Rearrangement in the Solvolysis of 3-Bromopentane in 60% Aqueous Ethanol

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Isomerically pure 3-bromopentane has been prepared from tri-1-ethylpropyl phosphite and hydrogen bromide and solvolysed in 60% aqueous ethanol. The detection of about 1% rearrangement products in both acid and weakly alkaline conditions supports the view that carbonium ion intermediates are formed in the reaction of at least a proportion of the molecules. The formation of 2-bromopentane is attributed to internal return in a close ion-pair and accounts for some, if not all, of the rearranged substitution products. No rearrangement occurs under more strongly alkaline conditions. The results are discussed in relation to previous work on s-alkyl bromides and s-alkyl sulphonates.

WHILST the solvolyses of s-alkyl bromides (*e.g.*, isopropyl, 1-methylheptyl) in 60% aqueous ethanol in neutral or acid conditions have been considered to proceed exclusively by the S_N1 mechanism,[1] they have also been found to show a greater dependance on solvent nucleophilicity than do the solvolyses of s-alkyl sulphonates.[2] The question of the extent to which intermediates are involved which may properly be described as carbonium ions has thus given rise to discussion.[2-4] It is difficult to make a clear distinction on kinetic grounds between an intermediate (which may involve some degree of covalent bonding between the solvent and the central carbon atom [5]) and a borderline S_N2 transition state in which solvent–carbon bonding makes only a small

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[1] (*a*) E. D. Hughes, C. K. Ingold, and U. G. Shapiro, *J. Chem. Soc.*, 1936, 225; (*b*) E. D. Hughes and U. G. Shapiro, *ibid.*, 1937, 117, 1192.

[2] S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700; A. Streitwieser, *Chem. Rev.*, 1956, **56**, 636.

[3] (*a*) M. C. Whiting, *Chem. in Brit.*, 1966, **2**, 482; (*b*) V. Gold, *J. Chem. Soc.*, 1956, 4633.

[4] W. L. Coburn, jun., E. Grunwald, and H. P. Marshall, *J. Amer. Chem. Soc.*, 1953, **75**, 5735.

[5] W. von E. Doering and H. H. Zeiss, *J. Amer. Chem. Soc.*, 1953, **75**, 4733.

contribution to the energetics of the process.[6] There is no clear evidence on the basis of a mass-law effect. Thus, whilst a small reduction in the first-order constant for the solvolysis of isopropyl bromide in 60% aqueous ethanol was observed in the presence of added sodium bromide,[1a] no detectable effect could be found for s-butyl bromide.[4] The overall stereochemical result in the solvolysis of an optically active s-alkyl bromide is further complicated by the gradual racemization of the starting material by bromide ion which builds up in solution as the reaction proceeds. Although allowance for this was made in earlier studies of the solvolysis of (+)-2-bromo-octane in 60% aqueous ethanol,[7] the corrected degrees of retention of optical purity reported are seen to be too low in the light of a more recent value for the optical rotation of the enantiomerically pure bromide.[8] An uncertainty also arises since the bromide used, by virtue of its method of preparation from hydrogen bromide,[7] most probably contained 3-bromo-octane (7—8%).[9] This may be unimportant if the two isomers solvolyse at closely similar rates, although the possibility of some fractionation in the final isolation of the alcohol as its hydrogen phthalate[7] cannot be excluded. More recent work on the solvolysis of (+)-2-bromo-octane in 60% aqueous ethanol has yielded the corresponding alcohol with a net inversion of 49%,[10] which, after application of the previously used correction factor,[7] corresponds to 93% net inversion in the hydrolytic displacement.

