420. *Addition of Free Radicals to Unsaturated Systems. Part XIII.* Direction of Radical Addition to Chloro-*1 : 1*-difluoroethylene.*

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Free-radical attack on chloro-1 : 1-difluoroethylene is predominantly and probably exclusively on the CF_2 group. Photochemical reaction of the olefin with trifluoroiodomethane yields the compound $CF_3{\cdot}CF_2{\cdot}CHClI$ and with hydrogen bromide the compound $CF_2Br{\cdot}CH_2Cl$; structures are proved. The polarisation of the olefin during reactions involving ionic intermediates is $\overset{\delta+}{CF_2}{:}\overset{\delta-}{CHCl}$. The results are discussed, and an earlier report in the literature is corrected.

TRIFLUOROIODOMETHANE shows no dark reaction with chloro-1 : 1-difluoroethylene, but irradiation of the mixture with light of wavelength >2200 Å (silica vessels) or >3000 Å (Pyrex vessels) gives a high yield of a compound $CF_3{\cdot}[C_2HClF_2]{\cdot}I$. Only small amounts of hexafluoroethane and chlorotrifluoromethane are formed as by-products by combination of two trifluoromethyl radicals and abstraction of chlorine.

That the main product is 3-chloro-1 : 1 : 1 : 2 : 2-pentafluoro-3-iodopropane (I) formed by attack of the CF_3 radical on the CF_2 group of the olefin, and not the isomer (II), is shown by spectroscopic and chemical evidence.

$CF_3{\cdot}CF_2{\cdot}CHClI$	$CF_3{\cdot}CHCl{\cdot}CF_2I$	$CF_3{\cdot}CF_2{\cdot}CHCl_2$	$CF_3{\cdot}CHCl{\cdot}CF_2Cl$
(I)	(II)	(III)	(IV)

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* Part XII, *J.*, 1956, 61.

The maximum in the ultraviolet spectrum of a compound R·CF_2I in light petroleum solution varies from 267 mμ when R = alkyl to 271 mμ when R = perfluoroalkyl.[1] The corresponding position for a compound R·CHClI is 278—280 mμ (see Table). There is sufficient difference between these characteristic positions for them to be used diagnostically. The product from the reaction of trifluoroiodomethane and chloro-1 : 1-difluoroethylene has maximum absorption at 280 mμ in light petroleum (Table) and thus contains the R·CHClI chromophore.

Ultraviolet spectra in light petroleum.

	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$		$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
CF_3·CF_2·CHClI ...	280	345	233	70	CF_2Cl·CHClI	279	260	229	35
CF_3·CHCl·CHClI	280	400	243	150	$CHCl_2$·CHClI	278	420	232	55
CF_3·CHF·CHClI	280	400	229	55	CF_3·CH_2·CHClI ...	278	430	231	40

Reaction of the 1 : 1 adduct with chlorine gave 3 : 3-dichloro-1 : 1 : 1 : 2 : 2-pentafluoropropane (III); under similar conditions, the halide (II) would have given 1 : 2-dichloro-1 : 1 : 3 : 3 : 3-pentafluoropropane (IV). Compound (III) contains a C_2F_5 group; an authentic specimen, synthesised from pentafluoropropanol, as follows :

$$C_2F_5{\cdot}CH_2{\cdot}OH \longrightarrow C_2F_5{\cdot}CH_2{\cdot}O{\cdot}SO_2{\cdot}C_6H_4Me \xrightarrow{KCl} C_2F_5{\cdot}CH_2Cl \xrightarrow{Cl_2} C_2F_5{\cdot}CHCl_2$$

had an infrared spectrum identical with that of the dichloro-compound obtained from (I). An authentic specimen of the dichloride (IV) was prepared by reaction of chlorine with 1 : 1 : 3 : 3 : 3-pentafluoropropene.[2] The dichlorides (III) and (IV) are readily distinguished by the presence or absence of strong bands in their infrared spectra at 13·18 μ (III) and 11·10 μ (IV).

