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

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[Reprint Order No. 4819.]

The photochemical reaction of trifluoroiodomethane with 1 : 1-difluoroethylene yields only the compound $CF_3\cdot CH_2\cdot CF_2I$, *i.e.*, the trifluoromethyl radical attacks exclusively the $:CH_2$ 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 trifluoroiodomethane, to vinyl chloride and vinyl fluoride was shown to be exclusively to the $:CH_2$ group (Part II, *J.*, 1953, 1199). The present study is concerned with the highly polarised olefin 1 : 1-difluoroethylene.

Trifluoroiodomethane and 1 : 1-difluoroethylene show no dark reaction, but react smoothly on exposure to light of wave-length >3000 Å, with liberation of only traces of iodine, to give exclusively $CF_3\cdot(C_2H_2F_2)\cdot I$. Light of wave-length >2200 Å (silica reaction vessels) appreciably increases the rate of formation of $CF_3\cdot(C_2H_2F_2)\cdot I$; small amounts of products of higher boiling point are also formed. Infra-red spectroscopic examination shows that the two products $CF_3\cdot(C_2H_2F_2)\cdot I$ are identical. The product is formed by a chain reaction of the type postulated earlier :

$$CF_3I \xrightarrow{h\nu} CF_3\cdot + I\cdot$$

$$CF_3\cdot + C_2H_2F_2 \longrightarrow CF_3\cdot(C_2H_2F_2)\cdot \xrightarrow{CF_3I} CF_3\cdot(C_2H_2F_2)\cdot I + CF_3\cdot$$

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

$$\underset{\text{(I)}}{CF_3\cdot CH_2\cdot CF_2I} \qquad \underset{\text{(II)}}{CF_3\cdot CF_2\cdot CH_2I} \qquad \underset{\text{(III)}}{CF_3\cdot CH:CF_2}$$

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 :

$$\text{(I)} \longrightarrow \text{(III)}$$

$$EtO^- + CF_3\cdot CH:CF_2 \longrightarrow CF_3\cdot\overset{-}{C}H\cdot CF_2\cdot OEt \xrightarrow{EtOH} CF_3\cdot CH_2\cdot CF_2\cdot OEt + EtO^-$$

The susceptibility of fluoro-olefins to nucleophilic attack and the resistance of compounds which contain a CF_2I group to S_N2 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.

	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε		$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
$CF_3\cdot CF_2\cdot CF_2I$	271	240	215	13	$CF_3\cdot CH_2I$ ...	262	265	—	—
$CF_3\cdot CH_2\cdot CF_2I$	271	290	219	24	$CF_2Cl\cdot CH_2I$...	263	500	212	20
$CH_2Cl\cdot CF_2I$ ...	269	340	228	55	$CF_2Br\cdot CH_2I$	266	420	239	230

The ultra-violet absorption maximum of 1-chloro-2 : 2-difluoro-2-iodoethane at 269 mμ is shifted only slightly to the blue relative to a fully-fluorinated iodo-compound (*e.g.*, C_3F_7I). The maximum for (I), at 271 mμ, is thus at the predicted position. By contrast, a compound of the type $R\cdot CH_2I$ (where R = perfluoroalkyl) will have an absorption maximum close to that for 1 : 1 : 1-trifluoro-2-iodoethane (262 mμ), and the difference between the spectra

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

of compounds $\geqslant C{\cdot}CH_2{\cdot}CF_2I$ and $\geqslant C{\cdot}CF_2{\cdot}CH_2I$ is sufficiently large to be used diagnostically (see also *J.*, 1953, 1764).

The direction of addition of ionic reagents to 1 : 1-difluoroethylene was established by reaction with iodine monobromide. The product is 1-bromo-1 : 1-difluoro-2-iodoethane (IV), since when the iodine is replaced by chlorine, only 1-bromo-2-chloro-1 : 1-difluoroethane (V) is obtained. The infra-red spectrum of (V) is identical with that of the product from hydrogen bromide and 1-chloro-2 : 2-difluoroethylene (unpublished results); this reaction could not yield the 1-bromo-2-chloro-2 : 2-difluoroethane (VI) which would have been obtained from 1 : 1-difluoroethylene if the direction of addition of iodine monobromide had been reversed:

$$CF_2{:}CH_2 \xrightarrow{I^+Br^-} \underset{(IV)}{CF_2Br{\cdot}CH_2I} \xrightarrow{Cl_2} \underset{(V)}{CF_2Br{\cdot}CH_2Cl} \xleftarrow{HBr} CF_2{:}CHCl$$

cf. $$CF_2{:}CH_2 \xrightarrow{IBr} CF_2I{\cdot}CH_2Br \longrightarrow CF_2Cl{\cdot}CH_2Br \quad (VI)$$

