The Retentive Solvolysis of 1-Phenylethyl Chloride in Binary Mixtures of the Carboxylic Acid with Nitromethane or the Nitrile

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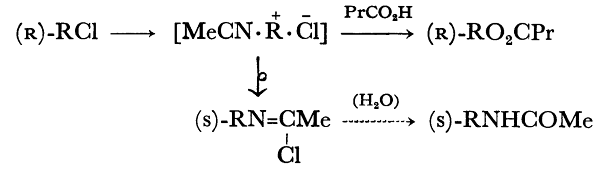
It has been previously demonstrated that a nucleophilic co-solvent, such as di-*n*-butyl ether[1] or acetone,[2] intervenes in the acetolysis of 1-butyl-1-*d* *p*-nitrobenzenesulfonate[1] or the methanolysis of 2-octyl *p*-bromobenzenesulfonate,[2] thus affording a by-product derived from the co-solvent and the substrate for the respective solvolyses. We wish now to report on some novel examples which clearly indicate that such intervention leads the S_N1 solvolysis, otherwise inversive, to become a retentive solvolysis.

When the butyrolysis was conducted on optically active 1-phenylethyl chloride (0.10M) in the presence of sodium butyrate (0.100N) at 100°C, in accord with a standard tendency in the S_N1 solvolysis of this system, 1-phenylethyl butyrate with a net (3.5%) inversion of configuration was obtained in an 82% yield, along with styrene in a 14% yield.

In contrast to this, in a binary mixture of butyric acid with acetonitrile (80.0 mol%) the butyrolysis yielded 1-phenylethyl butyrate with a 2.9% *retention* of configuration, accompanied by a predominant (97%) racemization. In addition, a by-product, *N*-1-phenylethylacetamide, isolated from the reaction mixture, when worked-up with water, had a net (3.2%) inverted configuration; this amide may stem from the net-inverted *N*-1-phenylethylacetimidoyl chloride, which was a product of the S_N2-like reaction of the ion-pair intermediate with acetonitrile. These results can be explained by the following reaction scheme, which includes a back-side shielding[3] of the ion-pair intermediate by the C≡N group of acetonitrile and also a subsequent front-side attack of butyric acid on the shielded intermediate:



Similarly, a net retention of configuration was observed in the propionolysis and in the valerolysis in the binary mixtures of the respective carboxylic acids with acetonitrile. Nitromethane, as a co-solvent, also exhibited a similar retentive function in the butyrolysis. These results are presented in Table 1, along with the first-order solvolysis rate constant for each run.

The nitriles other than acetonitrile (*viz.*, fumaronitrile, malononitrile, and acrylonitrile) were also found to be effective co-solvents in changing the steric course of the butyrolysis from a net inversion to a net retention. In Fig. 1 the extents of the retention (or inversion) of 1-phenylethyl butyrate are plotted against the concentrations of the added nitriles. There is a decided trend towards higher retentions in solvents with higher nitrile concentrations, but there is no simple correlation between the structure of the nitrile and the extent of retention. However, compared with acetonitrile or malononitrile, acrylonitrile and fumaronitrile show no specific effectiveness for the retention; this indicates that their C=C groups are scarcely responsible for the back-side shielding of the ion-pair intermediate.

Table 1. The net steric course and the rates in the solvolysis of 1-phenylethyl chloride (100°C)[a]

Solvent acid	Net steric course for $R'CO_2R$[b]	Net steric course for RNHCOMe[c]	10^5k_1 (sec^{-1})
Acetic	2.94% inv.	—	58.1
Acetic[d]	racem.	2.96% inv.	28.1
Propionic	0.75% inv.	—	5.03
Propionic[e]	2.77% ret.	2.05% inv.	14.1
Butyric	3.53% inv.	—	1.98
Butyric[f]	2.90% ret.	3.22% inv.	6.62
Butyric[h]	0.89% ret.	—	19.2
Valeric	5.94% inv.	—	0.89
Valeric[g]	2.73% ret.	4.69% inv.	7.80

a) In the presence of the sodium salts of the respective acids. b) Yield: 34—82%. c) Yield: 5—10%. d—g) +MeCN (67.9, 68.1, 80.0, and 67.5 mol%, respectively). h) +$MeNO_2$ (79.9 mol%).

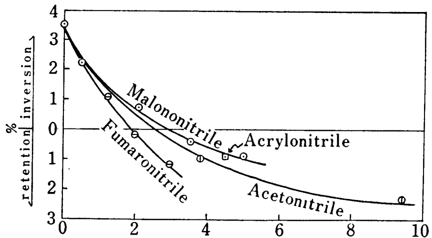


Fig. 1. Extents of retention (or inversion) of 1-phenylethyl butyrate (100°C).

In view of these results, the retentive S_N1 hydrolysis of some aralkyl *p*-nitrobenzoates in the aqueous acetone solvent, found by Goering and his collaborators,[4] may be attributed to the back-side shielding by acetone. Furthermore, our previous observation[5] that the hydrolysis of 1-phenylethyl chloride in aqueous acrylonitrile (97 wt%) affords 1-phenylethyl alcohol with a net (6.3%) retained configuration can be interpreted as involving back-side shielding by acrylonitrile.

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