The extent to which alkyl rearrangement provides evidence of carbonium ion character in the solvolysis of an s-alkyl halide has received very little attention. A preliminary examination by g.l.c.[10] of the products of solvolysis of 2-bromo-octane in 60% aqueous ethanol showed however that the octanol formed contained no more than 0·5% of the rearranged isomer (octan-3-ol) and in view of the incomplete resolution of 2- and 3-bromo-octane obtainable at that time the possible presence of this amount of 3-isomer in the starting material could not be definitely excluded. We have therefore turned our attention to the solvolysis of 3-bromopentane, (*a*) since the complete resolution of this material from 2-bromopentane has been achieved,[11] and (*b*) since it offers twice the statistical chance of rearrangement afforded by the 2-isomer. 3-Bromopentane was prepared by the interaction of tri-1-ethylpropyl phosphite with a carefully restricted amount of hydrogen bromide[8a] and was shown to contain no detectable 2-isomer (certainly $<0{\cdot}1\%$). The purity was further confirmed by solvolysis in ethanolic 1·6N-potassium hydroxide which yielded, in addition to olefinic products, pentan-3-ol which was isomerically pure. In 60% aqueous ethanol at 80 °C the solvolysis was essentially complete in 50 hours ($t_{\frac{1}{2}}$ *ca.* 11·5 h). Periodic sampling and analysis by g.l.c. showed that the pentanol formed contained *ca.* 1% of the rearranged product (pentan-2-ol). A similar proportion of rearranged ether was also detected in the final product although the resolution of the isomeric ethyl 1-methylbutyl and ethyl 1-ethylpropyl ethers by g.l.c. was not as good as that of the alcohols. As it was shown that the products did not isomerize, and that the possible olefinic by-products did not undergo hydration under reaction conditions, a small but definite amount of rearrangement in the solvolysis is indicated. Of considerable interest in the present work was the appearance during solvolysis of small amounts of 2-bromopentane. The proportion present, expressed as a percentage of the total bromopentane in solution, increased slowly from *ca.* 0·5% at 6 h to 2·0% at 20 h but was not measured thereafter as the total amount of bromide remaining was then too small. It was demonstrated that the 2-bromopentane was not formed by the recombination of pentene and hydrogen bromide under reaction conditions, nor did it arise by interaction of the alcohol or ether with hydrogen bromide. Had the solvolytic process been significantly reversible, the repeated formation of pentyl bromide (with rearrangement[9]) would have given rise to a steadily increasing percentage of rearranged alcohol and ether on prolonged heating. This, however, was not the case; the composition of the final product remained constant for a further 79 h at 80 °C after solvolysis was complete. It seems most probable therefore, in view of the lack of clear evidence for external return in similar systems,[4] that the 2-bromopentane was formed as the result of internal return, with rearrangement, in a close ion-pair. Ion pairs have been suggested as important intermediates in the solvolyses of 1-methylheptyl sulphonates in aqueous dioxan[12] and in acetic acid.[13] In the latter solvent, rearranged products and starting materials were also detected. The rearranged alcohol and ether detected in the present studies must have been formed, at least in part, from the solvolysis of rearranged bromide. The percentages involved were however too small to show with certainty whether the whole of the rearranged products arose by this route or whether some rearrangement accompanied the displacement process. In either case it is clear that the extent of covalent bonding between the solvent and the central carbon atom is sufficiently small for there to be effective competition by neighbouring hydrogen in at least a proportion of the molecules (Scheme 1) and to this extent an intermediate which may justifiably be called a carbonium ion must be present.

This is distinctly different from the result in aqueous 1·6N-ethanolic potassium hydroxide in which no detect-

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[6] M. L. Bird, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1954, 634.

[7] E. D. Hughes, C. K. Ingold, and S. Masterman, *J. Chem. Soc.*, 1937, 1196.

[8] (*a*) E. J. Coulson, W. Gerrard, and H. R. Hudson, *J. Chem. Soc.*, 1965, 2364; (*b*) H. M. R. Hoffmann, *ibid.*, 1964, 1249.

[9] W. Gerrard and H. R. Hudson, *J. Chem. Soc.*, 1964, 2310.

