Addition of Free Radicals to Unsaturated Systems. Part VIII. The Direction of Radical-addition to Alkyl- and Perfluoroalkyl-acetylenes.*

By K. Leedham and R. N. Haszeldine.

[Reprint Order No. 4910.]

The photochemical reaction of trifluoroiodomethane with the compounds $RC{\vdots}CH$ yields only $CF_3\cdot[CH{:}CR]_n\cdot CH{:}CRI$, where $R = CF_3$, C_2F_5, or CH_3, and $n = 1$ or 2. Heptafluoroiodopropane similarly reacts with trifluoromethylacetylene to give $C_3F_7\cdot[CH{:}C\cdot(CF_3)]_n\cdot CH{:}CI\cdot CF_3$. The rate but not the direction of addition of the perfluoroalkyl radical to an acetylene $RC{\vdots}CH$ is affected by the inductive effect of R. Alternative syntheses for $CF_3\cdot CH{:}CH\cdot CF_3$ and $CF_3\cdot CH{:}CH\cdot CH_3$, and ultra-violet and infra-red spectra are reported.

In attempting to determine how the direction of addition of a radical to an unsaturated system is influenced by the substituents on the unsaturated system, olefins of the type $RCH{:}CH_2$ were studied in Part II (Haszeldine and Steele, *J.*, 1953, 1199). The present communication describes a similar study with acetylenes, $RC{:}CH$. The perfluoroalkyl radicals CF_3 and C_3F_7 were used, prepared by the photolysis of the corresponding fluoroalkyl iodide, and the reasons for the choice of such radicals, and the assumptions made, have been stated earlier (*J.*, 1952, 2504).

Trifluoromethylacetylene and trifluoroiodomethane do not react at room temperature in the absence of light. The photochemical reaction proceeds smoothly and with liberation of only small amounts of iodine. The 1 : 1 addition product could be (I) or (II), but replacement of its iodine atom by hydrogen by means of zinc and hydrochloric acid gives a high yield of the known *trans*-hexafluorobut-2-ene (III) which can be derived only from (I).

$CF_3\cdot CH{:}CI\cdot CF_3$	$(CF_3)_2C{:}CHI$	$CF_3\cdot CH{:}CH\cdot CF_3$	$(CF_3)_2C{:}CH_2$
(I)	(II)	(III)	(IV)

The infra-red spectrum of the reduction product establishes the *trans*-configuration, and shows that the known hexafluoro*iso*butene (IV), which would have been obtained from (II), is not formed. It is noteworthy that the zinc–hydrochloric acid reduction is stereospecific.

---

* Part VII, Haszeldine and Steele, *J.*, 1954, 923.

The 1 : 1 addition product is thus 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-iodobut-2-ene (I), formed by a chain reaction of the type postulated earlier :

$$CF_3I \xrightarrow{h\nu} CF_3\cdot + I\cdot$$
$$CF_3\cdot + CF_3{\cdot}C{\vdots}CH \longrightarrow CF_3{\cdot}\dot{C}{:}CH{\cdot}CF_3$$
$$CF_3{\cdot}\dot{C}{:}CH{\cdot}CF_3 + CF_3I \longrightarrow CF_3{\cdot}CI{:}CH{\cdot}CF_3 + CF_3\cdot \longrightarrow \text{etc.}$$

The 1 : 1 adduct has the same constitution whether light which only trifluoroiodomethane can absorb (>3000 Å) or light which both fluoro-iodide and acetylene can absorb (>2200 Å) is used to initiate the reaction; the reaction under the former conditions (Pyrex vessels) is appreciably slower than when the latter conditions (silica vessels) are used.

A 1 : 2 addition product is also formed by the reaction of trifluoroiodomethane with trifluoromethylacetylene. That this is (V) or (VI), and not (VII) or (VIII), is shown by analytical and spectroscopic results. A compound such as (VII) would be formed by addition of trifluoroiodomethane to (I), and a compound such as (VIII) would be obtained by the not improbable combination of two resonance-stabilised $CF_3{\cdot}CH{:}\dot{C}{\cdot}CF_3$ radicals, followed by addition of trifluoroiodomethane to the resultant tetrakistrifluoromethylbutadiene. The absence of compounds such as (VIII) illustrates the efficiency of the chain transfer and, to a lesser extent, the propagation steps, in the reaction mechanism. Since the 1 : 1 addition product is 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-iodobut-2-ene, the trifluoromethyl radical must attack the ${\vdots}CH$ in trifluoromethylacetylene to give $CF_3{\cdot}CH{:}\dot{C}{\cdot}CF_3$; the attack of this radical on a second molecule of the acetylene will also occur at the ${\vdots}CH$ carbon atom, so that the propagation step is

