocalization of the charge from the 2- to the 1- and 6-positions required by the currently proposed nonclassical structure. We have failed to find any independent experimental kinetic evidence to support the proposal that cations of the norbornyl type exist as nonclassical resonance hybrids,^{2,9} rather than as an equilibrating pair of ions^{9a,10} (IV). Moreover,



the classical tertiary norbornyl cations exhibit precisely those properties, such as enhanced rates, high *exo/endo* rate ratios, and *exo* substitution, previously considered to be characteristic of the nonclassical norbornyl structure.¹

It must be concluded that formulation of the norbornyl cation as an equilibrating pair of classical ions (IV) is in better agreement with all of the experimental data presently available.

(7) If the observed *exo/endo* rate ratio for norbornyl brosylate is the result of participation in the *exo*, but not in the *endo*, we can arrive at an estimate of the nonclassical resonance stabilization in the transition state. Correction of the *exo/endo* rate ratio of 350 for internal return results in a relative rate of ionization of 1350. This is equivalent to 5 kcal. By adding 1 kcal. to correct for the higher ground-state energy of the more strained *endo* brosylate, we arrive at a value of 6 kcal./mole for the stabilization of the transition state for *exo*-norbornyl brosylate, as compared to the presumably classical transition state for the *endo* isomer. (It is customary to assume that resonance effects are only partially developed in the transition state. Consequently, nonclassical resonance would be considerably larger in the norbornyl cation.) It should be noted that the additional resonance stabilization afforded by the phenyl group in the *t*-cumyl as compared with the *t*-butyl chloride transition state is of the same order of magnitude (Table I). It is evident that the proposed nonclassical resonance stabilization is sufficiently large so that, if really present, it should exhibit some experimentally observable effects.

(8) Private communication from Professor P. von R. Schleyer.

(9) (a) T. P. Neville, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939); (b) F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature*, **168**, 65 (1951).

(10) H. Meerwein and K. van Emster, *Ber.*, **55**, 2500 (1922).

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Racemization and Radiochloride Exchange of *p*-Chlorobenzhydryl Chloride in a Series of Solvents¹ Sir:

Ion pair return during solvolysis causes the polarimetric rate constant, k_{α} , for formation of racemic starting material and product from *p*-chlorobenzhydryl chloride (RCI) to exceed the titrimetric rate constant, k_t , by a substantial factor in acetic acid^{2a} and by a smaller one in 80% acetone.^{2b} Similarly, in the aprotic solvent acetone,^{2c} k_{α} is much larger than the first-order radiochloride exchange rate constant, k_e , with low concentrations of added labeled LiCl. Several other aprotic solvents have now been studied so that the available data provide some perspective over a considerable solvent spectrum and point up the striking solvent specificity of the (k_{α}/k_e) ratios.

Summarized in Table I are the k_{α}^0 and k_t^0 values in the solvolyzing solvents at or extrapolated to zero concentration of added salt. Also listed are k_{α}^0 , k_e^0 , and k_{2e} values in four aprotic solvents.³ In MeNO₂, MeCN, and HCONMe₂ (DMF), k_e values at low concentrations of labeled Bu₄NCl are fitted to eq. 1, where k_{2e} is the slope and k_e^0 is the intercept of a plot of k_e vs. [Bu₄NCl]. In all three cases k_{α}^0 exceeds k_e^0 by a substantial factor.

$$k_e = k_e^0 + k_{2e}[\text{Bu}_4\text{NCl}] \quad (1)$$

$$\log k_{\alpha}^0 = 4.22 + 2.02 \log k_1 \quad (2)$$

As regards mechanisms associated with k_{α}^0 , k_e^0 , and k_{2e} , it is clear that k_{α}^0 is associated with ionization² of RCI. This conclusion is supported by the variation

TABLE I

POLARIMETRIC (k_{α}^0), TITRIMETRIC (k_t^0), AND EXCHANGE (k_e^0 AND k_{2e}) RATE CONSTANTS FOR *p*-CHLOROBENZHYDRYL CHLORIDE AT 75.0°

Solvent	$10^4 k$, sec. ⁻¹			$10^3 k_{2e}$, M ⁻¹ sec. ⁻¹
	k_{α}^0	k_t^0	k_e^0	
AcOH ^{2a}	68 ^{a,c} (21,300) ^b	1.8 ^{a,c}		
80% Me ₂ CO ^{2b}	60 ^a (11,650) ^b	23.1 ^a		
MeNO ₂	145		3.25	1.03
MeCN	60.7		0.2	1.23
HCONMe ₂	18.9		5.0	2.00
Me ₂ CO ^{2c}	1.38		<0.03	1.90

