685. *The Rearrangement of Some Dibromopropyl Esters.*

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A new rearrangement of dibromopropyl esters is described, in which a simultaneous migration of a bromine atom and an acyloxy-group takes place. The direction and rate of the migration appear to depend on the nature of the acyl group.

The preparation of 1 : 3-dibromo-2-propyl benzoate (I; R = Ph) by the reaction of 1 : 3-dibromopropan-2-ol (II) with benzoyl chloride has been reported by Hurd and Pilgrim (*J. Amer. Chem. Soc.*, 1933, **55**, 1195), but later workers (Andreva and Chernov, *Chem. Abs.*, 1940, 7572) have claimed that it could not be prepared in this way. During other work it became necessary to obtain samples of the benzoates of both of the dibromopropanols (II and III) for infra-red spectral studies. Benzoylation of both dibromopropanols, however, produced the same dibromopropyl benzoate, the products having identical infra-red spectra with their chief maxima at 7·05, 8·5, 9·5, 9·75, and 11·9 μ. In order to decide which of the two possible esters this product represented, it was dehalogenated by catalytic hydrogenation in presence of palladised strontium carbonate, and the infra-red spectrum of the product was compared with the spectra of the two isomeric propyl benzoates (Table 1, *a* and *b*). The debrominated ester was identified as *n*-propyl benzoate, from which it was concluded that the original ester was 2 : 3-dibromopropyl benzoate. It is evident, therefore, that during benzoylation of 1 : 3-dibromopropan-2-ol with benzoyl chloride, a rearrangement to the isomeric dibromopropyl benzoate (IV; R = Ph) takes place.

$CH_2Br\cdot CH(O\cdot COR)\cdot CH_2Br$ (I)

$CH_2Br\cdot CH(OH)\cdot CH_2Br$ (II)

$CH_2Br\cdot CHBr\cdot CH_2\cdot OH$ (III)

$CH_2Br\cdot CHBr\cdot CH_2(O\cdot COR)$ (IV)

When acetyl or butyryl chloride was heated with each of the isomeric dibromopropanols, distinct dibromopropyl esters were obtained in each case. The products obtained after catalytic debromination were shown by their infra-red absorption spectra to be the acetates and butyrates of the isomeric propyl alcohols (Table 1; *c*, *d*, *e*, and *f*).

Table 1. *Characteristic infra-red absorption bands of propyl and dibromopropyl esters.*

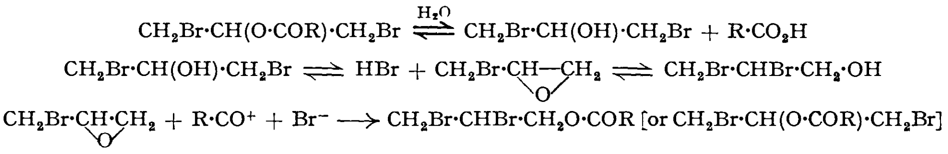
Ester	$\lambda_{max.}$ for characteristic bands (μ)
a, *iso*Propyl benzoate	8·7, 10·8, 11·75, 12·1
b, *n*-Propyl benzoate	8·6, 10·3, 10·7, 10·95, 11·8
c, *iso*Propyl butyrate	9·55, 12·15
d, *n*-Propyl butyrate	10·0, 10·9, 11·9
e, *iso*Propyl acetate	8·45, 8·7, 9, 10·45
f, *n*-Propyl acetate	8·55, 9·5, 10·25, 13·2
g, 2 : 3-Dibromopropyl benzoate	7·05, 8·5, 9·5, 9·75, 11·9

Table 2. *Variation in characteristic absorption bands of dibromopropyl acetates due to interconversion at* 100°.

	Absorption (%) of esters			
Reaction	10·25 μ	10·8 μ	11·2 μ	12·2 μ
2 : 3-Dibromopropanol + AcCl; 3 hr.	60	nil	53	nil
2 : 3-Dibromopropanol + AcCl; 36 hr.	52	40	40	28
2 : 3-Dibromopropyl acetate + HCl gas; 84 hr.	50	50	40	30
1 : 3-Dibromopropan-2-ol + AcCl; 3 hr.	48	50	30	34

In all of the acylations described, the reaction time was 1—3 hr., and it seemed possible that the apparent absence of rearrangement during acetylation and butyrylation was due to the rearrangement in these cases being slow. When the time of reaction was prolonged, definite infra-red spectral evidence of the formation of some 1 : 3-dibromo-2-propyl acetate from 2 : 3-dibromopropan-1-ol and acetyl chloride was found (Table 2). When a sample of pure 2 : 3-dibromopropyl acetate was saturated with hydrogen chloride at 20° and heated in a sealed tube at 100° for 36 hr., the product was shown by comparison of infra-red spectra to be almost wholly the 1 : 3-dibromo-2-propyl ester (Table 2). In the case of the acetates, therefore, the rearrangement takes place in the opposite direction to that of the benzoates, but much more slowly, and it is likely that it is acid-catalysed.

