Classical Carbonium Ions. Part 9.[1] Rates of Solvolysis of Nitroaryl Ethers in Aqueous Ethanol

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1-Adamantyl 2,4-dinitrophenolate and t-butyl 2,4-dinitrophenolate undergo solvolysis reactions in aqueous ethanol at rates which accurately fit the Winstein–Grunwald equation, the low *m* values indicating that solvation of the leaving group distinguishes weakly between water and ethanol. 1-Adamantyl picrate behaves similarly, but secondary picrates react both by alkyl–oxygen heterolysis and by bimolecular aromatic substitution. This fact limits the use of picrate as a leaving group in mechanistic work in such solvents.

WE have recently emphasised [2,3] the advantages of tri- and di-nitrophenyl ethers as substrates in solvolysis reactions: ease of preparation, crystallinity, and convenience in spectrophotometric assay. These claims have been endorsed.[4] Nevertheless, new leaving groups are at a substantial disadvantage relative to toluene-*p*-sulphonate, *etc.*, simply because they are new, and the extent of their compliance with well-known relationships is unknown. We now remedy this for the Winstein–Grunwald equation [5] $k/k_0 = mY$, and the solvent system ethanol–water, in three representative cases, not because we consider these media suitable for the study of solvolysis (their choice was unfortunate, because of the non-ideality of such mixtures, which is probably the cause of 'Thurber-shaped plots' [6]), but merely because of their historical importance.

Provided that 0.05M-potassium acetate was present, good first-order behaviour was observed for the solvolysis of t-butyl and 1-adamantyl 2,4-dinitrophenyl ethers in aqueous ethanol over a range of compositions, otherwise plots were curved, because of incomplete ionisation of 2,4-dinitrophenol. Rates of reaction at 74.2 and 119.6°, respectively, are given in Table 1. Both sets of data fitted the equation accurately, giving *m* values much lower than those of t-butyl chloride at 25° (1 by definition) and of 1-bromoadamantane at 50° (1.16; ρ 0.997).[7] Correlation coefficients were, indeed, better than for the latter results, perhaps because two of these values had to be extrapolated from rates measured at other temperatures. The important difference in sensitivity to solvent composition between these ethers and the corresponding halides presumably implicates the preferential solvation of the halide ion by water as the largest single energy term in going from starting material to transition state.[8] Since one is usually concerned with a comparison between one organic residue and another, it is, of course, a further advantage to use leaving groups which are themselves less sensitive to solvation, the term of interest then being relatively important.[5] We have recorded aqueous-ethanolysis rates for allylic 2,4-dinitrophenyl ethers,[9] which again were measured without difficulty and gave good Winstein–Grunwald plots; for reactive systems 2,4-dinitrophenolate thus appears to be a highly satisfactory leaving group, preferable in most respects to *p*-nitrobenzoate, *etc.*, now that initial preparative difficulties [3] are largely overcome.[9]

TABLE 1

Rates of solvolysis

mol % H_2O [a]	Y	$10^5k/s^{-1}$ [b]	mol % H_2O [a]	Y	$10^5k/s^{-1}$ [c]	mol % H_2O [a]	Y	$10^5k/s^{-1}$ [d]
94.3	3.15	209 [e]						
92.9	3.05	209 [e]						
88.5	2.55	112 [f]				80.5	1.98	5 850 ± 220
82.9	2.20	75.8				69.2	1.17	1 600 ± 30
76.5	1.65	44.2	72.0	1.35	40.9	66.8	1.02	1 490
68.4	1.12	21.7	69.2	1.17	34.4	52.9	0.30	690 ± 12
44.8	0.00	6.9	52.9	0.30	9.9	22.2	−0.93	122 ± 1
13.0	−1.33	1.59	22.2	−0.93	1.63	13.6	−1.33	72
0.0	−2.03	0.78	14.1	−1.30	1.15	0.0	−2.03	31 ± 1