Although 1-bromo-1 : 1-difluoro-2-iodoethane (IV) contains a carbon–iodine bond which is (presumably) weaker than the carbon–bromine bond by 11—12 kcal./mole, reaction of (IV) with mercurous fluoride causes exclusively replacement of *bromine* by fluorine, to give the known 1 : 1 : 1-trifluoro-2-iodoethane ($CF_2Br{\cdot}CH_2I \longrightarrow CF_3{\cdot}CH_2I$); 1 : 1-difluoroethylene is a major by-product. This shows that the presence of other halogen, and the absence of hydrogen, on the carbon atom carrying the halogen atom to be replaced, has a marked influence on the ease of reaction.

Discussion.—The main factor influencing the direction of addition of the trifluoromethyl radical to 1 : 1-difluoroethylene is considered to be the relative stabilities of the intermediate radicals $CF_3{\cdot}CH_2{\cdot}CF_2{\cdot}$ and $CF_3{\cdot}CF_2{\cdot}CH_2{\cdot}$, but a full discussion of the factors affecting the stability of these and other radicals is deferred to a later paper.

Two alternative suggestions may be considered at this stage and discarded: A mechanism which could be invoked to explain certain of the results recorded earlier in this series is that the addition occurs *via ionic* intermediates $CF_3^-\ I^+$ from trifluoroiodomethane. Thus, for chlorotrifluoroethylene, $\overset{\delta-}{CF_3}\overset{\delta+}{I} + \overset{\delta+}{CF_2}{:}\overset{\delta-}{CFCl} \longrightarrow CF_3{\cdot}CF_2{\cdot}CFClI$ as actually found (Part III). The mechanism is clearly wrong, however, since, apart from arguments against ionic mechanisms given in earlier papers, the present communication shows that 1 : 1-difluoroethylene yields $CF_3{\cdot}CH_2{\cdot}CF_2I$, whereas by the ionic mechanism $CF_3{\cdot}CF_2{\cdot}CH_2I$ would have been produced.

A second concept which has to be considered is that the trifluoromethyl radical might attack the olefinic carbon atom which which it will form the stronger bond. Thus, since the CF_2–CF_2 carbon–carbon bond in a fluorocarbon is very probably stronger than that in CH_2–CH_2 in a hydrocarbon, it could be argued that the free radical would attack a ${:}CF_2$ group in preference to a ${:}CH_2$ group, or to a ${:}CFCl$ or $-CF{:}$ group. Although this theory would predict the product successfully for $CF_2{:}CFCl$ ($\longrightarrow CF_3{\cdot}CF_2{\cdot}CFClI$) or $CF_3{\cdot}CF{:}CF_2$ ($\longrightarrow CF_3{\cdot}CFI{\cdot}CF_2{\cdot}CF_3$), it fails with 1 : 1-difluoroethylene, and is therefore considered unsuitable for general application.

EXPERIMENTAL

The reaction vessels were sealed Pyrex or silica tubes which were filled from a vacuum system, and sealed *in vacuo*. Care was taken to exclude air, moisture, etc., which might catalyse ionic or free-radical reactions. The products were distilled in a vacuum-system or in short fractionating columns designed to give minimum hold-up. Trifluoroiodomethane (*J.*, 1951, 584), hydrogen bromide, hydrogen chloride, and chlorine were dried and stored *in vacuo* before use.

Reaction of 1 : 1-*Difluoroethylene with Trifluoroiodomethane.*—The olefin was a commercial specimen which was further purified by distillation *in vacuo* (Found: *M*, 64·0. Calc. for $C_2H_2F_2$: *M*, 64·0); its purity was checked by infra-red spectroscopic examination, and it was peroxide-free.

(a) *In Pyrex vessels.* The olefin (5·1 g., 0·079 mole) and trifluoroiodomethane (14·8 g., 0·076 mole) were exposed to ultra-violet light for 28 days in a Pyrex vessel (capacity 600 ml.)

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_5HF_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-*pentafluoropropane* (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.

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