

Isomer Ratios from the Bromination of Allyl Chloride in Water, Methanol, Acetic Acid, and Trifluoroacetic Acid

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In a hydroxylic solvent HOR (water, methanol, acetic acid, or trifluoroacetic acid), bromine reacts with allyl chloride to yield 1,2-dibromo-3-chloropropane together with the 1-bromo-2-OR and 2-bromo-1-OR products. As expected the yield of the dibromide increases as the nucleophilicity of the solvent is decreased, but the ratio of the other two isomeric products remains approximately constant at 30 : 70 over the range of solvents studied. The results, together with those obtained by other workers for similar electrophilic additions, are discussed in terms of the structures of the intermediate carbocations.

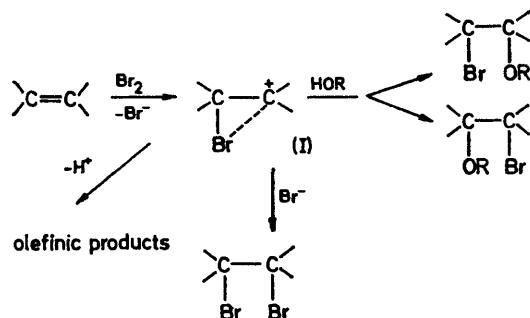
THE orientation of addition in a two-stage electrophilic process involving an unsymmetrical alkene and an unsymmetrical reagent was first discussed in terms of Markownikoff's rule. Later this was rationalised in terms of the electronic and steric effects of substituents in the alkene and the relative stabilities of the possible carbocation intermediates, and by implication, of the transition states leading to the formation of these intermediates. Whereas the addition of hydrogen halides generally leads to only one isomer, there are many cases known, for

example in halogenation, where both regioisomers are formed. The mechanisms of these reactions have been discussed^{1,2} in terms of intermediates in which there is a considerable degree of bridging between the electrophile and the carbocationic centre [such as the bromonium ion(I)]. These intermediates can undergo proton loss to give various olefinic products, reaction with bromide ion

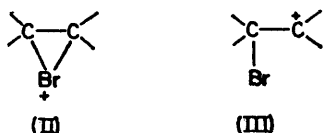
¹ P. B. D. de la Mare and R. Bolton, 'Electrophilic Additions to Unsaturated Systems,' Elsevier, Amsterdam, 1966, p. 116.

² R. C. Fahey, *Topics Stereochem.*, 1968, **3**, 239.

to give the dibromide, and attack by the solvent HOR, at either carbon atom (with a 1,2-bromine shift in one case) to give the two isomeric bromo-OR products. Any other added nucleophile can compete with Br^- and HOR for capture of the intermediate. Here the species (I) is



written as a partially bridged ion, with an electrostatic ion-dipole interaction between the bromine atom and the carbon atom bearing the formal positive charge. Some authors³ prefer to describe these intermediates as fully bridged three-membered ring bromonium ions(II).



Olah and his co-workers⁴ have identified such species in highly stabilising acid media; this does not necessarily mean that these ions are intermediates in electrophilic bromination reactions in hydroxylic solvents. Peterson and his co-workers⁵ have concluded that five-membered ring halogenonium ions are involved in the addition of trifluoroacetic acid to alkenes and alkynes, but there is no evidence for five-membered ring bromonium ions in the bromination of alkenes in a number of hydroxylic solvents.⁶ Generally free carbocations of the type (III) are not postulated as intermediates in electrophilic brominations as they cannot account for the *trans*-addition generally observed in such reactions. There is also evidence against the involvement of such species from the detailed analysis⁷ of the orientation of proton loss from carbocations produced by electrophilic additions. In much of the early work on halogenation of alkenes in hydroxylic solvents the ratios of dihalide to halogeno-OR products (e.g. halogenomethyl ether from methanolic solution,⁸ and halogenoacetates from acetic acid⁹) were measured, but no attempt was made to determine the relative proportions of the two possible regioisomers in

³ E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, New York, 1959, p. 523; J. G. Traynham, *J. Chem. Educ.*, 1963, 392.

⁴ G. A. Olah and P. E. Peterson, *J. Amer. Chem. Soc.*, 1968, **90**, 4675; G. A. Olah, *Science*, 1970, **168**, 1298.