That the 1 : 1 adduct obtained from trifluoroiodomethane and chloro-1 : 1-difluoroethylene did not contain even traces of isomer (II) was confirmed by its reaction with zinc and ethanol. Under these conditions, compound (II), like (IV), would have given 1 : 1 : 3 : 3 : 3-pentafluoropropene in high yield, but this olefin[2] was not detected spectroscopically. More than 1—2% of (II) present in the original CF_3·[C_2HClF_2]·I would have been detected by the procedure used. 3-Chloro-1 : 1 : 1 : 2 : 2-pentafluoropropane and 2 : 3 : 3 : 3-tetrafluoropropene were the major products, arising by reduction of the iodine and fluoride elimination :

$$CF_3{\cdot}CF_2{\cdot}CHClI \xrightarrow{Zn} CF_3{\cdot}CF_2{\cdot}CHCl{\cdot}ZnI \xrightarrow{EtOH} CF_3{\cdot}CF_2{\cdot}CH_2Cl$$
$$CF_3{\cdot}CF_2{\cdot}CH_2Cl \longrightarrow CF_3{\cdot}CF_2{\cdot}CH_2{\cdot}ZnCl \longrightarrow CF_3{\cdot}CF_2{\cdot}CH_2^- \longrightarrow F^- + CF_3{\cdot}CF{:}CH_2$$

A control experiment showed that the chloropentafluoropropane reacts with zinc and ethanol under similar conditions to give the tetrafluoropropene. The corresponding iodo-compound gives a high yield of the tetrafluoropropene ($C_2F_5{\cdot}CH_2I \longrightarrow CF_3{\cdot}CF{:}CH_2$).

Hydrogen bromide does not react with chloro-1 : 1-difluoroethylene in the dark at room temperature; the rapid reaction occurring on irradiation (>2200 Å) yields 1-bromo-2-chloro-1 : 1-difluoroethane (V) quantitatively. The structure of this was proved by its ready de-halogenation, on treatment with zinc and ethanol, to 1 : 1-difluoroethylene[1] in high yield; the other possible product, (VI), could not yield difluoroethylene in this way. Attack by the bromine atom is thus on the CF_2 group of the olefin :

$CF_2Br{\cdot}CH_2Cl$	$CHF_2{\cdot}CHClBr$	$CF_2Cl{\cdot}CH_2Cl$	$CF_3{\cdot}CH_2Cl$
(V)	(VI)	(VII)	(VIII)

$$Br{\cdot} + CF_2{:}CHCl \longrightarrow CF_2Br{\cdot}CHCl{\cdot} \xrightarrow{HBr} CF_2Br{\cdot}CH_2Cl + Br{\cdot}$$

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[1] Haszeldine and Steele, *J.*, 1954, 923.

[2] *Idem, J.*, 1955, 3005.

The polarisation of the double bond in chloro-1 : 1-difluoroethylene during reactions involving ionic intermediates is shown to be $\overset{\delta+}{CF_2}{:}\overset{\delta-}{CHCl}$ by thermal reaction with hydrogen chloride to give 1 : 2-dichloro-1 : 1-difluoroethane (VII), an authentic sample of which was prepared by treatment of 1 : 1-difluoroethylene with chlorine. This polarisation is supported by the formation of 2-chloro-1 : 1 : 1-trifluoroethane (VIII) by reaction of the olefin with hydrogen fluoride,[3] by the base-catalysed addition of ethanol[4] to give 2-chloro-1 : 1-difluoroethyl ethyl ether :

$$EtO^- + CF_2{:}CHCl \longrightarrow EtO\cdot CF_2\cdot CHCl^- \xrightarrow{EtOH} EtO\cdot CF_2\cdot CH_2Cl + EtO^-$$

and by the formation of 2-chloro-1 : 1-difluoro-1-iodoethane $CF_2I\cdot CH_2Cl$ on reaction with hydrogen iodide.[5]

The evidence summarised above thus shows that radical and atomic attack on chloro-1 : 1-difluoroethylene is predominantly, and probably exclusively, on the CF_2 group. This again[6] shows that a radical does not behave as an electrophilic reagent during its attack on unsaturated systems. The concept being adopted that intermediate radical stability determines the direction of radical addition to an olefin, it follows that the radical $\dot{C}F_3\cdot CF_2\cdot CHCl$ is more stable than $CF_3\cdot CHCl\cdot \dot{C}F_2$, *i.e.*, to a first approximation replacement of only one hydrogen of a CH_2 group by chlorine gives a radical more stable than one produced by replacement of both hydrogens in the CH_2 group by fluorine.

