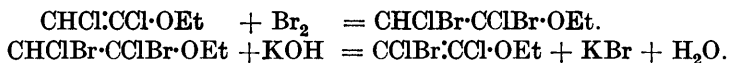


CXLIX.— $\alpha\beta$ -Dichloro- $\beta$ -bromovinyl Ethyl Ether.

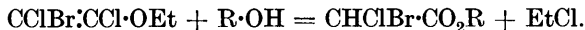
By ISOBEL AGNES SMITH.

By brominating  $\alpha\beta$ -dichlorovinyl ethyl ether and then heating the addition product, Crompton and Triffitt (J., 1921, **119**, 1874) obtained chlorobromoacetyl chloride. If the addition product is not heated but is treated at once with alcoholic potash,  $\alpha\beta$ -dichloro- $\beta$ -bromovinyl ethyl ether is obtained in good yield :

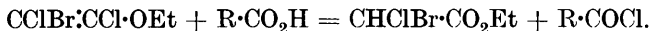


This ether resembles  $\alpha\beta$ -dichlorovinyl ethyl ether in its reactions towards ethyl alcohol and phenol (compare Crompton and Vander-

stichele, J., 1920, **117**, 691). The reactions, however, take place less readily, considerable heating being necessary to induce the ether to react. The reactions with ethyl alcohol, phenol,  $\beta$ -naphthol, and quinol were studied and in each case gave rise to the corresponding ester:

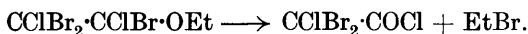


The ether was also found to resemble  $\alpha\beta$ -dichlorovinyl ethyl ether in its reactions with acids, concentrated sulphuric acid, glacial acetic acid, and benzoic acid being selected as typical acids for the comparison. In each case ethyl chlorobromoacetate was obtained and, in the latter two cases, the acid chlorides of the reacting acids:



In the experiment with glacial acetic acid a secondary reaction took place on prolonged heating. No acid chloride could then be detected, but in addition to ethyl chlorobromoacetate considerable quantities of ethyl acetate and chlorobromoacetic acid were obtained.

When brominated,  $\alpha\beta$ -dichloro- $\beta$ -bromovinyl ethyl ether gave  $\alpha\beta$ -dichloro- $\alpha\beta\beta$ -tribromodiethyl ether, which on exposure to moist air readily lost its halogen and passed into oxalic acid. On being heated in the absence of moisture, the ether was converted into chlorodibromoacetyl chloride, a reaction which also took place slowly on allowing the compound to remain in a sealed tube for several weeks at the ordinary temperature.



Chlorine appeared to act on  $\alpha\beta$ -dichloro- $\beta$ -bromovinyl ethyl ether in a similar manner.

#### EXPERIMENTAL.

*$\alpha\beta$ -Dichloro- $\beta$ -bromovinyl Ethyl Ether.*—To 100 g. of  $\alpha\beta$ -dichlorovinyl ethyl ether (Crompton and Vanderstichele, J., 1920, **117**, 691), cooled in a freezing mixture of ice and salt, 34 c.c. of bromine were run in slowly, the coloration then being permanent. The product was added to a solution of potassium hydroxide (60 g. of KOH, 40 c.c. of water, 310 c.c. of absolute alcohol) and, after  $\frac{1}{2}$  hour, sodium bromide having separated, the mixture was poured into 2 l. of water. The oil thus produced was washed with water, dried over soda-lime, and fractionally distilled, 100 g., b. p. 172—177°, being obtained.  *$\alpha\beta$ -Dichloro- $\beta$ -bromovinyl ethyl ether* is a colourless liquid, b. p. 177°/754 mm.,  $d_4^{20}$  1.6565,  $d_4^{25}$  1.6478,  $d_4^{30}$  1.6422,  $n_D^{17}$  1.50427; whence  $[R_L]_D^{17}$  39.24 (Found: Cl, 32.1; Br, 36.2.  $\text{C}_4\text{H}_5\text{OCl}_2\text{Br}$  requires Cl, 32.2; Br, 36.3%).

Ethyl alcohol, phenol, and  $\beta$ -naphthol, by interaction with this ether, gave ethyl, phenyl, and  $\beta$ -naphthyl chlorobromoacetate, respectively, the product being identified in each case by its physical properties and by analysis. Quinol gave quinol bischlorobromoacetate, m. p. 122—123°. Concentrated sulphuric acid gave ethyl chlorobromoacetate, whereas acetic acid and benzoic acid yielded ethyl chlorobromoacetate together with acetyl chloride and benzoyl chloride, respectively, the acid chlorides being identified by conversion into the corresponding anilide and amide.

