NOTES

Isolation of Glycollic Acid from Periodate-degraded Starch

Soluble starch, 2.0 g, in water (100 ml) was oxidized with periodic acid in the usual manner. After no further periodate was consumed, the solution was neutralized with barium carbonate and filtered. The polyaldehyde was reduced with potassium borohydride followed by mild acid hydrolysis. The mixture was further treated with bromine to oxidize glycollic aldehyde to the corresponding carboxylic acid. The solution was finally neutralized (PbCO₃), evaporated to dryness, borate removed, and an aqueous solution of the residue deionized. The neutral effluent was shown to contain erythritol, glycerol, and a trace of glucosylerythritol as deduced from hydrolysis of this component and the resulting equimolar ratio of glucose and erythritol. Glycollic acid was eluted from the anion exchange resin with dilute alkali and the free acid regenerated. The solution was evaporated and the residue heated (80° C) under high vacuum. Because of the possible volatility of the lactonized product, a cold finger apparatus was used. The product was reduced with potassium borohydride and the reaction mixture worked up in the usual manner. Ethylene glycol was identified chromatographically and as the di-p-nitrobenzoate, m.p. and mixed m.p. 145-146° C. As theoretically required, the molecular proportion of ethylene glycol was approximately equivalent to the combined molecular proportions of glycerol and erythritol.

Borohydride Reduction of Starch Polyalcohol Hydrolyzate

A quantity of starch (2 g) which had been treated with periodate, borohydride, and hydrolyzed with weak acid (7) in that order was re-treated with potassium borohydride to reduce glycollic aldehyde to ethylene glycol. Jayme and Satre (19) used a similar but somewhat less satisfactory procedure to characterize glycollic aldehyde. The mixture was worked up in the usual manner. The oily residue was chromatographed and found to contain erythritol, glycerol, and ethylene glycol. The relative molar quantity of each was determined by the periodate - chromotropic acid procedure (17, 18) and the combined molar quantity of glycerol and erythritol was equivalent to the molar quantity of ethylene glycol as theoretically required. The components were separated by paper chromatography and each compound further identified as the solid p-nitrobenzoate: ethylene glycol p-nitrobenzoate had m.p. and mixed m.p. 144-145° C, glycerol p-nitrobenzoate had m.p. and mixed m.p. 194-196° C, and erythritol p-nitrobenzoate had m.p. and mixed m.p. 249-252° C.

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THE DIMER OF BROMOTRIFLUOROETHYLENE

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Park, Holler, and Lacher (1) have briefly reported that dimerization of bromotrifluoroethylene takes place at 210° in the presence of the polymerization inhibitor Terpene-B.

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They suggested that the dimer is 1,2-dibromohexafluorocyclobutane since debromination gives hexafluorocyclobutene. They also suggested that their product was an approximately 50:50 mixture of the cis and trans forms. During the course of a study of the reactions of bromotrifluoroethylene with compounds containing As—As and P—P bonds (2) a product of molecular formula $C_4F_6Br_2$ was often obtained; therefore, it was decided to investigate further the preparation and structure of this compound.

It has now been found that dimerization of bromotrifluoroethylene occurs under quite mild conditions, giving a product which can be debrominated to give hexafluorocyclobutene. The infrared spectrum of this product is very similar to that of the product obtained by the bromination of hexafluorocyclobutene. However, extra bands are present in the spectrum of the dimer. Both these spectra are similar to that of the cyclic dimer of chlorotrifluoroethylene. The retention times of the dimer and the bromination product are identical on a dinonylphthalate column at 100°.

The ¹⁹F n.m.r. spectrum of the bromination product (Fig. 1(*a*)) shows an AB quartet



(lines 1–4) and an absorption due to one other nonequivalent fluorine (line 5). This pattern would be expected from a pure isomer of 1,2-dibromohexafluorocyclobutane, the two adjacent equivalent CF₂ groups giving rise to the AB pattern and the other absorption being due to the two equivalent fluorines on the two adjacent CFBr groups (3). The coupling constant for the AB system, 205 cycles/sec, is of the same order as that found for similarly fluorinated cyclobutanes (3). The ¹⁹F n.m.r. spectrum of the dimer is shown in Fig. 1(*b*), and if the bands corresponding to those in Fig. 1(*a*) are removed then the spectrum of Fig. 1(*c*) remains. This last spectrum is again what would be expected from a pure isomer of 1,2-dibromohexafluorocyclobutane, consisting of an AB pattern (lines 1', 2', 3', 4') (coupling constant 213 cycles/sec) and one other line (line 5').