It was pointed out earlier[7] that radical stability decreases in the order tertiary > secondary > primary, where the terms tertiary, secondary, and primary indicate the number of atoms or groups other than hydrogen attached to the α-carbon atom and do not necessarily refer to the carbon skeleton. It was also noted[7] that, by suitable choice of stabilising groups or atoms R and R′ in a secondary radical $RR'CH\cdot$, the stability of a secondary radical can in special cases by made greater than that of a tertiary radical which carries groups or atoms which have only a weak stabilising effect on the radical. The greater stability of the secondary radical $CF_3\cdot CF_2\cdot \dot{C}HCl$ ($R = C_2F_5$, $R' = Cl$) compared with the tertiary radical $CF_3\cdot CHCl\cdot \dot{C}F_2$ thus exemplifies this overlap region between secondary and tertiary radicals. It is similarly clear that attack by a trifluoromethyl radical or bromine atom on an olefin such as $CF_3\cdot CF{:}CHCl$ will be on the CF group, since the secondary radical $CF_3\cdot CFR\cdot \dot{C}HCl$ will be more stable than the tertiary radical $CF_3\cdot \dot{C}F\cdot CHClR$ (R = perfluoroalkyl, Br, etc.).

The ease of radical attack on chloro-1 : 1-difluoroethylene is roughly comparable with that on chlorotrifluoroethylene.[8] The propagation step ($CF_3\cdot CF_2\cdot \dot{C}HCl + CF_2{:}CHCl \longrightarrow CF_3\cdot CF_2\cdot CHCl\cdot CF_2\cdot \dot{C}HCl$) occurs less readily than with chlorotrifluoroethylene, however, and it is thus comparatively easy to obtain the 1 : 1 adduct in good yield by use of an excess of the chain-transfer agent.

Park, Seffl, and Lacher[9] considered that the reaction of trifluoroiodoethylene with chloro-1 : 1-difluoroethylene gave 3-chloro-1 : 1 : 2 : 4 : 4-pentafluoro-4-iodobut-1-ene ($CF_2{:}CFI + CF_2{:}CHCl \longrightarrow CF_2{:}CF\cdot CHCl\cdot CF_2I$), thus intimating that radical attack takes place on a CHCl group before a CF_2 group. Since attack of both a trifluoromethyl radical and a bromine atom is actually on the CF_2 group of the olefin, it is extremely unlikely that the $CF_2{:}CF\cdot$ radical would attack the CHCl group of the olefin. The product actually obtained by Park *et al.* is clearly 4-chloro-1 : 1 : 2 : 3 : 3-pentafluoro-4-iodobut-1-ene $CF_2{:}CF\cdot CF_2\cdot CHClI$.

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[3] Henne and Arnold, *J. Amer. Chem. Soc.*, 1948, **70**, 758.
[4] B.P. 583,874; *Chem. Abs.*, 1947, **41**, 5142.
[5] Haszeldine and Osborne, *J.*, 1956, 61.
[6] Haszeldine and Steele, *J.*, 1953, 1199 *et seq.*
[7] Haszeldine, *J.*, 1953, 3565.
[8] Haszeldine and Steele, *J.*, 1953, 1592.
[9] Park, Seffl, and Lacher, *J. Amer. Chem. Soc.*, 1956, **78**, 59.

EXPERIMENTAL

*Preparation of Chloro-*1 : 1-*difluoroethylene.*—The olefin, b. p. −18·0° (Found : *M*, 98·5. Calc. for C_2HClF_2 : *M*, 98·5), was prepared from 1 : 1-dichlorodifluoroethylene in 98% yield by photochemical reaction with hydrogen bromide followed by debromochlorination; its purity was checked by means of its infrared spectrum.

*Reaction of Chloro-*1 : 1-*difluoroethylene with Trifluoroiodomethane.*—(a) *In Pyrex vessels.* The olefin (3·08 g., 0·031 mole) and trifluoroiodomethane (12·6 g., 0·064 mole), sealed in a 600-ml. Pyrex tube, did not react in the dark during 14 days. The lower portion of the tube was then shielded and the vapour phase was exposed to ultraviolet light for 28 days to give unchanged reactants (14·4 g., 91%) and 3-*chloro*-1 : 1 : 1 : 2 : 2-*pentafluoro*-3-*iodopropane* (1·20 g., 94%), b. p. 102°, n_D^{20} 1·404 (Found : C, 12·5; H, 0·5. C_3HClF_5I requires C, 12·2; H, 0·3%).

