

336. Salt Effects in Rearrangement of 1-Phenylallyl Chloride.

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Salts strongly accelerate the rearrangement of 1-phenylallyl chloride to *trans*-cinnamyl chloride in *NN*-dimethylformamide. Results for a few 1 : 1 electrolytes at 80° suggest that the accelerating effect varies inversely with the size of the anion and is surprisingly unaffected by the size of the cation. Such a result implies that ion pairs are about as effective as isolated anions in promoting the rearrangement.

trans-Cinnamyl chloride and tetraethylammonium chloride undergo isotopic exchange in the same solvent by what appears to be an S_N2 mechanism.

1-PHENYLALLYL CHLORIDE is a good material for the study of allylic rearrangements because formation of the conjugated *trans*-3-phenylallyl (cinnamyl) chloride is virtually irreversible and can be followed easily by ultraviolet spectrophotometry.

We have studied this rearrangement in *NN*-dimethylformamide at 80°, both uncatalyzed and in the presence of some added salts. The results are indicated in the Figure.

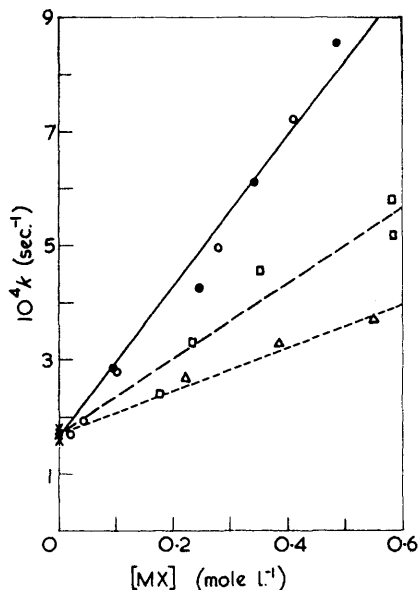
The first-order rate constants for the rearrangement can be fitted well by an equation of the form, $k = a + b[\text{MX}]$, where MX is the added salt. The uncatalyzed experiments give $a = 1.70 \times 10^{-4} \text{ sec.}^{-1}$. Values of b are presented in the Table.

Catalytic effects of salts on rearrangement of 1-phenylallyl chloride.

| Salt | LiCl | NEt ₄ Cl | NEt ₄ NO ₃ | NEt ₄ ClO ₄ |
|--|------|---------------------|----------------------------------|-----------------------------------|
| 10 ⁴ <i>b</i> (l. mole ⁻¹ sec. ⁻¹) | 13.1 | 12.8 | 6.6 | 3.8 |

3 M

The data for the uncatalyzed reaction and for the effect of lithium chloride seem to be in satisfactory agreement with the measurements of Valkanas and Waight¹ on the same system. Tetraethylammonium nitrate and perchlorate clearly exert kinetic salt effects of considerable magnitude. Referees have pointed out that the b values for the chlorides might contain contributions from rearrangement proceeding by an S_N2' mechanism. However, the pattern of salt effects is the same as those observed by Ross and Labes² for the solvolysis of *t*-butyl bromide in the same solvent and by Winstein, Smith, and Darwish³ for the ionization of *t*-butyl bromide in acetone. In all three of these studies, chloride and bromide salts cause accelerations that are larger by factors of 2–3 than are



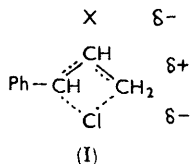
Effect of salts on first-order rate constants for rearrangement of 1-phenylallyl chloride in *NN*-dimethylformamide. \times , without added salt. \bullet , LiCl. \circ , NEt_4Cl . \square , NEt_4NO_3 . \triangle , NEt_4ClO_4 .

the accelerations caused by nitrates and perchlorates. Since the *t*-butyl bromide reactions do not offer any obvious mechanisms for acceleration by a specific common ion, we prefer to regard as non-specific the chloride effects observed here.

In the other two studies^{2,3} as well as in the present one, the kinetic salt effects seem to depend only on the nature of the anion and are remarkably independent of the nature of the (singly charged) cation. It is also surprising that the rate of reaction is a linear function of salt concentration in a range where the ions are probably appreciably associated.

Apparently ion pairs are about as effective as free anions at aiding the rearrangement. Such a conclusion differs from observed behaviour when an organic molecule undergoes direct substitution by an anion.⁴

Our observations could be accommodated to a transition state of the form (I) where the anion (or ion pair) X and the migrating Cl might share the net negative charge and be on opposite sides of the plane determined by the three allylic carbon atoms. The anion would then serve to neutralize the developing positive centre associated with chloride migration.



