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 ^{19}F 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 ^{19}F 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 dilute aqueous solution, has the isolation of a monohaloindole (3-iodoindole) been successful (1, 2). The reaction of chlorine and bromine with indole is reported to yield "a mixture of higher substitution products" (3) which apparently could not be resolved.

A more successful route to 3-bromo- and 3-chloro-indole, devised by Weissgerber (3), involved the action of halogens on N-benzoylindole. Sulphuryl chloride has been reported to convert indole to 3-chloroindole or to 2,3-dichloroindole depending upon the amount of halogenating agent used (4). Buu-Hoï (5) found that the reaction of N-bromosuccinimide with N-benzoylindole gave a reasonably good yield of 3-bromo-N-benzoylindole which could readily be hydrolyzed to 3-bromoindole (3). More recently Yanovskaya (6) reported that in dioxane solution at 0° the action of dioxane dibromide on indole gave a 60% yield of 3-bromoindole.

Certain work in progress in this laboratory required a considerable quantity of 3-bromoindole. Although Weissgerber's procedure gave reasonably good results and produced 3-bromoindole from indole in an overall yield of about 45% (3), this route is time consuming. Accordingly, the preparation of the haloindole was attempted following the procedure reported by Yanovskaya (6). However, in our hands, the reaction in purified dioxane solvent (7, p. 284) gave only a very small amount of material, which spontaneously decomposed on attempts at its purification, in the manner characteristic of 3-bromoindole. The temperature of the reaction solvent could not be reduced to 0°, as reported, since the solvent and contents solidified below 8°. Hence we carried out the bromination at 8–10°, but otherwise as described (6). The same procedure, modified by the addition of a small amount of diethyl ether as diluent for the dioxane to permit attainment of 0° reaction temperature gave the same "tarry" material as before and little or no 3-bromoindole.

In the above reactions it was noted that hydrogen bromide evolved from the solution, especially near the end of the bromination reaction. Since Weissgerber found that 3-bromoindole decomposed readily when impure, or when in the presence of strong mineral acids, it was felt that some means of neutralizing or removing the acid would improve the reaction. The solvent pyridine proved to be the answer to the problem. When the halogenation was carried out using pyridine as solvent, indole could be converted to 3-bromoindole with dioxane dibromide in 48% yield. Use of pyridinium bromide perbromide as halogenating agent and pyridine as solvent and carrying the reaction out at 0–2° increased the yield of pure 3-bromoindole to at least 64%.

EXPERIMENTAL

To a solution of 4.0 g (0.034 mole) of indole in 40 ml of reagent pyridine cooled to 0–2°, was added slowly 10.8 g (0.034 mole) of pyridinium bromide perbromide (7, p. 65) dissolved in 30 ml of pyridine. The rate of addition was such that the temperature of the reaction mixture did not rise above 2°. When addition was complete, the solution was poured into cold ether and the resulting mixture freed from insoluble material by filtration. The cold ether solution was washed several times with cold dilute aqueous hydrochloric acid to remove the pyridine. The residual ether solution of the haloindole was then washed first with cold dilute aqueous sodium hydroxide, then with water. The dried ether solution ($MgSO_4$) was freed from ether and the residue crystallized from *n*-heptane and decolorized with charcoal if necessary. Yield, 4.3 g (64%) of pure 3-bromoindole melting at 65–66° (decomp.).

When dioxane dibromide was used as brominating agent in pyridine solution the same procedure gave 3-bromoindole in 48% yield.

In the recrystallization procedure, it is important not to heat the solution above 60° since 3-bromoindole, which deposits in the flask, begins to decompose at 65°. 3-Bromoindole may be kept satisfactorily if placed under a solvent such as pentane and stored at −20°. Otherwise even very pure material undergoes slow decomposition.

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