$CF_3{\cdot}CH{:}C(CF_3){\cdot}CH{:}CI{\cdot}CF_3$ (V)

$CF_3{\cdot}CH{:}C(CF_3){\cdot}C(CF_3){:}CHI$ (VI)

$(CF_3)_2CH{\cdot}CI_2{\cdot}CF_3$ (VII)

$CF_3{\cdot}CH{:}C(CF_3){\cdot}C(CF_3)_2{\cdot}CHI{\cdot}CF_3$ (VIII)

$$CF_3{\cdot}CH{:}\dot{C}{\cdot}CF_3 + CF_3{\cdot}C{\vdots}CH \longrightarrow CF_3{\cdot}CH{:}C(CF_3){\cdot}CH{:}\dot{C}{\cdot}CF_3,\ \text{etc.}$$

followed by the chain-transfer step

$$CF_3{\cdot}CH{:}C(CF_3){\cdot}CH{:}\dot{C}{\cdot}CF_3 + CF_3I \longrightarrow CF_3{\cdot}CH{:}C(CF_3){\cdot}CH{:}CI{\cdot}CF_3 + CF_3\cdot$$

The 1 : 2-adduct is thus very probably 1 : 1 : 1 : 6 : 6 : 6-hexafluoro-2-iodo-4-trifluoromethylhexa-2 : 4-diene (V) and not (VI). As will be reported later, (V) can be converted into 1 : 2 : 4-tristrifluoromethylbutadiene.

Trifluoroiodomethane similarly reacts smoothly with pentafluoroethylacetylene to give 1 : 1 and 1 : 2 addition products. The constitutions of these products are assumed to be (IX) and (X) by analogy with the reactions with trifluoromethylacetylene.

$CF_3{\cdot}CH{:}CI{\cdot}C_2F_5$ (IX)

$CF_3{\cdot}CH{:}C(C_2F_5){\cdot}CH{:}CI{\cdot}C_2F_5$ (X)

$C_3F_7{\cdot}CH{:}CI{\cdot}CF_3$ (XI)

$C_3F_7{\cdot}CH{:}C(CF_3){\cdot}CH{:}CI{\cdot}CF_3$ (XII)

Attack on trifluoromethylacetylene proceeds as smoothly with a heptafluoropropyl as with a trifluoromethyl radical, and (XI) and (XII), the analogous products to (I) and (V), are obtained; their assumed constitution is supported by their spectra (see Table).

The photochemical reaction of trifluoroiodomethane with methylacetylene is much more rapid than with trifluoromethylacetylene. There is no dark reaction, and only slight attack on the methyl group to give the $\dot{C}H_2{\cdot}C{:}CH$ radical during the photochemical reaction, since only very small amounts of fluoroform could be detected. High yields of a 1 : 1 and what is probably a 1 : 2 addition product were obtained, and spectroscopic examination showed that the 1 : 1 adduct was the same whether Pyrex or silica vessels were used. The 1 : 1 adduct is (XIII), since the iodine atom can be replaced by hydrogen in high yield to give only the known 1 : 1 : 1-trifluorobut-2-ene (XV); infra-red spectroscopic examination shows that the isomeric trifluoro*iso*butene (XVI), b. p. 6·4°, is absent. This compound would have been formed if trifluoroiodomethane addition to propyne had taken place in the opposite sense to that shown by (XIII). Attack of the trifluoromethyl radical is thus exclusively on the ${\vdots}CH$ carbon atom of propyne with a reaction mechanism similar to that for the perfluoroalkylacetylenes given above. The 1 : 2-addition product will have the constitution shown by (XIV).