⁵ P. E. Peterson, *Accounts Chem. Res.*, 1971, 407.

⁶ S. R. Hooley and D. L. H. Williams, *J.C.S. Perkin II*, 1975, 503.

⁷ P. B. D. de la Mare and A. Salama, *J. Chem. Soc.*, 1956, 3337; P. Ballinger, P. B. D. de la Mare, and D. L. H. Williams, *J. Chem. Soc.*, 1960, 2467.

the latter product. Later work,¹⁰ often based upon kinetic analysis of the isomer mixture, showed that the orientation was a function of the electrophile. This was interpreted for halogenation in terms of the increasing degree of bridging along the series $\text{Cl} < \text{Br} < \text{I}$ in accord with the increasing neighbouring group interaction of the halogen. It was suggested¹¹ that the orientation of addition might be affected by the nucleophilicity of the solvent, although little detailed investigation of this aspect had been reported. We have attempted to establish this point in the present work, by examining the product ratios obtained in the bromination of allyl chloride in water, methanol, acetic acid, and trifluoroacetic acid. It is known that the halogenation of allyl halides¹⁰ leads to a mixture of products, with the non-Markownikoff product dominating, although for the addition of hydrogen halides to allyl chloride¹² only the 1,2-dihalogenopropane products have been reported.

EXPERIMENTAL

Commercial allyl chloride was purified by fractional distillation before use. Methanol, acetic acid, and trifluoroacetic acid were distilled from bromine. Brominations were carried out by addition of an excess of allyl chloride to bromine (ca. 0.05M) in the appropriate solvent. In some cases sodium bromide was present. When reaction was complete, the solvent was removed, in the case of methanol, acetic acid, and trifluoroacetic acid, and the residue was examined by g.l.c. For the reaction in water, the products were extracted into ether, the extract was dried and evaporated, and the residue was examined by g.l.c. The yield of each product was determined by integration of the g.l.c. peak; the traces were all obtained by using a gas density balance. The figures were reproducible to within $\pm 2\%$.

Products from the Water Reaction.—This gave two peaks only in the g.l.c. trace with a small separation. The products were identified as 1-bromo-3-chloropropan-2-ol, and 2-bromo-3-chloropropan-1-ol by comparison with authentic samples.¹³ The i.r. spectrum of the total product was identical with the product of addition of hypobromous acid to allyl chloride. There was no indication of any olefinic products, nor of the dibromide, even when the reaction mixture contained 0.1M-sodium bromide.

Products from the Methanol Reaction.—Three peaks were observed in the g.l.c. trace, two close together and the third with longer retention time. The first two were separated from the third by preparative g.l.c. Material from peak three was 1,2-dibromo-3-chloropropane (Found: C, 15.5; H, 2.3; total halogen 82.5. Calc. for $\text{C}_3\text{H}_5\text{Br}_2\text{Cl}$: C, 15.3; H, 2.1; total halogen 82.5%). The combined peaks one and two gave analytical figures consistent with the methyl ether of bromochloropropanol (Found: C, 25.5; H, 4.7; total halogen, 61.7. Calc. for $\text{C}_4\text{H}_8\text{BrClO}$: C, 25.6; H, 4.3; total halogen, 61.6%). A commercial sample of 1-bromo-3-chloropropan-2-ol was converted into its methyl ether by

⁸ C. F. Irwin and G. F. Hennion, *J. Amer. Chem. Soc.*, 1941, **63**, 858.

⁹ W. Bockemuller and F. W. Hoffmann, *Annalen*, 1935, **519**, 165.

¹⁰ Ref. 1, p. 135.

¹¹ Ref. 1, p. 134.

¹² M. S. Kharasch, S. C. Kleiger, and F. R. Mayo, *J. Org. Chem.*, 1939, **4**, 430; A. L. Henne and F. W. Haekle, *J. Amer. Chem. Soc.*, 1941, **63**, 2692.

¹³ D. L. H. Williams, Ph.D. Thesis, London, 1960.

reaction with diazomethane and used in the g.l.c. experiments to identify the appropriate isomer in the reaction product. Similarly the 2-acetoxy- and 2-trifluoroacetoxy-derivatives of 1-bromo-3-chloropropan-2-ol were prepared by reaction with acetic anhydride and trifluoroacetic anhydride respectively, so that the appropriate isomers could be identified from the bromination reactions in acetic acid and trifluoroacetic acid.

