

*Addition of Free Radicals to Unsaturated Systems. Part VII.**
1 : 1-Difluoroethylene.

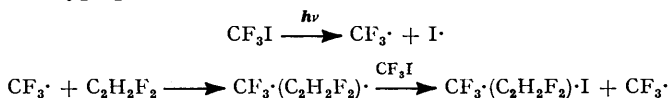
By R. N. HASZELDINE and B. R. STEELE.

[Reprint Order No. 4819.]

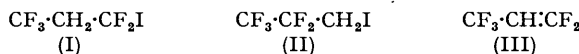
The photochemical reaction of trifluoriodomethane with 1 : 1-difluoroethylene yields only the compound $\text{CF}_3\cdot\text{CH}_2\cdot\text{CF}_2\text{I}$, *i.e.*, the trifluoromethyl radical attacks exclusively the $\cdot\text{CH}_2$ group. Proof of constitution is given. Iodine monobromide and 1 : 1-difluoroethylene yield only 1-bromo-1 : 1-difluoro-2-iodoethane; the iodo-compound is converted into 1 : 1 : 1-trifluoro-2-iodoethane by means of mercurous fluoride.

THE direction of addition of a trifluoromethyl radical, derived from trifluoriodomethane, to vinyl chloride and vinyl fluoride was shown to be exclusively to the $\cdot\text{CH}_2$ group (Part II, *J.*, 1953, 1199). The present study is concerned with the highly polarised olefin 1 : 1-difluoroethylene.

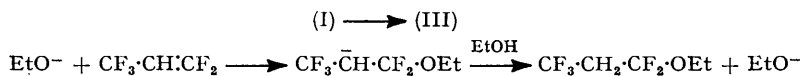
Trifluoriodomethane and 1 : 1-difluoroethylene show no dark reaction, but react smoothly on exposure to light of wave-length $>3000 \text{ \AA}$, with liberation of only traces of iodine, to give exclusively $\text{CF}_3\cdot(\text{C}_2\text{H}_2\text{F}_2)\cdot\text{I}$. Light of wave-length $>2200 \text{ \AA}$ (silica reaction vessels) appreciably increases the rate of formation of $\text{CF}_3\cdot(\text{C}_2\text{H}_2\text{F}_2)\cdot\text{I}$; small amounts of products of higher boiling point are also formed. Infra-red spectroscopic examination shows that the two products $\text{CF}_3\cdot(\text{C}_2\text{H}_2\text{F}_2)\cdot\text{I}$ are identical. The product is formed by a chain reaction of the type postulated earlier :



and could be (I) or (II). That it is 1 : 1 : 1 : 3 : 3-pentafluoro-3-iodopropane (I), to an extent of at least 85% and probably exclusively, is shown by its dehydroiodination by



means of solid potassium hydroxide to give a high yield of the known 1 : 1 : 3 : 3 : 3-pentafluoropropene (III). 1 : 1 : 1 : 2 : 2-Pentafluoro-3-iodopropane (II) would not be converted into (III) by this method. The dehydroiodination can also be effected by means of ethanolic potassium hydroxide, but the yields of the olefin are considerably reduced, since formation of an ether occurs :



The susceptibility of fluoro-olefins to nucleophilic attack and the resistance of compounds which contain a CF_2I group to $\text{S}_{\text{N}}2$ reactions are well established. Clear distinction between (I) and (II) can also be made from the ultra-violet spectra in light petroleum shown in the annexed Table.

	λ_{max}	ϵ	λ_{min}	ϵ		λ_{max}	ϵ	λ_{min}	ϵ
$\text{CF}_3\cdot\text{CF}_2\cdot\text{CF}_2\text{I}$	271	240	215	13	$\text{CF}_3\cdot\text{CH}_2\text{I}$...	262	265	—	—
$\text{CF}_3\cdot\text{CH}_2\cdot\text{CF}_2\text{I}$	271	290	219	24	$\text{CF}_2\text{Cl}\cdot\text{CH}_2\text{I}$...	263	500	212	20
$\text{CH}_2\text{Cl}\cdot\text{CF}_2\text{I}$...	269	340	228	55	$\text{CF}_2\text{Br}\cdot\text{CH}_2\text{I}$	266	420	239	230

The ultra-violet absorption maximum of 1-chloro-2 : 2-difluoro-2-iodoethane at $269 \text{ m}\mu$ is shifted only slightly to the blue relative to a fully-fluorinated iodo-compound (*e.g.*, $\text{C}_3\text{F}_7\text{I}$). The maximum for (I), at $271 \text{ m}\mu$, is thus at the predicted position. By contrast, a compound of the type $\text{R}\cdot\text{CH}_2\text{I}$ (where R = perfluoroalkyl) will have an absorption maximum close to that for 1 : 1 : 1-trifluoro-2-iodoethane ($262 \text{ m}\mu$), and the difference between the spectra

* Part VI. Jander and Haszeldine, *J.*, 1954, 696.

the lower portion of which was shielded. Fractionation gave unchanged reactants (7.0 g.) and liquid products (12.6 g.) which were redistilled, to give 1 : 1 : 1 : 3 : 3-pentafluoro-3-iodopropane (11.6 g., 90%), b. p. 72.0°, n_D^{20} 1.373 (Found: C, 14.1; H, 1.1. $C_3H_2F_5I$ requires C, 13.9; H, 0.8%) (infra-red spectrum, C.S. 98*).