It was at first thought that epibromohydrin might be an intermediate in the rearrangement, according to some such scheme as :

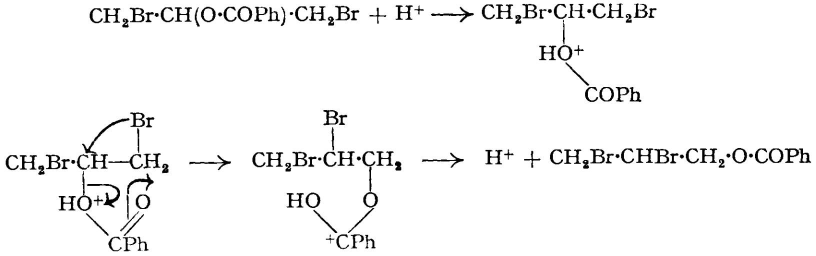


$$CH_2Br{\cdot}CH(O{\cdot}COR){\cdot}CH_2Br \overset{H_2O}{\rightleftharpoons} CH_2Br{\cdot}CH(OH){\cdot}CH_2Br + R{\cdot}CO_2H$$
$$CH_2Br{\cdot}CH(OH){\cdot}CH_2Br \rightleftharpoons HBr + CH_2Br{\cdot}\underbrace{CH{-}CH_2}_{O} \rightleftharpoons CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}OH$$
$$CH_2Br{\cdot}\underbrace{CH{\cdot}CH_2}_{O} + R{\cdot}CO^+ + Br^- \longrightarrow CH_2Br{\cdot}CHBr{\cdot}CH_2O{\cdot}COR\ [\text{or } CH_2Br{\cdot}CH(O{\cdot}COR){\cdot}CH_2Br]$$

However, any such mechanism includes the reaction of a carbonium ion or an oxide with a bromine anion, and in the presence of the high concentration of chloride ion present in the reaction mixture, chlorobromopropyl esters should be found in the products. No trace of chlorine could be detected in any of the esters produced, and this mechanism cannot therefore obtain.

When benzoyl chloride was caused to react with an excess of 1 : 3-dibromopropan-2-ol, the products were 2 : 3-dibromopropyl benzoate and unchanged 1 : 3-dibromopropanol. This excludes the possibility that the alcohol rearranges before benzoylation, and it seems that formation of the 2 : 3-dibromopropyl ester takes place by an exceedingly rapid rearrangement of either the 1 : 3-dibromo-2-propyl benzoate or an intermediate complex.

The following mechanism for the rearrangement is proposed :



$$CH_2Br{\cdot}CH(O{\cdot}COPh){\cdot}CH_2Br + H^+ \longrightarrow CH_2Br{\cdot}\underset{\underset{COPh}{HO^+}}{CH}{\cdot}CH_2Br$$
$$CH_2Br{\cdot}\underset{HO^+}{CH}{-}\overset{Br}{CH_2} \longrightarrow CH_2Br{\cdot}\overset{Br}{CH}{\cdot}\underset{O}{CH_2} \longrightarrow H^+ + CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}O{\cdot}COPh$$

When Me replaces Ph, the rearrangement takes place in the opposite direction and much more slowly.

EXPERIMENTAL

Preparation of Reference Materials.—1 : 3-Dibromopropan-2-ol was prepared by Fuson and Babcock's method (*Org. Synth.*, **14**, 42).

2 : 3-*Dibromopropanol.* Allyl alcohol (1 mol.) in dry carbon tetrachloride (10 vols.) was treated slowly with bromine (2 mols.) in twice its volume of dry carbon tetrachloride at <25° (ice-cooling). The resulting solution was washed with 2N-sodium carbonate and dried (Na_2SO_4), and the solvent removed by distillation. Fractional distillation of the residue under reduced pressure gave 2 : 3-dibromopropanol, b. p. 116°/15 mm.

n-*Propyl acetate and benzoate, and* iso*propyl acetate and benzoate.* Commercial esters (B.D.H.) were redistilled, fractions used having b. p. 101°, 230°, 81°, and 218°, respectively.

n-*Propyl butyrate and* iso*propyl butyrate.* These esters were prepared by the sulphuric acid-catalysed esterification of the appropriate propanols with butyric acid. *n*-Propyl butyrate had b. p. 142·5°, and *iso*propyl butyrate, b. p. 128°.

Preparation of Dibromopropyl Esters.—The appropriate dibromopropanol (1 mol.) and the acid halide (1·1 mols.) were heated together at 100° for 3 hr. The resulting mixture was diluted with ether, and washed with sodium hydrogen carbonate solution until free from acid, and then with water. After being dried (Na_2SO_4), the ether was evaporated off and the residue distilled under reduced pressure. The product was redistilled under reduced pressure for the preparation of a sample for determination of infra-red spectrum. B. p.s of 1 : 3- and 2 : 3-dibromopropyl esters were identical, *viz.* : acetates, 68°/3 mm.; butyrates, 118°/6·5 mm.; 2 : 3-dibromopropyl benzoate, 165°/3 mm. The isomers were readily distinguishable by their infra-red spectra and those of the propyl esters produced on catalytic dehalogenation.

Catalytic Dehalogenation of Dibromopropyl Esters.—The ester (1 g.) and 2% palladised strontium carbonate catalyst (0·5 g.) in methanol (50 c.c.) were shaken for 24 hr. in hydrogen; absorption was then complete. After filtration and evaporation, distillation gave the propyl ester, which was redistilled for determination of infra-red spectrum. Yields were approx. 80%.

Infra-red spectra were determined on the liquid esters, with a Perkin–Elmer 12.B recording spectrograph.

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