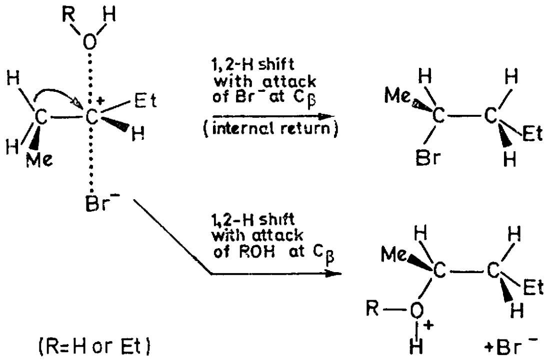
[10] W. Gerrard and H. R. Hudson, *Nature*, 1964, **204**, 876.

[11] B. A. Chaudri, H. R. Hudson, and W. S. Murphy, *J. Chromatog.*, 1967, **29**, 218.

[12] H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.*, 1965, **87**, 287, 292; R. A. Sneen and J. W. Larsen, *ibid.*, 1966, **88**, 2593; 1969, **91**, 362.

[13] A. Streitwieser and T. D. Walsh, *J. Amer. Chem. Soc.*, 1965, **87**, 3686.

able rearrangement was observed. In dilute alkali (0·53N) a small percentage of rearranged alcohol was also formed, indicating that some degree of carbonium ion character persists under such conditions. The possibility of a concerted process of rearrangement with attack by solvent at the β-carbon atom (Scheme 2) cannot be entirely excluded although it appears unlikely, since there is no reason, if this were so, why the lyate anion should not behave similarly in the more strongly alkaline solution.



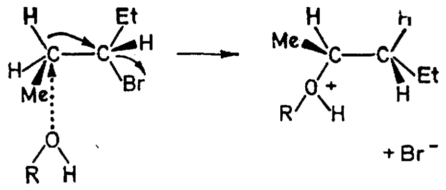
SCHEME 1

TABLE 1

Solvolysis of 3-bromopentane in 60% aqueous ethanol

No.	Et_2CHBr/g	60% Aq. EtOH/ml	Time/h	Concn./M of KOH, HBr *etc.*/M Initial	Final	Product composition/% [a] Et_2CHOH	$Pr^iMeCHOH$	Et_2CHOEt	$Pr^iMeCHOEt$
1	4·0	86	51	0	0·30 HBr	76·2	0·8	23·0	trace
2	3·4	74	50 [b]	0	0·29 HBr	72·4	1·0	25·8	0·3
3	4·5	100	7	0·53	0·24 KOH	67·1	0·7	32·2	N.D. [c]
4	3·0	65	7	0·53	0·24 KOH	66·2	0·6	33·2	N.D.
5	3·5	75	5	1·60	1·30 KOH	58·7	N.D.	41·3	N.D.

[a] Calculated for the alcohols and ethers only. Mean values by analysis on different columns. Olefinic products were barely detectable in expts. 1 and 2; pent-2-ene (3%) was detected during expt. 4; pent-2-ene (12% *cis*, 88% *trans*) was the principal product (90%) in expt. 5. [b] The final composition was unchanged after a further 79 h at 80 °C. 2-Bromopentane was detected as follows (h, % 2-isomer in total bromopentane present): 6, 0·5; 15, 0·8; 20, 2·0. [c] Not detectable.



SCHEME 2

The relatively small percentage of rearrangement is notable. This could be interpreted as being due to the fact that the majority of molecules react *via* a borderline S_N2 transition state, only a small fraction forming genuine intermediates, or alternatively, if all or most form carbonium intermediates, to the fact that the latter are very short-lived and rearrangement is rare since there is no appreciable change in stability associated with the 1,2-hydride shift between the two isomeric s-alkyl carbonium ions. A greater degree of carbonium ion character is evident in the acetolyses of 1-methylheptyl *p*-nitrobenzenesulphonates,[14] which afford higher proportions (3—6%) of rearranged products. As much as 10—20% rearrangement to isomeric s-alkyl carbonium ions may occur in the deamination of 4-amino-octane and its derivatives.[3a]