$CF_3\cdot CH{:}CI\cdot CH_3$	$CF_3\cdot CH{:}C(CH_3)\cdot CH{:}CI\cdot CH_3$	$CF_3\cdot CH{:}CHMe$	$CF_3\cdot CMe{:}CH_2$
(XIII)	(XIV)	(XV)	(XVI)

The vinylic C–H and the C:C stretching vibrations in the infra-red, and the ultra-violet spectra of certain of the above compounds, are shown in the Table. The C:C stretching absorption in the substituted butadienes is doubled, indicating *cis–trans*-isomerism about one or both of the double bonds; the vinylic C–H absorption appears at its characteristic wave-length. The ultra-violet absorption of compounds of the type $R_F\cdot CH{:}CI\cdot R_F$ is characteristic, and sufficiently different from that of compounds $R_F\cdot CH{:}CI\cdot Alk$ (where R_F = perfluoroalkyl) to be used diagnostically.

Discussion.—The reaction of HX (X = F, Cl, or Br) with propyne under conditions favouring ionic intermediates yields only compounds $CH_3\cdot CX{:}CH_2$, *i.e.*, propyne is polarised as $CH_3\cdot\overset{\delta+}{C}\equiv\overset{\delta-}{CH}$ in such reactions. By contrast, trifluoromethylacetylene reacts with HX (X = F, Cl, Br, I, OMe, OEt, or NR_2) to give $CF_3\cdot CH{:}CHX$ (*J.*, 1952, 3490), *i.e.*, is polarised as $CF_3\cdot\overset{\delta-}{C}\equiv\overset{\delta+}{CH}$. As shown above, free-radical attack on these acetylenes is *exclusively* on the terminal carbon atom, *i.e.*, the *direction* of free-radical attack on a terminal acetylene is independent of the inductive or hyperconjugative effects of R in $R\cdot C{\vdots}CH$, since these act in opposite directions when R = CH_3 and R = CF_3. The apparent polarisation of the triple bond does affect markedly, however, the *rate* of reaction; the rate is much greater when R = CH_3 than when R = CF_3.

	Infra-red		Ultra-violet spectra (in light petroleum)			
	C–H	C:C	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
$CF_3\cdot CH{:}CI\cdot CF_3$, b. p. 75·5° ...	3·25μ	6·00 6·07 triplet 6·14	243 222	3250 4250	236 —	3150 —
$CF_3\cdot CH{:}CI\cdot C_2F_5$, b. p. 85°......	3·27	6·07	248 226	3000 4000	240 —	2900 —
$C_3F_7\cdot CH{:}CI\cdot CF_3$, b. p. 110° ...	3·25	6·06	248 226	3450 4400	240 —	3250 —
$CF_3\cdot CH{:}CI\cdot CH_3$, b. p. 94·5° ...	3·24	6·07	260 230 215	350 3800 3500	251·5 221·5 —	320 3100 —

		Infra-red bands (μ)	
Compound	B. p./mm.	C–H	C:C
(V)	60°/77	3·25	5·90, 6·10
(X)	87/100	3·25	5·94, 6·16
(XII)	75/70	3·25	5·92, 6·10
(XIV)	55/7	3·24	6·03, 6·23

It was shown earlier that the photochemical reaction of hydrogen bromide with trifluoromethylacetylene gave only 1-bromo-3 : 3 : 3-trifluoropropene (*J.*, 1952, 3490); Kharasch, McNab, and McNab (*J. Amer. Chem. Soc.*, 1935, **57**, 2463) showed that the " peroxide effect " in the reaction of hydrogen bromide with propyne gave 1 : 2-dibromopropane. In both reactions, the initial attack of the bromine atom is thus directed in the same way as a free perfluoroalkyl radical :

$$Br\cdot + RC{\vdots}CH \longrightarrow R\dot{C}{:}CHBr \xrightarrow{HBr} RCH{:}CHBr + Br\cdot, \text{ etc.}$$

Bader, Cross, Heilbron, and Jones (*J.*, 1949, 619) showed that radical attack during the peroxide-induced reaction of thiolacetic acid with monosubstituted acetylenes was on the terminal carbon atom of the alkyne. The trichloromethyl radical from trichloroiodomethane also attacks the terminal carbon atom in 3 : 3 : 3-trifluoropropyne (Haszeldine, *J.*, 1953, 922) :

$$CF_3\cdot C{\vdots}CH + CCl_3I \xrightarrow{h\nu} CF_3\cdot CI{:}CH\cdot CCl_3$$

Free-radical attack on propyne and trifluoromethylacetylene is thus very similar to the corresponding reactions with propylene and 3 : 3 : 3-trifluoropropene (*J.*, 1952, 2504; 1953, 1199) where attack is exclusively on the terminal CH_2 group. It can be concluded that the intermediate free radicals $R'H{:}\dot{C}R$ are more stable than the radicals $RR'C{:}\dot{C}H$, but a full discussion is deferred, as with the results of papers presented earlier in this series, to a paper in course of preparation.