^a 25.0°. ^b Extrapolated from values at 25.0°. ^c From data with either LiOAc or Bu₄NOAc; erroneously high k values previously reported^{2a} for Bu₄NOAc.

of k_{α}^0 over a range of 4.2 powers of ten as solvent ionizing power varies. In fact, $\log k_{\alpha}^0$ in all six solvents at 75° is linear in $\log k_1$ for *p*-methoxyneophyl toluenesulfonate,⁴ the slope of the plot being 2.0 (eq. 2). Further, k_{α}^0 in MeNO₂ shows an appropriate α -deuterium isotope effect, k_H/k_D being 1.05.

The k_{2e} values for the slopes of the plots of k_e vs. [Bu₄NCl] are nearly identical in the four aprotic

(1) Research sponsored by the National Science Foundation.

(2) (a) S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1010 (1960); (b) S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Letters*, **No. 22**, 12 (1960); (c) S. Winstein, A. Ledwith, and M. Hojo, *ibid.*, **No. 10**, 341 (1961).

(3) In all four aprotic solvents, RCI is sufficiently stable for attainment of the calculated statistical distribution of radiochloride in the exchanges.

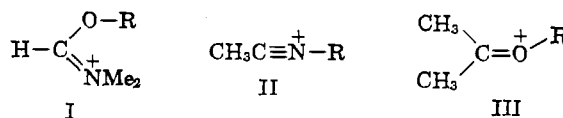
(4) S. Smith, A. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

solvents. Further, in MeNO₂, MeCN, and Me₂CO, the k_{2e} values for *p*-chlorobenzhydryl chloride are either nearly identical with or somewhat larger than those for the unsubstituted benzhydryl chloride. The available evidence suggests that the k_{2e} values are rate constants for SN2 attack^{2c} on covalent RCl. A similar conclusion has been reached by Pocker⁵ in the case of bromide exchange of benzhydryl bromide in MeNO₂.

The k_e^0 intercept values represent rate constants for formation of capturable intermediates extrapolated to zero salt concentration. In MeNO₂, MeCN, and DMF, the k_e^0 values are smaller than those for benzhydryl chloride by factors of 2.4–2.5, so that the *p*-Cl substituent effect is in line with the idea that k_e^0 is associated with ionization of RCl. For benzhydryl bromide in MeNO₂, Pocker⁵ observed the same intercept values from bromide exchange or reaction with triethylamine, and he also noted common ion depression of the amine reaction by bromide salt. On this basis, he concluded that the capturable intermediate is the dissociated carbonium ion. Analogously, the capturable intermediate for the k_e^0 values in all four aprotic solvents may well be a dissociated species.⁶

In Table II are summarized k_a^0/k_t^0 ratios for the solvolyzing solvents and k_a^0/k_e^0 ratios for the aprotic ones. These values are lower limits for the ratio of

the tendency for such nucleophilic solvent intervention is high for DMF⁸ and low for CH₃CN.



While an ion like I would be sufficiently long-lived to become a dissociated cation (free of the counter chloride ion), the nucleophilic intervention of DMF in the radiochloride exchange scheme must occur at a stage of ionization–dissociation of RCl earlier than the dissociated R⁺ ion. If DMF attacks a carbonium chloride ion pair, one can understand k_e^0 being sensitive to solvent nucleophilicity, while k_a^0 is not.

(8) See, e.g., F. C. Chang and R. T. Blickenstaff, *J. Am. Chem. Soc.*, **80**, 2906 (1960), for nucleophilic attack by DMF; for related effects of MeNO₂ and Me₂CO, see Y. Pocker, *J. Chem. Soc.*, 240 (1958); H. Burton and G. W. H. Cheeseman, *ibid.*, 832 (1953); R. A. Sneen and H. Weiner, *J. Am. Chem. Soc.*, **85**, 2181 (1963).