(b) *In silica vessels.* In a typical small-scale experiment, the olefin (1·26 g., 0·013 mole) and trifluoroiodomethane (6·3 g., 0·032 mole) in a 200-ml. silica tube were similarly irradiated for 6 days to give unchanged trifluoroiodomethane (3·8 g., 60%), liquid products (3·44 g.), and a mixture (0·15 g.) of hexafluoroethane and chlorotrifluoromethane (analysed by infrared spectroscopy). Distillation of the liquid products gave 3-chloro-1 : 1 : 1 : 2 : 2-pentafluoro-3-iodopropane (2·7 g., 72%), b. p. 102°, shown by infrared spectroscopic examination to be identical with the material obtained as in (a) above, and a residue (0·6 g.) of $CF_3\cdot[CF_2\cdot CHCl]_2\cdot I$ (Found : C, 15·4; H, 0·5. $C_5H_2Cl_2F_7I$ requires C, 15·4; H, 0·5%). The conditions used in the above reaction were designed to prevent the propagation reaction as much as possible.

Reaction of 3-*Chloro*-1 : 1 : 1 : 2 : 2-*pentafluoro*-3-*iodopropane with Chlorine.*—In a typical experiment, the iodo-compound (2·40 g., 0·0081 mole) was mixed with chlorine (0·40 g., 0·0056 mole) in a 50-ml. Pyrex tube and exposed to ultraviolet light for 2 days. Mercury was then added and the liquid products were distilled *in vacuo*, to give unchanged iodo-compound (*ca.* 0·6 g.), and a fraction redistilled through a small column to give 3 : 3-*dichloro*-1 : 1 : 1 : 2 : 2-*pentafluoropropane* (1·00 g., 87%), b. p. 53°/771 mm., n_D^{20} 1·326 (Found : C, 17·4; H, 0·7%; *M*, 200. $C_3HCl_2F_5$ requires C, 17·7; H, 0·5%; *M*, 203). This compound shows strong infrared bands at 3·30, 7·42, 7·46, 8·10, 8·28, 8·74, 9·23, 9·60, 10·06, 11·91, 12·50, 13·18, 13·97, and 14·05 μ.

Synthesis of 3 : 3-*Dichloro*-1 : 1 : 1 : 2 : 2-*pentafluoropropane.*—Reaction of an excess of 3-chloro-1 : 1 : 1 : 2 : 2-pentafluoropropane (3·31 g.) with chlorine (0·75 g.) and water (2 ml.) in a 20-ml. Pyrex tube exposed to a Hanovia arc for 2 days gave 3 : 3-dichloro-1 : 1 : 1 : 2 : 2-pentafluoropropane (61%) (Found : *M*, 202), b. p. (isoteniscope) 50°/735 mm.; its infrared spectrum was identical with that of the compound prepared by reaction of the compound (I) with chlorine.

Synthesis of 3-*Chloro- and* 3-*Iodo*-1 : 1 : 1 : 2 : 2-*pentafluoropropane.*—The toluene-*p*-sulphonate of pentafluoropropanol [10] (7·7 g.), prepared in the conventional manner, was treated with a 100% excess of potassium chloride in refluxing diethylene glycol monobutyl ether for 4 hr. The volatile product, condensed in liquid oxygen, was transferred to an apparatus for manipulation of volatile compounds, and distilled to give 3-*chloro*-1 : 1 : 1 : 2 : 2-*pentafluoropropane* (71%) (Found : C, 21·4; H, 1·5%; *M*, 168. $C_3H_2ClF_5$ requires C, 21·4; H, 1·4%; *M*, 168·5), b. p. 28° (isoteniscope).

Reaction of the toluene-*p*-sulphonate (6·9 g.) with potassium iodide (100% excess) similarly yielded 3-iodo-1 : 1 : 1 : 2 : 2-pentafluoropropane (75%) (Found : *M*, 259. Calc. for $C_3H_2F_5I$: *M*, 260), b. p. 72°. The iodo-compound (2·7 g.), sealed *in vacuo* in a 10-ml. Pyrex tube containing chlorine (10% excess) and kept in the dark for 3 days, then exposed to ultraviolet light for 8 hr., gave a volatile product which when washed with cold dilute aqueous sodium hydroxide and distilled *in vacuo* was identified as 3-chloro-1 : 1 : 1 : 2 : 2-pentafluoropropane (77%) (Found : *M*, 169. Calc. for $C_3H_2ClF_5$: *M*, 168·5).

Tiers, Brown, and Reid [11] used lithium halides to convert the toluene-*p*-sulphonates of fluoro-alcohols into the corresponding halides, but reported that the sodium halides were ineffective; satisfactory yields can clearly be obtained by using potassium halides.