EXPERIMENTAL

Tri-1-*ethylpropyl Phosphite*.—Phosphorus trichloride (48·1 g, 1·02 mol. equiv.) was added dropwise (70 min) to a stirred, ice-cold mixture of pentan-3-ol (90·2 g, 3 mol. equiv.) (Fluka AG; isomerically pure by g.l.c.) and dimethylaniline (126·4 g, 3·06 mol. equiv.) in light petroleum (b.p. 30—40°) (400 ml). Removal of the dimethylanilinium chloride (158·7 g, 2·95 mol. equiv.) by filtration was followed by repeated distillation to give tri-1-ethylpropyl phosphite (21·7 g, 0·46 mol. equiv.), b.p. 94°/0·25 mm., n_D^{20} 1·4389 (Found: P, 10·3. Calc. for $C_{15}H_{33}O_3P$: P, 10·6%) [^{31}P δ(p.p.m.) −142 singlet, relative to H_3PO_4].

3-*Bromopentane*.—Anhydrous hydrogen bromide (4·7 g, 0·82 mol. equiv.) was passed slowly (87 min) into tri-1-ethylpropyl phosphite (20·5 g, 1 mol. equiv.) at 0 °C. A further quantity of the phosphite (21·2 g) was similarly treated with hydrogen bromide (4·0 g, 0·7 mol. equiv.) during 75 min. The volatile products were in each case removed at 0·3 mmHg and room temperature, trapped (−80 °C), washed, and dried (K_2CO_3). Distillation of the combined products gave: (i) 1·1 g, b.p. 114—116°, n_D^{20} 1·4412; (ii) 3-bromopentane (8·9 g), b.p. 116—117·5°, n_D^{20} 1·4450, which contained no detectable 2-isomer (g.l.c.). Further quantities were made similarly.

TABLE 2

Relative retention times

	Squalane	PEG	DBDT
Column temp./°C	40	55	40
N_2 inlet pressure/lb in^{-2}	30—36	12—15	20
trans-Pent-2-ene	0·10	0·08	0·10
cis-Pent-2-ene	0·10	0·08	0·11
Ethyl 1-methylbutyl ether	0·68	0·14	1·09
Ethyl 1-ethylpropyl ether	0·68	0·14	1·00
Pentan-2-ol	0·80	1·13	4·64
Pentan-3-ol	0·80	1·00	3·77
2-Bromopentane	1·00	0·30	1·68
3-Bromopentane	1·08	0·30	1·78

The lower limit for the detection of 2-bromopentane in 3-bromopentane was shown to be not greater than 0·1% by the analysis of synthetic mixtures on the squalane column.

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[14] N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc.* (*B*), 1968, 355.

Solvolysis of 3-Bromopentane.—Solutions of 3-bromopentane (*ca.* 0·3M) in 60% aqueous ethanol (60 vol. absolute ethanol plus 40 vol. water) were heated under reflux at 80 °C (oil-bath) until no alkyl halide was detectable (g.l.c.). Potassium hydroxide was present as specified in experiments 3, 4, and 5. Samples taken periodically were analysed by g.l.c. on three columns as described below. Final compositions are given in Table 1.

Gas–Liquid Chromatography.—Analyses were performed on a Perkin-Elmer F.11 flame ionization chromatograph with N_2 carrier gas and stainless steel columns as follows: (*a*) 4 m × 1/16 in o.d., containing 10% squalane on 80—100 mesh Chromosorb W; (*b*) 4 m × 1/8 in o.d., containing 10% polyethylene glycol 400 (PEG) on 60—80 mesh Chromosorb W; and (*c*) 4 m × 1/8 in o.d., containing 10% di-n-butyl D-tartrate (DBDT) on 85—100 mesh Celite. Relative retention times were determined for authentic samples as in Table 2.

Absence of Addition Reactions of Pent-2-ene.—A mixture (1·85 g) of pentenes (1-ene, 5·0%; *cis*-2-ene, 35·6%; *trans*-2-ene, 59·4%) was added to 60% aqueous ethanol (85·0 ml) containing hydrogen bromide (1·05 g, 0·15M) and the mixture was heated at 80 °C for 50 h. Most of the pent-2-ene escaped to a trap (−80 °C). No addition product was detectable.

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