(b) *In silica vessels.* Irradiation for 4 days of trifluoroiodomethane (13.5 g., 0.069 mole) and the olefin (4.2 g., 0.066 mole) in a 200-ml. silica vessel gave unchanged trifluoroiodomethane (1.5 g.) and 1 : 1 : 1 : 3 : 3-pentafluoro-3-iodopropane (13.2 g., 83%), identical with that obtained as in (a) above, and a fraction of higher b. p. (2.0 g.).

Dehydroiodination of 1 : 1 : 1 : 3 : 3-Pentafluoro-3-iodopropane.—The iodo-compound (4.0 g.) was slowly added to powdered potassium hydroxide (10 g.) in a Pyrex flask fitted with a water condenser, and after 4 hours' heating to 100° the volatile products were swept out by a stream of dry nitrogen and transferred to a vacuum-system. Distillation gave 1 : 1 : 3 : 3 : 3-pentafluoropropene (1.70 g., 85%), b. p. -20.7° (Found: M , 132. Calc. for C_3HF_5 : M , 132), identified by means of its infra-red spectrum (C.S. 100*). Henne and Waalkes (*J. Amer. Chem. Soc.*, 1946, 68, 496) report b. p. -21°.

Treatment of 1 : 1 : 1 : 3 : 3-pentafluoro-3-iodopropane (6.0 g.) with 10% ethanolic potassium hydroxide (20 ml.) at room temperature (2 hr.), then at 80° (2 hr.), gave volatile products which were washed with water and distilled, to give 1 : 1 : 3 : 3 : 3-pentafluoropropene (1.02 g., 34%) (Found: M , 133. Calc. for C_3HF_5 : M , 132), identified by means of its infra-red spectrum. The contents of the reaction flask were treated with an excess of water, and the lower layer was dried (P_2O_5) and distilled, to give 1-ethoxy-1 : 1 : 3 : 3 : 3-pentafluoropropene (1.0 g., 25%), b. p. 77°, n_D^{20} 1.326 (Found: C, 33.6; H, 3.8. $C_5H_7OF_5$ requires C, 33.7; H, 3.9%), shown by its infra-red spectrum to be very slightly contaminated by an olefin. Treatment of the ether with chlorine in an attempt to remove the olefin caused extensive breakdown.

Reaction of 1 : 1-Difluoroethylene with Iodine Monobromide.—The olefin (7.5 g., 0.12 mole) and iodine monobromide (24 g., 0.12 mole) were set aside for 24 hr. in the dark. The liquid product (31 g.) was shaken with aqueous sodium thiosulphate and distilled from phosphoric anhydride, to give 1-bromo-1 : 1-difluoro-2-iodoethane (30 g., 95%), b. p. 84°/216 mm., n_D^{20} 1.504 (Found: C, 9.1; H, 0.7. $C_2H_2BrF_2I$ requires C, 8.8; H, 0.7%). C.S. 99*.

The iodo-compound (2.0 g., 0.007 mole) was sealed with chlorine (0.52 g., 0.007 mole), set aside in the dark for 1 day, then exposed to ultra-violet light for 1 day. After treatment with mercury the product was distilled, to give 1-bromo-2-chloro-1 : 1-difluoroethane (1.10 g., 83%), b. p. 71°/770 mm., n_D^{20} 1.404. The infra-red spectrum of this compound (C.S. 101*) was identical with that of the compound prepared by the reaction of hydrogen bromide with 1-chloro-2 : 2-difluoroethylene.

Reaction of 1-Bromo-1 : 1-difluoro-2-iodoethane with Mercurous Fluoride.—The iodo-compound (3.50 g.) was heated at 140° during 4 hr. with mercurous fluoride (20 g.) in a Pyrex flask fitted with an air-condenser connected *via* glass tubing to a trap cooled in liquid oxygen. Dry nitrogen was then passed into the flask, and the condenser and connecting tube were heated so that material of b. p. <100° distilled into the trap. Distillation of the product *in vacuo* give 1 : 1 : 1 trifluoro-2-iodoethane (1.44 g., 53%), b. p. 55.0° (Found: M , 209. Calc. for $C_2H_2F_3I$: M , 210), 1 : 1-difluoroethylene (0.275 g., 33%), and a small amount of silicon tetrafluoride. Gilman and Jones (*J. Amer. Chem. Soc.*, 1943, 65, 2037) report b. p. 54.5—55.0°/730 mm. for 1 : 1 : 1-trifluoro-2-iodoethane.

The authors thank Allied Chemical and Dye Corporation General Chemical Division for a gift of 1 : 1-difluoroethylene. One of them (B. R. S.) is indebted to the Department of Scientific and Industrial Research for a Maintenance Allowance.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[Received, November 20th, 1953.]

* Spectra thus marked have been deposited with the Society. Photocopies, price 3s. 0d. per copy per spectrum, post free, may be obtained on application to the General Secretary, stating the C.S. number.