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Radiochlorine Exchange and Racemization of 1-Phenylethyl Chloride and *p*-Methylbenzhydryl Chloride in Nitromethane^{1,2}

Sir:

In the presence of added pyridine, the initial first-order rate coefficients of styrene, acid, and chloride ion production from 1-phenylethyl chloride at 99.8° in solvent nitromethane are practically identical (*i.e.*, dehydrohalogenation) and independent of pyridine concentration: $V_D = k_1^D[\text{RCl}]$ with $k_1^D = 0.29 \times 10^{-5} \text{ sec}^{-1}$. In the presence of added Et₄NCl³⁶, $V_D = k_1^D[\text{RCl}] + k_2^D[\text{RCl}][\text{Et}_4\text{NCl}]$ with $k_1^D = 0.29 \times 10^{-5} \text{ sec}^{-1}$ and $k_2^D \approx 2.0 \times 10^{-5} \text{ sec}^{-1} \text{ l. mole}^{-1}$, but the radiochlorine exchange³ is a strictly bimolecular process: $V_E = k_E[\text{RCl}] = k_2^E[\text{RCl}][\text{Et}_4\text{NCl}^{36}]$, with $k_2^E = 6.1 \times 10^{-3} \text{ sec}^{-1} \text{ l. mole}^{-1}$. For racemization we find $V_a = k_a[\text{RCl}] = k_1^a[\text{RCl}] + k_2^a[\text{RCl}][\text{Et}_4\text{NCl}^{36}]$, where $k_1^a = 1.2 \times 10^{-5} \text{ sec}^{-1}$ and $k_2^a = 12.4 \times 10^{-3} \text{ sec}^{-1} \text{ l. mole}^{-1}$. It will be noticed that in the unimolecular region, $[\text{NET}_4\text{Cl}] \rightarrow 0$, the polarimetric rate coefficient, k_1^a , for the formation of racemic starting material and product is about four times larger than the rate coefficient for chemical capture, $(k_1^D + k_1^E) \approx k_1^D$.⁴ The route corresponding to k_1^a is associated with ion pair return after reorganization^{4,5}; its free energy of activation is lower than that of

ionization rate to rate of chemical capture.² They are also lower limits to the ratio of rate of ionization to rate of formation of dissociated carbonium ions.² Very interesting is the large range of k_a^0/k_e^0 values in the aprotic solvents. Most striking are the values in MeNO₂, MeCN, and DMF, three solvents with essentially identical dielectric constants. In DMF the ratio is as low as 4, while in CH₃CN it is as high as 304. The most plausible single factor responsible for the large solvent specificity of the k_a^0/k_e^0 ratios in these three solvents is nucleophilic solvent intervention which makes k_e^0 a larger fraction of k_a^0 than it would otherwise be. For example, in the case of DMF, cation I would be an intermediate for the k_e^0 rate. Such solvent intervention is conceivable with the other aprotic solvents as well, salts of the I, II, and III types being known.⁷ The present data suggest that

(5) Y. Pocker, *J. Chem. Soc.*, 3939, 3944 (1959).

(6) With *p*-chlorobenzhydryl chloride and triethylamine in MeNO₂ at 75°, the situation is quite complex. First-order rate constants for the amine reaction, followed by amine consumption or chloride ion formation, obey an equation like (1) with the intercept the same as for chloride exchange. Further, in the presence of sufficient Et₃N, the exchange reaction with Bu₄NCl has its intercept k_e^0 value suppressed to *ca.* zero and its k_{2e} slope is relatively unaffected. The product of the amine reaction is not the RN⁺Et₃Cl⁻ salt, however. The latter, independently prepared, decomposes rapidly at 75° with chloride ion disappearance, and subsequently chloride ion slowly reappears.

(7) H. Meerwein, *et al.*, *Angew. Chem.*, **67**, 374 (1955); *Ber.*, **89**, 209, 2060 (1956).

(1) This work was supported in part by a grant from the National Science Foundation.

(2) Presented in part at the Nineteenth IUPAC Congress, London, 1963.

(3) The rate of loss of tracer from Et₄NCl³⁶ contains a term due to the dehydrohalogenation of 1-phenylethyl chloride (isotopic dilution) and a term due to substitution (isotopic exchange). To obtain the true component of isotopic exchange we corrected for dehydrohalogenation. The values thus obtained have also been confirmed by determining the rate of incorporation of Cl³⁶ into 1-phenylethyl chloride.

(4) In liquid SO₂, $k_1^a/(k_1^D + k_1^E) \approx 9$: Y. Pocker, *Trans. Faraday Soc.*, **55**, 1266 (1959); *cf.* also Y. Pocker, "Nucleophilic Substitution at a Saturated Carbon Atom in Nonhydroxylic Solvents," Vol. 1, Pergamon Press, New York, N. Y., 1961, pp. 227, 228.

(5) S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1010 (1960); S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Letters*, **No. 22**, 12 (1960); S. Winstein, A. Ledwith, and M. Hojo, *ibid.*, **No. 10**, 341 (1961); A. F. Diaz and S. Winstein, *J. Am. Chem. Soc.*, **86**, 5010 (1964).