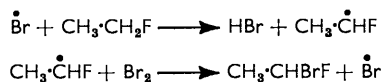


### 1234. Preparation of 1-Bromo-1-fluoroethane and 1-Bromo-1,1-difluoroethane

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KINETIC studies of the vapour-phase bromination of fluoroethanes have shown that the reactivity of the hydrogen atoms is strongly influenced by fluorine substituents.<sup>1</sup> Thus, in ethyl fluoride, the C-1 hydrogen (*i.e.*, on CH<sub>2</sub>F) is slightly activated and the C-2 hydrogen strongly deactivated relative to ethane, so that only methylene hydrogen atoms are abstracted by bromine atoms and the only chain-propagation steps are:



The products contain less than 0.1% of the alternative bromide, CH<sub>2</sub>Br·CH<sub>2</sub>F. In the same way, the bromination of 1,1-difluoroethane yields exclusively CH<sub>3</sub>·CBrF<sub>2</sub>.

The two bromides can therefore be made by direct bromination, as an alternative to Haszeldine and Osborne's method<sup>2</sup> of adding hydrogen bromide to the appropriate olefin in the dark, *e.g.*, they made CH<sub>3</sub>·CBrF<sub>2</sub> from CH<sub>2</sub>·CF<sub>2</sub> and we have made CH<sub>3</sub>·CHBrF from CH<sub>2</sub>·CHF using their procedure. Both preparations are about equally convenient and efficient but one utilises the olefin and the other the alkyl fluoride.

The infrared spectra of 1-bromo-1-fluoroethane and 1-bromo-1,1-difluoroethane have not previously been reported; using 50 mm. of vapour in an 8-cm. cell, the main features are: CH<sub>3</sub>·CHBrF 3040m, 1439w, 1391m, 1379m, 1255s, 1247s, 1242s, 1111vs, 1016m, 1003m, 907s, and 889s cm.<sup>-1</sup>; CH<sub>3</sub>·CBrF<sub>2</sub> 3058vw, 1439w, 1387s, 1190vs, 1111vs, 1030w, 969s, 901s, and 889s cm.<sup>-1</sup>. The p.m.r. spectrum of CH<sub>3</sub>·CHBrF in carbon tetrachloride at 33.5° had the following features: τ 7.96 (CH<sub>3</sub>, double doublet, *J*<sub>Me, H</sub> 5, *J*<sub>Me, F</sub> 21 c./sec.), 3.41 (CH, double quartet, *J*<sub>H, F</sub> 50.5 c./sec.).

#### EXPERIMENTAL

*Materials.*—Vinyl fluoride, 1,1-difluoroethane, and hydrogen bromide (Matheson), 1,1-difluoroethylene (Imperial Smelting Co.), and ethyl fluoride, made by the method of Edgell and Parts,<sup>3</sup> were purified by distillation.

*1-Bromo-1-fluoroethane.*—Ethyl fluoride (230 mm.; 1.20 mmoles) and bromine (220 mm.; 1.15 mmoles) were irradiated in a Pyrex vessel at 167° for 10 min., using a mercury lamp, after which 95% of the bromine had reacted. The products were pumped at -80° for 30 sec. to remove hydrogen bromide and residual bromine. Unchanged ethyl fluoride was recovered by distilling from -80° to a trap at -196°. The residue was purified by bulb-to-bulb distillations, and a middle cut was shown by g.l.c. to be a single compound (A) (85% based on C<sub>2</sub>H<sub>5</sub>F). It was identified as follows. After irradiation of a mixture of vinyl fluoride and hydrogen bromide, using a mercury lamp, two products were detected by g.l.c., one with the same retention time as the bromide (A). This component was isolated and its infrared spectrum was identical with that of compound (A) but quite different from that of CH<sub>2</sub>Br·CH<sub>2</sub>F,<sup>4</sup> hence (A) must be CH<sub>3</sub>·CHBrF. This is confirmed by its p.m.r. spectrum, given earlier.

<sup>1</sup> J. W. Coomber and E. Whittle, unpublished work.

<sup>2</sup> R. N. Haszeldine and J. E. Osborne, *J.*, 1956, 61.

<sup>3</sup> W. F. Edgell and L. Parts, *J. Amer. Chem. Soc.*, 1955, **77**, 4899.

<sup>4</sup> J. Simpson and E. K. Plyler, *J. Res. Nat. Bur. Stand.*, 1953, **50**, 223.

1-Bromo-1,1-difluoroethane.—1,1-Difluoroethane (230 mm.; 1.20 mmoles) and bromine (220 mm.; 1.15 mmoles) were irradiated at 167°, as above; after 22 hr., 99% of the bromine had reacted (a long photolysis time is required because  $\text{CH}_3\cdot\text{CHF}_2$  is much less reactive than  $\text{CH}_3\cdot\text{CH}_2\text{F}$ ). The products were passed through Carbosorb to remove hydrogen bromide and residual bromine. Unchanged  $\text{CH}_3\cdot\text{CHF}_2$  was separated from the bromide by g.l.c. using a 3-ft. column of 30% w/w tritolyl phosphate on Celite (the separation can also be done by distillation). The products contained only one bromide (B) (95% based on  $\text{CH}_3\cdot\text{CHF}_2$ ). It was identified as follows.  $\text{CH}_3\cdot\text{CBrF}_2$  was made by addition of hydrogen bromide to 1,1-difluoroethylene in the dark.<sup>2</sup> Its infrared spectrum and g.l.c. retention time were identical with those of compound (B). Also, the p.m.r. spectrum of a solution of (B) in carbon tetrachloride was identical with that in the literature.<sup>5</sup>

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<sup>5</sup> D. D. Ellerman, L. C. Brown, and D. Williams, *J. Mol. Spectroscopy*, 1961, **7**, 307.

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