EXPERIMENTAL

Trifluoroiodomethane (*J.*, 1951, 584), trifluoromethylacetylene (*J.*, 1951, 588, 2495; 1952, 3483), pentafluoroethylacetylene (*J.*, 1952, 3483), and heptafluoroiodopropane (*J.*, 1949, 2886) were thoroughly dried and stored in a vacuum system. Reactions were carried out in sealed 50-ml. Pyrex or silica tubes, with exclusion of moisture, oxygen, etc., which might catalyse ionic or free-radical reactions. A Hanovia lamp was used as source of ultra-violet radiation.

Reaction of Trifluoroiodomethane with 3 : 3 : 3-*Trifluoropropyne*.—Trifluoroiodomethane (4·0 g., 0·02 mole) and 3 : 3 : 3-trifluoropropyne (1·92 g., 0·02 mole) in a silica tube were exposed to ultra-violet light for 72 hr. with the liquid phase shielded from light. The small amount of iodine which had been liberated was removed by treatment with mercury, and the liquid products were distilled to give 1 : 1 : 1 : 4 : 4 : 4-*hexafluoro*-2-*iodobut*-2-*ene* (2·22 g., 38%), b. p. 75·5° (isoteniscope), n_D^{16} 1·3758 (Found : C, 16·4; H, 0·6%; *M*, 288. C_4HIF_6 requires C, 16·6; H, 0·4%; *M*, 290), and material of higher b. p. The latter was distilled through a small column, to give 1 : 1 : 1 : 6 : 6 : 6-*hexafluoro*-2-*iodo*-4-*trifluoromethylhexa*-2 : 4-*diene* (0·7 g., 9%), b. p. 60°/77 mm. (Found : C, 22·0; H, 0·7. $C_7H_2IF_9$ requires C, 21·9; H, 0·5%).

Irradiation of trifluoroiodomethane and 3 : 3 : 3-trifluoropropyne in a Pyrex tube for 10 days also gave 1 : 1 : 1 : 4 : 4 : 4-hexafluoro-2-iodobut-2-ene, shown to be identical with the compound obtained above by comparison of infra-red spectra.

Reduction of 1 : 1 : 1 : 4 : 4 : 4-*Hexafluoro*-2-*iodobut*-2-*ene*.—The compound (0·69 g.) was added dropwise (30 min.) to zinc dust (10 g.) and 10% hydrochloric acid (12 ml.) in a flask fitted with reflux condenser connected *via* rubber tubing to a trap cooled in liquid oxygen. The reactants were heated at 60° for 1·5 hr., with intermittent addition of concentrated hydrochloric acid (2 ml.). The gaseous contents of the flask were swept out with nitrogen, and the combined volatile products were fractionated to give *trans*-1 : 1 : 1 : 4 : 4 : 4-hexafluorobut-2-ene (0·27 g., 70%), b. p. (isoteniscope) 9·1° (Found : *M*, 165. Calc. for $C_4H_2F_6$: *M*, 164), identified by comparison of its b. p. and infra-red spectrum with those reported earlier (*J.*, 1952, 2504).

In a second experiment, magnesium (1 g.) was added to the zinc (15 g.) used for the reduction of the iodo-compound (1·97 g.); the yield of *trans*-hexafluorobut-2-ene was 78%.

Reaction of Pentafluoroethylacetylene with Trifluoroiodomethane.—The acetylene (2·54 g., 0·02 mole)and trifluoroiodomethane (3·46 g., 0·02 mole) were sealed in a silica tube and irradiated for 71 hr., affording unchanged trifluoroiodomethane and liquid products which were distilled to give 1 : 1 : 1 : 4 : 4 : 5 : 5 : 5-*octafluoro*-3-*iodopent*-2-*ene* (1·69 g., 29%), b. p. 84—86°, n_D^{16} 1·3623 (Found : C, 17·9; H, 0·6%; *M*, 338. C_5HIF_8 requires C, 17·6; H, 0·3%; *M*, 340), and 1 : 1 : 1 : 6 : 6 : 7 : 7 : 7-*octafluoro*-5-*iodo*-3-*pentafluoroethylhepta*-2 : 4-*diene* (*ca.* 0·3 g., 4%), b. p. 86—88°/100 mm. (Found : C, 22·4; H, 0·8. $C_9H_2IF_{13}$ requires C, 22·3; H, 0·4%).