RESULTS AND DISCUSSION

The results of the product analyses are shown in the Table. As expected, the yield of the dibromide increases from zero (in water) to 97% (in trifluoroacetic acid) as the nucleophilicity of the solvent decreases along the series H₂O, MeOH, AcOH, CF₃·CO₂H, thus

Product yields in the bromination of allyl chloride

Solvent	Added Br ⁻	% Dibromide	1-Br : 2-Br ratio
H ₂ O	0	0	30 : 70
H ₂ O	0.1M	0	26 : 74
MeOH	0	57	30 : 70
MeOH	0.2M	71	32 : 68
AcOH	0	73	29 : 71
CF ₃ ·CO ₂ H	0	97	29 : 71

allowing the bromide ion to compete more effectively as the nucleophile. The addition of sodium bromide increased the yield of dibromide for the reaction in methanol but had no effect upon the product from the reaction in water. Within the experimental error of the g.l.c. analyses, the isomer ratio of the other products (bromo-chloro-alcohols, bromo-chloro-methyl ethers, bromo-chloro-acetates, and bromo-chloro-trifluoroacetates) remains constant at 30 : 70 over the range of solvents studied, with the 2-bromo-isomer (the anti-Markownikoff product) in excess. This ratio is close to that reported¹⁴ for the products from the addition of hypobromous acid to allyl chloride in water (27 : 73). The results show that the orientation of addition is thus independent of the nature of the solvent, which acts as the nucleophile in reaction (competing with Br⁻) with the carbocation inter-

mediate. The solvent series represents a significant range of nucleophilic reactivities (as evidenced by the increasing dibromide yield) and also of molecular size.

Poutsma and Kartch¹⁵ have found similar results for the chlorination of pent-2-ene. There the products in a number of solvents, HOR, are the dichloride, various olefinic products, and the isomeric 2-Cl-3-OR and 2-OR-3-Cl products. The ratios of the yields of the latter two were found to be approximately constant for a number of solvents. de la Mare and Galandauer¹⁶ have found also that in the addition of bromine monochloride to propene in aqueous hydrochloric acid, although, as expected, the overall yield of bromohydrin product decreases as the hydrochloric acid concentration is increased, the fraction of 1-bromopropan-2-ol in the bromohydrin mixture remains constant, as does the fraction of 1-bromo-2-chloropropane in the bromo-chloropropane mixture. These fractions were however not the same, and it was suggested that two discrete intermediates were involved, one of type (I) which gives predominantly the Markownikoff orientation products, and the other a fully bridged bromonium ion of type (II) which leads predominantly to the anti-Markownikoff products. In other cases, changing the nucleophilic part of the reagent has little effect on the product ratios; for example the addition of hypobromous acid¹⁴ and of bromine monochloride¹⁷ to allyl chloride.

Our results for bromination and those of Poutsma and Kartch for chlorination can be accommodated by reaction schemes involving (a) only one intermediate of type (I), and (b) two intermediates (I) and (II). However the results do indicate that attack by the solvent at the carbon atom bearing the positive charge is not very sensitive to the steric requirements of the solvent. This tends to argue against reaction in which both isomeric products are produced from a fully bridged bromonium ion intermediate (II), where it is to be expected that attack would occur at the sterically favoured 1-carbon atom (by analogy with the ring-opening reactions of epoxides¹⁸), particularly for the larger solvent molecules, acetic acid and trifluoroacetic acid.

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¹⁴ P. B. D. de la Mare, P. G. Naylor, and D. L. H. Williams, *J. Chem. Soc.*, 1962, 443.

¹⁵ M. L. Poutsma and J. L. Kartch, *J. Amer. Chem. Soc.*, 1967, **89**, 6595.

¹⁶ P. B. D. de la Mare and S. Galandauer, *J. Chem. Soc.*, 1958, 36.

¹⁷ P. G. Naylor, Ph.D. Thesis, London, 1961.

¹⁸ R. E. Parker and N. S. Isaacs, *Chem. Rev.*, 1959, **59**, 737.