Bromination of hexafluorocyclobutene would be expected to give predominantly the trans isomer and since only one isomer appears to be present this must be the trans form. Consequently the spectrum of Fig. 1(c) is that of the cis isomer.

These results strongly indicate that the dimer of bromotrifluoroethylene is a mixture of *cis*- and *trans*-1,2-dibromohexafluorocyclobutane. The relative amounts of the isomers are given by the relative intensities of lines 5 and 5' (Fig. 1(*b*)). The proportion is therefore approximately 60% cis and 40% trans.

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EXPERIMENTAL

Volatile reagents and products were manipulated in a vacuum system. Infrared spectra were recorded on a Perkin-Elmer model 421 instrument. Nuclear magnetic resonance spectra were determined on neat liquids using a Varian spectrometer operating at 40 Mc/sec.

Dimerization of Bromotrifluoroethylene

In a typical experiment 17.4 g of bromotrifluoroethylene was heated in a sealed tube (50 ml) for 6 days at 100°. Unchanged monomer (12.5 g) was recovered. The reaction products were an involatile polymer (0.90 g), which remained in the tube, and 3.8 g of a volatile fraction, which condensed in a trap cooled to -78°. This fraction was purified by v.p.c. (dinonylphthalate on firebrick at 100°) and found to contain ca. 70% of the expected dimer (found: mol. wt., 323; calc.: mol. wt., 322). The infrared spectrum showed the following absorption bands (vapor): 1375 (s), 1278 (s), 1230 (vs), 1172 (vw), 1072 (vw), 1047 (vw), 1016 (w), 996 (w), 963 (w), 941 (w), 866 (s), 836 (s), 797 (w), 759 (w), 724 (w) cm⁻¹. The ¹⁹F n.m.r. spectrum (Fig. 1(b)) had absorption at 1667, 1872, 1880, 2082, 2199, 2249, 2460, 2487, 2703, 2855 cycles/sec to the high-field side of an internal benzotrifluoride reference.

In further experiments it was found that irradiation of the monomer for 5 hours in thick-walled Pyrex tubes using a 100-w ultraviolet lamp produced very little polymer (3%) and no dimer. Dimerization by heating at 100° was slow, e.g. 2% dimer and 1% polymer after 18 hours, but at higher temperatures the rate was faster, e.g. 45% dimer and 40% polymer after 48 hours at 150°.

Debromination of the Dimer

When the dimer (2.338 g), benzonitrile (5 ml), and zinc dust (2.0 g) were shaken at 20° for 4 hours, hexafluorocyclobutene (0.788 g; 67% yield) was obtained which was identified by its molecular weight of 163 (calc.: mol. wt., 162) and by its infrared spectrum.

Bromination of Hexafluorocyclobutene

The butene (16.6 g) and bromine (16.6 g) in a sealed tube were irradiated with a 100-w ultraviolet lamp for 8 hours (4). The crude 1,2-dibromohexafluorocyclobutane so obtained distilled at 96-97° (760 mm) (lit. value, 96-97° (4)) and was purified by v.p.c. The major component of the distillate (ca. 90%) had the same retention time on the dinonylphthalate column (100°) as did the dimer. The infrared spectrum of the bromination product showed the following absorption bands (vapor): 1375 (s), 1276 (s), 1230 (vs), 1193 (w), 1171 (w), 1071 (vw), 1046 (w), 996 (s), 946 (w), 846 (w), 840 (s), 759 (s), 636 (w) cm⁻¹. The ¹⁹F n.m.r. spectrum (Fig. 1(a)) had absorption at 1877, 2082, 2199, 2249, 2460 cycles/sec to the high-field side of an internal benzotrifluoride reference.

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THE PREPARATION OF 3-BROMOINDOLE

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The few reports in the literature describing attempts at the direct halogenation of indole in the pyrrole ring, with bromine, chlorine, or iodine (1-3), indicate that a vigorous reaction does indeed occur. However, only in the case of iodination, and then only in

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