¹ Valkanas and Waight, *J.*, 1959, 2720.

² Ross and Labes, *J. Amer. Chem. Soc.*, 1957, **79**, 4155.

³ Winstein, Smith, and Darwish, *Tetrahedron Letters*, 1959, No. 16, p. 24.

⁴ Evans and Sugden, *J.*, 1949, 270.

Such an interpretation implies that in *NN*-dimethylformamide an anion is more stabilized the greater the surface area over which the negative charge is dispersed. The opposite effect is observed in a protic solvent, and Valkanas and Waight¹ found that in ethanol at 25° the same rearrangement was accelerated more by lithium bromide than by lithium chloride. These effects of anion size on solvation energy are in agreement with the arguments of Miller and Parker⁵ about similar types of systems.

We have also studied the isotopic exchange of *trans*-3-phenylallyl chloride with $\text{NEt}_4^{36}\text{Cl}$ in *NN*-dimethylformamide. The total concentration of 1:1 electrolyte was maintained at 0.010 mole/l. by addition of tetraethylammonium perchlorate; this concentration is too low for significant kinetic salt effects if *b* is of the magnitude observed during the rearrangement reaction. At 30° the rate of exchange was of the first order each in cinnamyl chloride and in tetraethylammonium chloride, and the rate constant was 7.7×10^{-3} l. mole⁻¹ sec.⁻¹. A single run at 80° indicated a rate constant of 0.48 l. mole⁻¹ sec.⁻¹. These results suggest that 3-phenylallyl chloride undergoes exchange by an $\text{S}_{\text{N}}2$ mechanism with an activation energy of about 17.6 kcal. mole⁻¹.

It had also been our intention to study isotopic chloride exchange in a system undergoing rearrangement in order to learn more about the mechanism of this process. A recent communication by Waight and Weinstock⁶ indicates that similar studies have already been completed. Hence we are abandoning work on this system but are continuing studies of rearrangements of some substituted phenylallyl benzoates.

EXPERIMENTAL

Valkanas and Waight¹ prepared 1-phenylallyl chloride from the corresponding alcohol, but their procedure gave low yields in our hands. We had better success with the procedure of Caserio *et al.*⁷ Twice recrystallized cinnamyl alcohol was treated with thionyl chloride in ether. The 1-phenylallyl chloride initially produced tended to isomerize before reaction of the alcohol was complete, and the optimum time to stop the reaction was determined spectrophotometrically. Acid was then removed with triethylamine, the ether solution was evaporated, and the residue was dissolved in light petroleum (b. p. 30–60°). This solution was washed with cold sodium carbonate solution and water, and the petroleum was also evaporated. Fractional distillation of the residue gave a small amount of material with n_D^{25} 1.5385 and ϵ_{2530} 1100 (in ether). Hydrolysis and titration with silver nitrate indicated 98% of the theoretical amount of chloride. Since $\epsilon_{2530} = 20,000$ for cinnamyl chloride, contamination by this isomer was limited to no more than a few per cent. Apparently our material had less cinnamyl chloride than that prepared by Valkanas and Waight,¹ which had $\epsilon_{2530} = 1900$.

Commercial 3-phenylallyl chloride was fractionally distilled at reduced pressure and used without further purification.

Spectro-grade *NN*-dimethylformamide was used as solvent without further purification. Karl Fischer titration indicated less than 10⁻³% of water in it. Its conductivity was 1.7×10^{-6} mho.

Commercial tetraethylammonium bromide was converted into the hydroxide by the action of moist silver oxide. The various salts used in the kinetic runs were then prepared by neutralization with the appropriate acid.

Solutions used in studying the rearrangement reaction were diluted 1000-fold with ether, and the extinction at 2530 Å was measured with a Beckman spectrophotometer. Individual runs gave good first-order kinetics.

Solutions used to study the exchange reaction were treated with cold ether to precipitate the salt. This precipitate was dissolved in water, and the radioactivity of the solution was measured with a thin-walled Geiger tube. The solution from this measurement was also

⁵ Miller and Parker, *J. Amer. Chem. Soc.*, 1961, **83**, 117; Parker, *J.*, 1961, 1328; *Quart. Rev.*, 1962, **16**, 163.

⁶ Waight and Weinstock, *Proc. Chem. Soc.*, 1961, 334.

⁷ Caserio, Dennis, de Wolfe, and Young, *J. Amer. Chem. Soc.*, 1955, **77**, 4182.

titrated with silver nitrate solution, and the specific activity of the chloride was computed and compared with that of the initial tetraethylammonium chloride.

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