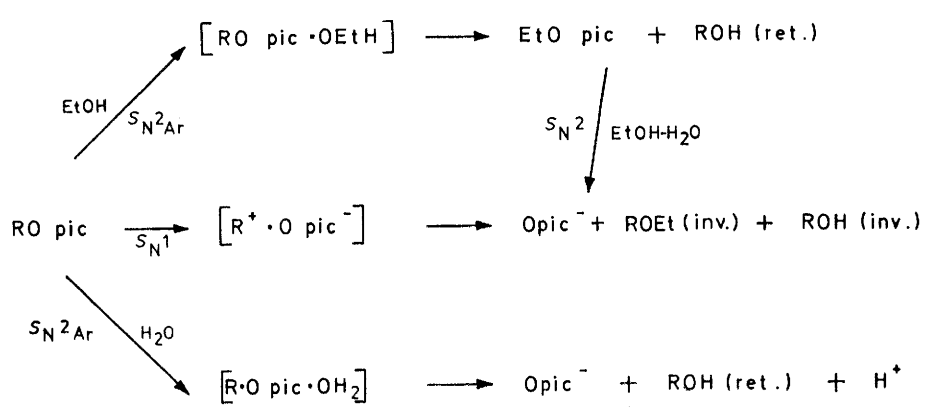
[a] Aqueous ethanol. [b] t-Butyl-2,4-dinitrophenolate, 74.2°, *m* 0.476, ρ 0.9997. [c] 1-Adamantyl 2,4-dinitrophenolate, 119.6°, *m* 0.602, ρ 0.9992. [d] 1-Adamantyl picrate, 49.1°, *m* 0.564, ρ 0.9996. In 70 and 90% acetone by weight (Y 0.13 and −1.86) the last substrate had at 50° $10^5k = 605 \pm 15$ and 99 ± 2, giving *m* 0.39; in methanol, $Y = -1.09$, $10^5k = 63.8$; in acetic acid (ref. 2), $Y = -1.67$, $10^5k = 46$. Standard deviations, derived from the Guggenheim plot, are given in the cases where they were calculated. [e] Two runs each, coincidentally all giving 209. [f] Duplicate runs, 111 and 113.

Table 1 also includes data for 1-adamantyl picrate [2] at 49.1°, which gave an excellent correlation with *m* and a slope very close to that of the 2,4-dinitrophenyl ether at 119.6°. This tends to confirm the relative unimportance of differential solvent effects (water–ethanol) for such leaving groups, and suggests that reactive picrates may also be studied in this way. For 1-adamantyl picrate at 50° rates of solvolysis in methanol and in two concentrations of aqueous acetone were also measured. When added to the log *k versus* Y plot, the familiar phenomenon of 'dispersion' [5] was evident; although the aqueous ethanol points defined an excellent line, the point for methanol lay *ca.* 0.2 units below the line, while the points for aqueous acetone defined a line of smaller slope, lying above it. The point for acetic acid, however, was (within experimental error) on the line.

When some other alkyl picrates were subjected to aqueous ethanolysis signs were observed that the known

S_N2_{Ar} process[10] was not negligible relative to direct heterolysis. Reactions no longer consistently showed first-order kinetics, presumably because of the reactions in the Scheme.

The deviation from first-order kinetics was obvious in the cases R = isopropyl and methyl, but not for R = 4-t-butylcyclohexyl at 74° in ethanol. In this case the observed rate was fortuitously equal to the ethanolysis rate of ethyl picrate, so that diversion of starting material to ethyl picrate made no difference to spectrophotometric assay of picrate ion concentration. When this reaction was terminated at apparent half-completion, ethyl picrate was isolated by t.l.c. and found to be present in about the calculated quantity; similarly, methyl picrate was largely converted on heating in ethanol to ethyl picrate.



SCHEME

The products obtained in the acetolysis of *cis*- and *trans*-4-t-butylcyclohexyl toluene-*p*-sulphonates[11] and picrates[2] have been described, and also the solvolysis products of the arenesulphonates in 50% aqueous ethanol.[11] When the ethanolysis and aqueous-ethanolysis products of the corresponding picrates were examined (see Table 2), the two outstanding differences were the presence of large amounts of ' retained ' alcohol (especially in the case of the *trans*-alcohol), and the absence of detectable amounts of rearranged products, especially of rearranged olefin. Hydride shift is certainly less important in these solvents than in acetic acid, and less important in picrate than in arenesulphonate solvolysis; nevertheless, the results of Table 2 should not be taken to prove it absent, especially as appreciable yields of rearranged, inverted alcohols could have co-chromatographed with the retained, unrearranged alcohols from the S_N2_{Ar} reaction.

Use of picrate as a leaving group in solvolysis reactions in ethanol or aqueous ethanol (as opposed to acetic acid and less nucleophilic solvents) evidently requires caution; as a guide, *cis*- and *trans*-4-t-butylcyclohexyl picrates react to the extent of 83.5 and 40% by alkyl–oxygen fission in ethanol, and 93 and 50% in 68.4 mol% aqueous ethanol at 74°, an increase in temperature probably favouring alkyl–oxygen fission. The rate of the S_N2_{Ar} reaction presumably varies somewhat with the alkyl residue present, but much less than that of the simultaneous S_N1 process. Picrate should thus be considered as lying between normal carboxylate residues, *e.g.* 3,5-dinitrobenzoate, and arenesulphonate in respect of the ratio of the two reactions, and may resemble 2,6-disubstituted benzoate residues. Solvolysis of picrates is so much less sensitive to solvent polarity than solvolysis of halides or arenesulphonates that no generalisation can be made about relative reactivity in partially aqueous systems.