Reaction of Heptafluoroiodopropane with 3 : 3 : 3-*Trifluoropropyne*.—Heptafluoroiodopropane (23·3 g., 0·088 mole) and 3 : 3 : 3-trifluoropropyne (4·72 g., 0·033 mole) were irradiated in a Pyrex tube for 13 days. Distillation gave unchanged heptafluoroiodopropane (8·16 g., 35%), 1 : 1 : 1 : 4 : 4 : 5 : 5 : 6 : 6 : 6-*decafluoro*-2-*iodohex*-2-*ene* (8·90 g., 38%), b. p. 110°, n_D^{13} 1·3575 (Found : C, 18·6; H, 0·4. C_6HIF_{10} requires C, 18·5; H, 0·2%), and 1 : 1 : 1 : 6 : 6 : 7 : 7 : 8 : 8 : 8-*decafluoro*-2-*iodo*-4-*trifluoromethylocta*-2 : 4-*diene* (*ca.* 1 g.), b. p. 83°/56 mm. (Found : C, 21·8; H, 0·4. $C_9H_2IF_{13}$ requires C, 22·3; H, 0·4%).

Reaction of Propyne with Trifluoroiodomethane.—In a typical experiment, trifluoroiodomethane (17·5 g., 0·089 mole), sealed in a silica tube with propyne (3·72 g., 0·093 mole), was exposed to ultra-violet light for 17 hr. with the liquid phase shielded from light, to give liquid products (18·2 g., 86%). These were distilled to give 1 : 1 : 1-*trifluoro*-3-*iodobut*-2-*ene* (16·2 g., 89%), b. p. 94·5°, n_D^{20} 1·4352 (Found : C, 20·2; H, 1·7. $C_4H_4IF_3$ requires C, 20·3; H, 1·7%), and a residue of higher b. p. Only traces of fluoroform were detected by infra-red spectroscopic examination. An experiment in a Pyrex tube also gave 1 : 1 : 1-trifluoro-3-iodobut-2-ene, shown to be identical with the compound prepared as above by comparison of infra-red spectra.

The products of higher b. p. from several experiments were combined and distilled to give what is probably the 1 : 2 addition product, 1 : 1 : 1-trifluoro-5-iodo-3-methylhexa-2 : 4-diene, b. p. 54—55°/7 mm.

Blank experiments in which propyne was irradiated alone, or in presence of iodine, showed that it did not isomerise to allene.

Reduction of 1 : 1 : 1-*Trifluoro*-3-*iodobut*-2-*ene*.—The iodo-compound (2·10 g.) was added to zinc dust (15 g.), magnesium (1 g.), and 50% hydrochloric acid (20 ml.), kept at room temperature (5 hr.), then heated slowly to 100° (2 hr.). The volatile products passed through a reflux water-condenser, were collected in a trap cooled by liquid oxygen, and then distilled *in vacuo* to give 1 : 1 : 1-trifluorobut-2-ene (83%), b. p. (isoteniscope) 16·5° (Found : *M*, 110. Calc. for $C_4H_5F_3$: *M*, 110), and unchanged 1 : 1 : 1-trifluoro-3-iodobut-2-ene (0·16 g.). Apart from 1 : 1 : 1-trifluorobut-2-ene, there was no material boiling in the region 0—30°. The trifluorobutene was identified by comparison of the infra-red spectrum of its dichloride (prepared by reaction with chlorine in the dark) with that of the dichloride similarly prepared from a known specimen of 1 : 1 : 1-trifluorobut-2-ene, b. p. 20° (Haszeldine and Steele, *J.*, 1953, 1199).

One of us (K. L.) is indebted to Courtauld's Scientific and Educational Trust for grants (1950—1952) during the tenure of which this work was carried out.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, December* 21*st*, 1953.]