

Anal. Calcd. for $C_{12}H_9NO_2$ (215.20): C, 66.97; H, 4.22; N, 6.51. Found: C, 66.92; H, 4.20; N, 6.28.

Attempted reaction of indole and maleic and fumaric acids under alkaline hydrolysis conditions. Indole (7.06 g., 0.0602 mole) and maleic acid (3.49 g., 0.0301 mole) were refluxed for 3 hr. with 30% aqueous potassium hydroxide solution (100 cc.). The reaction mixture was cooled, extracted with ether (3–50 cc. portions), and the ether evaporated, yielding crude indole (6.88 g., 97%), m.p. 39–43°.

In an identical experiment, with fumaric acid in place of maleic acid, the recovery of crude indole was 7.05 g., 100%, m.p. 39–43°.

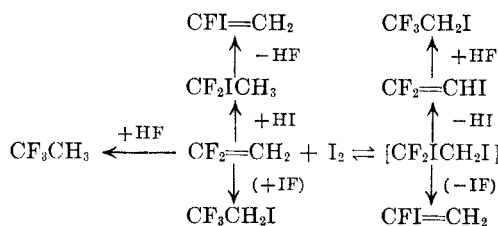
SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS 14, MINN.

Thermal Reaction of 1,1-Difluoroethylene with Iodine¹

MURRAY HAUPTSCHNEIN, ARNOLD H. FAINBERG, AND MILTON BRAID

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1,1-Difluoroethylene has been found to react thermally with iodine to form quite unexpectedly, 1,1,1-trifluoro-2-iodoethane as the major product. Another principal product of the reaction was an olefin boiling at *ca.* 40°, for which the structure 1-fluoro-1-iodoethylene is proposed. Two minor products were also identified in the reaction mixture, 1,1-difluoro-1-iodoethane and 1,1-difluoro-2-iodoethylene, as well as some polymeric material. In the presence of the very large excess of 1,1-difluoroethylene used in the present work, 1,1,1-trifluoroethane was a major by-product.²



It is obvious that the conditions employed in the single experiment reported herein were not designed to produce the iodine-containing products in optimum yields, which, of course, would be greatly improved by use of an excess of iodine.

(1) The work herein reported was carried out under contract between the Office of Naval Research and the Pennsalt Chemicals Corp. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) All of the products isolated can be related schematically through the iodine adduct of 1,1-difluoroethylene (not isolated) as shown below:

EXPERIMENTAL

Thermal reaction of 1,1-difluoroethylene with iodine. Into a 170-ml. monel autoclave were placed 63.5 g. (0.25 mole) of crystalline iodine. The autoclave was cooled in liquid nitrogen, and 80 g. (1.25 moles) of 1,1-difluoroethylene were condensed in it by means of gaseous transfer *in vacuo*. After heating at 185° with shaking for 160 hr., during which the pressure dropped from 3200 to 1300 p.s.i., the autoclave was cooled to room temperature and vented at atmospheric pressure into a liquid nitrogen-cooled receiver.

The recovered product consisted of 53 g. of material, gaseous at room temperature, shown by infrared analysis to consist only of unreacted $\text{CH}_2=\text{CF}_2$ (mostly) and CF_3CH_3 ,³ 53 g. of liquid product, and 37 g. of solids, containing some polymeric material and unreacted iodine. Distillation of the liquid product gave 38 g. of liquid boiling below 55°, and 14 g. of polymer boiling above 145°.

Fractional distillation of a 25-g. portion⁴ of the liquid product through a 2 ft. \times 8 mm. Mini-Cal Podbielniak column gave several fractions totalling 8 g., b.p. 40–46°, n_D^{20} 1.39–1.41 and 16 g. of $\text{CF}_3\text{CH}_2\text{I}$, b.p. 54–55°, center cut: b.p. 55.0° (756 mm.), n_D^{20} 1.3962, reported⁵ b.p. 55.0°, n_D^{25} 1.3981. Its infrared spectrum was identical with that of an authentic sample prepared by iodide displacement on 2,2,2-trifluoroethyl *p*-toluenesulfonate. Principal infrared bands for $\text{CF}_3\text{CH}_2\text{I}$: 3.36, 6.81, 7.01, 7.43, 7.78, 8.19, 8.90, 9.44, 11.9, 14.9 μ .

The infrared spectrum of the fractions b.p. 40–46° showed that the mixture consisted principally of an olefin A, b.p. *ca.* 40°, with a double bond stretching band at 6.09, 6.14 μ (doublet). Also indicated were minor amounts of a second olefin B, boiling virtually at the same temperature as A (perhaps slightly higher), having a double bond stretching band at 5.79 μ , and a saturated compound boiling several degrees higher than the olefins, and exhibiting remarkably intense C—H stretching bands at 3.33 and 3.40 μ .

The saturated compound was identified as $\text{CH}_3\text{CF}_2\text{I}$, reported⁶ b.p. 45°, n_D^{19} 1.4183 on the basis that the infrared spectrum of the mixture contained the nine major peaks found⁷ for an authentic sample. Olefin B was similarly identified spectroscopically as $\text{CF}_2=\text{CHI}$, reported⁸ b.p. 35.5° at 622 mm.

Olefin A has principal peaks in the infrared at 6.09, 6.14, *ca.* 8.3, 8.68, 8.95, 9.55, 9.60, 10.20, 11.03, 11.82, and 12.26 μ . Its double bond stretching frequency is consistent with a $\text{CH}_2=\text{CFX}$ type of structure,⁹ and the structure $\text{CH}_2=\text{CFI}$, is proposed.

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(3) A.P.I. Research Project 44, Catalog of Infrared Spectral Data, No. 979.

(4) This portion was not an entirely representative sample of the 38 g. of liquid boiling below 55°, but was richer in the least volatile component.

(5) G.V.D. Tiers, H. A. Brown, and T. S. Reid, *J. Am. Chem. Soc.*, **75**, 5978 (1953).

(6) R. N. Haszeldine, *J. Chem. Soc.*, 61 (1956).

(7) R. N. Haszeldine, private communication: 3.34, 3.40, 7.20, 8.47, 9.03, 9.07, 10.40, 11.27, 11.35 μ .

(8) Private communication of J. D. Park; M. Hein, Ph.D. Thesis, University of Colorado (1954): 5.80, 7.62, 7.68, 8.77, 8.85, 10.52, 10.63, 13.58 μ .

(9) *E.g.*, the double-bond stretching frequency of $\text{CH}_2=\text{CClF}$ is 6.08 μ . See I. P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945).