The solvolysis of a compound RX in a solvent HY can be affected by proton transfer from HY to incipient X^- at the transition state; the importance of this process (and, at the same time, of the attenuated nucleophilic assistance observed even in most ' S_N1 ' reactions[12]) can be measured by comparing rates of solvolysis in acetic acid (*Y* —1.67) and in aqueous ethanol of a similar *Y* value. Diphenylmethyl fluoride gives a ratio of 5 000,[5] indicating extensive proton transfer to F^-. For 1-adamantyl picrate the value is 0.87, but for the 2,4-dinitrophenolate it is 12, so that here proton transfer from HOAc is significant. As would be expected, picrates show no very dramatic catalysis in trifluoroacetic acid, but 2,4-dinitrophenolates are inconveniently reactive.[12] With primary and secondary substrates nucleophilic interaction of the incipient cation with solvent affects this ratio, so that the high reactivity of

TABLE 2

Products from aqueous ethanolysis of t-butylcyclohexyl picrates at 74°

mol % H_2O	$C_{10}H_{18}$	*c*-4-OEt	*t*-4-OEt	*c*-4-OH	*t*-4-OH
0.02 [a]	80	0	20	(16.5) [c]	0.2
0.02 [b,d]	55	44	0.7	0.2	(60) [c]
1.5 [b]	56	41	0.5	1.7	(63) [c]
17.9 [b]	57	29	0.2	13	(68) [c]
31.2 [b]	61	22	0.9	17	(68) [c]
68.4 [b]	68	8.4	0.4	23	(50) [c]
68.4 [a]	77	0	3	(7.0) [c]	20

[a] *cis*-Picrate used. [b] *trans*-Picrate used. [c] Yield of retained alcohol, assumed to be formed in S_N2_{Ar} reaction, therefore ignored in working out yields of solvolysis products. [d] $k = 9.5 \times 10^{-6}\ s^{-1}$. Here ' $C_{10}H_{18}$ ' is 4-t-butylcyclohexene, free from isomers; *c*-4-OEt means *cis*-4-t-butylcyclohexyl ethyl ether, *etc.*

ethyl picrate in ethanol (k 9.5 × 10^{-6} s^{-1} at 74°) in (presumably) a straightforward S_N2 process is expected.

EXPERIMENTAL

The preparation of the substrates and general methods of following reactions and calculating results have all been described.[2,3] Methanol and ethanol were dried by distillation from the magnesium alkoxide and had water contents of 0.012 and 0.008%, respectively (Karl Fischer). Acetone was distilled from potassium permanganate and dried over magnesium sulphate, then potassium carbonate. Solvolysis reactions carried out at 74° or below were followed *in situ*, using 0.05M-potassium acetate as buffer salt and 400 nm as the analytical wavelength; the Guggenheim method was employed in calculating results. Reactions at higher temperatures required solutions in ampoules (2 ml each), infinity readings being obtained after *ca.* 10 half-lives, in duplicate, the run being accepted only when they concurred.

In product analysis our methods were based on ref. 13, using a Perkin-Elmer F11 instrument with flame-ionisation detector and 2 m stainless steel columns ($\frac{1}{8}$ in outside diameter) packed with 12% ' GEO 100 ' (glycerol–ethylene oxide condensation product similar to Carbowax). Peak areas were assumed proportional to (height × width at half height), and molar response factors to the number of carbon atoms. The temperature was 110°, increased after elution of olefin and ethers to 140°, and the identity of the peaks was deduced from the similarity of their retention times to those formed in the aqueous alcoholysis of *trans*-4-t-butylcyclohexyl *p*-bromobenzenesulphonate,[11] which was repeated for the purpose. *trans*-Decalin was used as an internal standard in measuring yields of retained alcohol, and yields of other products are quoted on the basis that all other products total 100%.

In measuring ethyl picrate formed in ethanolysis reactions t.l.c. on silica was employed, diethyl ether being the solvent, and ammonia the visualising reagent. R_F Values were: *trans*-4-t-butylcyclohexyl picrate, 0.70; ethyl picrate, 0.55; methyl picrate 0.45.

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