*Action of Bromine on  $\alpha\beta$ -Dichloro- $\beta$ -bromovinyl Ethyl Ether.*—The ether (80 g.) was brominated at 0°,  $\alpha\beta$ -dichloro- $\alpha\beta\beta$ -tribromodiethyl ether separating as a solid. After recrystallisation from light petroleum, this ether (yield 82 g.) had m. p. 28—29°,  $d_4^{20}$  2.2297,  $d_4^{30}$  2.2138,  $n_D^{20}$  1.56833; whence  $[R_L]_D^{20}$  55.88 (Found: Cl, 18.8; Br, 63.9.  $C_4H_5OCl_2Br_3$  requires Cl, 18.7; Br, 63.2%). It is readily soluble in the cold in acetone, alcohol, carbon tetrachloride, benzene or xylene, and insoluble in cold or hot water.

*Action of Heat on  $\alpha\beta$ -Dichloro- $\alpha\beta\beta$ -tribromodiethyl Ether.*—The ether was heated at about 60° in a hard glass tube drawn out to a fine capillary. Ethyl bromide was evolved and the ether changed almost quantitatively into chlorodibromoacetyl chloride. This was identified by conversion into chlorodibromoacetamide, which, mixed with an authentic specimen, melted at 127—128°. The acid chloride was further characterised by conversion into the *anilide*, which, after crystallisation from aqueous alcohol, melted at 102—103° (Found: N, 4.4.  $C_8H_6ONClBr_2$  requires N, 4.3%).

*Action of Chlorine on  $\alpha\beta$ -Dichloro- $\beta$ -bromovinyl Ethyl Ether.*—Dry chlorine was readily absorbed by  $\alpha\beta$ -dichloro- $\beta$ -bromovinyl ethyl ether at 0°, but the product could not be obtained crystalline, nor any uniform material by distillation under reduced pressure. On exposure to moist air, the product was largely converted into oxalic acid; and when it was heated at 60° for several hours in a tube drawn out to a capillary, dichlorobromoacetyl chloride (identified by conversion into dichlorobromoacetamide) was formed. These results indicated the presence of  $\alpha\alpha\beta\beta$ -tetrachloro- $\beta$ -bromodiethyl ether, but this could not be isolated.

*Molecular Refractivities.*—The molecular refractivity of  $\alpha\beta$ -dichloro- $\beta$ -bromovinyl ethyl ether, obtained from the observed refractivity by the Lorenz and Lorentz formula, is slightly lower than that calculated by means of Eisenlohr's atomic refractivities, and that of  $\alpha\beta$ -dichloro- $\alpha\beta\beta$ -tribromodiethyl ether is somewhat higher. The refractivities of the allied compounds  $\alpha\beta$ -dichlorovinyl ethyl ether and  $\alpha\beta\beta$ -trichlorovinyl ethyl ether were therefore determined for comparison; the former has  $d_4^{20}$  1.2037,  $d_4^{25}$  1.1972,  $d_4^{30}$  1.1909,

$n_D^{16.5^\circ}$  1.45584, and the latter has  $d_4^{20^\circ}$  1.3409,  $d_4^{25^\circ}$  1.3343,  $d_4^{30^\circ}$  1.3280,  $n_D^{16^\circ}$  1.47551.

	[ $R_L$ ] <sub>D</sub> .		Diff.
	Found.	Calc.	
$\alpha\beta$ -Dichloro- $\beta$ -bromovinyl ethyl ether .....	39.24	39.35	-0.11
$\alpha\beta$ -Dichlorovinyl ethyl ether .....	31.71	31.582	+0.13
$\alpha\beta\beta$ -Trichlorovinyl ethyl ether .....	36.73	36.449	+0.28
$\alpha\beta$ -Dichloro- $\alpha\beta\beta$ -tribromodiethyl ether .....	55.88	55.34	+0.54

The somewhat anomalous behaviour of  $\alpha\beta$ -dichloro- $\beta$ -bromovinyl ethyl ether may be connected with the *cis-trans* isomerism which it should exhibit, but attempts to isolate the isomerides from the product prepared as above were not successful.

The author desires to express her thanks to Mr. Holland Crompton for much advice and criticism.

BEDFORD COLLEGE,  
UNIVERSITY OF LONDON.

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