Reaction of 1 : 1 : 3 : 3 : 3-*Pentafluoropropene with Chlorine.*—The olefin (0·85 g.), prepared by dehydroiodination of 1 : 1 : 3 : 3 : 3-pentafluoro-1-iodopropane,[3] was sealed in a Pyrex tube with chlorine (0·48 g.) and exposed to daylight for 24 hr., then to ultraviolet light for 4 hr.

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[10] Haszeldine and Leedham, *J.*, 1953, 1548.

[11] Tiers, Brown, and Reid, *J. Amer. Chem. Soc.*, 1953, **75**, 5978.

Mercury was added and the product was distilled to give 1 : 2-*dichloro*-1 : 1 : 3 : 3 : 3-*pentafluoropropane* (1·15 g., 90%), b. p. 51°, n_D^{20} 1·323 (Found: C, 17·2; Cl, 34·5%; *M*, 203. $C_3HCl_2F_5$ requires C, 17·7; Cl, 35·0%; *M*, 203). This compound shows strong infrared bands at 3·35, 7·45, 7·90, 8·25, 8·65, 8·87, 9·55, 10·10, 11·10, 12·13, 12·29, 14·07, 14·16, 14·55, and 14·85 μ.

Action of Zinc and Ethanol on 3-*Chloro*-1 : 1 : 1 : 2 : 2-*pentafluoro*-3-*iodopropane*.—The iodo-compound (4·12 g.) was slowly added to a well-stirred mixture of zinc dust (15 g.) and refluxing ethanol (30 ml.). After 5 hr. the volatile products which had been formed were carried through the water-condenser by a stream of dry nitrogen and collected in a trap cooled to −183°. Distillation *in vacuo* gave a fraction shown by infrared spectroscopy to be free from 1 : 1 : 3 : 3 : 3-pentafluoropropene. 3-Chloro-1 : 1 : 1 : 2 : 2-pentafluoropropane (40%) and 2 : 3 : 3 : 3-tetrafluoropropene (30%) were identified as the main products by spectroscopy. The olefin was removed by reaction with chlorine in the dark, and the dichloride, after separation from the monochloro-compound by distillation, was treated with zinc and ethanol to regenerate the olefin. Further spectroscopic examination then confirmed the original analysis.

3-Chloro-1 : 1 : 1 : 2 : 2-pentafluoropropane was shown to react with zinc and ethanol in a sealed tube at 70° to give 2 : 3 : 3 : 3-tetrafluoropropene (53%). 1 : 1 : 1 : 2 : 2-Pentafluoro-3-iodopropane similarly gave the olefin in 87% yield.

Reaction of Chloro-1 : 1-*difluoroethylene with Hydrogen Bromide*.—The olefin (0·75 g., 0·0076 mole) and hydrogen bromide (0·615 g., 0·0076 mole) were sealed in a 100-ml. Pyrex tube and kept in the dark for 6 weeks; no reaction occurred. When the olefin (3·20 g., 0·0325 mole) and hydrogen bromide (2·66 g., 0·0328 mole) were sealed in a 200-ml. silica tube, and the vapour phase was exposed to ultraviolet light, immediate reaction was seen and after 6 hr. distillation gave 1-*bromo*-2-*chloro*-1 : 1-*difluoroethane* (5·80 g., 99%), b. p. 70·2°/776 mm., n_D^{20} 1·404 (Found: C, 13·4; H, 1·3. $C_2H_2BrClF_2$ requires C, 13·4; H, 1·1%).

The bromo-compound (3·51 g.), dissolved in ethanol (5 ml.), was slowly added to a stirred mixture of zinc dust (10 g.) and refluxing ethanol (10 ml.) and after a further 2 hr. the volatile products were swept from the apparatus by a stream of nitrogen. Distillation *in vacuo* gave 1 : 1-difluoroethylene (1·20 g., 95%) (Found: *M*, 63·5. Calc. for $C_2H_2F_2$: *M*, 64), identified by its infrared spectrum.

Reaction of Chloro-1 : 1-*difluoroethylene with Hydrogen Chloride*.—The olefin (1·08 g., 0·11 mole) and hydrogen chloride (0·72 g., 0·02 mole), sealed in a 150-ml. Pyrex tube, did not react at 250° for 2 days. Reaction occurred at 270° and after 2 days distillation gave hydrogen chloride (0·368 g.) and 1 : 2-dichloro-1 : 1-difluoroethane (1·40 g., 91%), b. p. 47°, identified by its infrared spectrum.

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