Addition of Free Radicals to Unsaturated Systems. Part X. The Reaction of Hydrogen Bromide with Tetrafluoroethylene and Chlorotrifluoroethylene.*

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The photochemical reaction of hydrogen bromide with tetrafluoroethylene yields $H{\cdot}[C_2F_4]_n{\cdot}Br$, where $n = 1, 2, 3$, etc. Chlorotrifluoroethylene similarly yields $H{\cdot}[CFCl{\cdot}CF_2]_n{\cdot}Br$ and the bromine atom thus attacks the CF_2 group of the olefin; poly(chlorotrifluoroethylene) is formed by head-to-tail addition. The mechanisms of the reactions and in particular the fate of the hydrogen atoms are discussed.

THAT hydrogen bromide can react with olefins by mechanisms involving either electrophilic attack or attack by a bromine atom is now well established. An unsubstituted olefin is particularly susceptible to electrophilic attack, however, and it is thus difficult to suppress the reaction involving ionic intermediates even under conditions which strongly favour the radical mechanism. Unsubstituted olefins do not polymerise readily under the conditions normally used for their reaction with hydrogen bromide under free-radical conditions, and the chain-propagation reaction in the sequence below has never been reported when R or R′ = alkyl, aryl, etc. Such a propagation reaction would clearly provide strong support for a free-radical mechanism.

$$HBr \longrightarrow H\cdot + Br\cdot$$

$$Br\cdot + CR_2{:}CR'_2 \longrightarrow CR_2Br{\cdot}CR'_2\cdot \quad \text{Initiation}$$

$$CR_2Br{\cdot}CR'_2\cdot + CR_2{:}CR'_2 \longrightarrow CR_2Br{\cdot}CR'_2{\cdot}CR_2{\cdot}CR'_2\cdot \text{ etc.} \quad \text{Propagation}$$

$$CR_2Br{\cdot}CR'_2\cdot + HBr \longrightarrow CR_2Br{\cdot}CHR'_2 + Br\cdot \longrightarrow \text{etc.} \quad \text{Transfer}$$

Polyhalogeno-olefins resist electrophilic attack yet, as pointed out in earlier papers, are still sensitive to free-radical attack. By use of polyhalogeno-olefins, and in particular of polyfluoro-olefins, it should thus be possible to observe two effects during photochemical reaction with hydrogen bromide : (*a*) the free-radical reaction to the complete exclusion of the ionic reaction, and (*b*) the polymerisation of the fluoro-olefin.

Hydrogen bromide and tetrafluoroethylene (R = R′ = F) do not react at room temperature in absence of light, but readily combine when exposed to light of wave-length > 3000 Å (Pyrex vessels). When approximately equimolar quantities are used the product is almost completely 1-bromo-1 : 1 : 2 : 2-tetrafluoroethane and only traces of products with a higher boiling point are formed, thus revealing the efficiency of the chain-transfer step relative to the propagation step. It is noteworthy that molecular hydrogen, even in traces, is not produced during the photochemical reaction, thus showing either that the reaction chain is very long so that only infinitesimal amounts of hydrogen are produced, or that the hydrogen atom produced by the photolysis of a molecule of hydrogen bromide in the initial step combines with the olefin in some way, probably by initial formation of the dihydro-olefin and generation of a bromine atom :

$$H\cdot + CF_2{:}CF_2 \longrightarrow CHF_2{\cdot}CF_2\cdot$$

$$CHF_2{\cdot}CF_2\cdot + HBr \longrightarrow CHF_2{\cdot}CHF_2 + Br\cdot$$

This is followed by the usual chain reaction

$$Br\cdot + CF_2{:}CF_2 \longrightarrow CF_2Br{\cdot}CF_2\cdot$$

$$CF_2Br{\cdot}CF_2\cdot + HBr \longrightarrow CF_2Br{\cdot}CHF_2 + Br\cdot \longrightarrow \text{etc.}$$

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* Part IX, Haszeldine, Leedham, and Steele, *J.*, 1954, 2040.

The fate of the hydrogen atom in the mechanism proposed for the photochemical reaction of hydrogen bromide with olefins has hitherto been ignored. The above suggestion is not implausible, since there is no reason to assume that the hydrogen atom is unreactive and incapable of attacking the double bond of tetrafluoroethylene, or that the $CHF_2{\cdot}CF_2$ radical should fail to abstract hydrogen from hydrogen bromide in a manner similar to the $CF_2Br{\cdot}CF_2$ radical. It is evident that if the reaction chain is long, the actual amount of 1 : 1 : 2 : 2-tetrafluoroethane produced is extremely small, and the fact that this compound could not be detected in the reaction products suggests that the reaction chain is long; experiments on a larger scale might render its spectroscopic detection possible.

A simple mechanism similar to that postulated above to explain the fate of the hydrogen atom can be applied to the reactions involving the photochemical reaction of bromotrichloromethane with olefins. In these reactions the fate of the bromine atom produced in the step

$$CCl_3Br \xrightarrow{h\nu} CCl_3{\cdot} + Br{\cdot}$$

has always been ignored, and it has somewhat arbitrarily been concluded that the CCl_3 radical initiates all the reaction chains:

$$CCl_3{\cdot} + CR_2{:}CR'_2 \longrightarrow CCl_3{\cdot}CR_2{\cdot}CR'_2{\cdot} \xrightarrow{CCl_3Br} CCl_3{\cdot}CR_2{\cdot}CR'_2Br + CCl_3{\cdot} \longrightarrow \text{etc.}$$

There is no reason why a bromine atom produced by photolysis of bromotrichloromethane should not attack the olefin in the same manner as a bromine atom produced from hydrogen bromide; after the first step, however, a CCl_3 radical will be generated:

$$Br{\cdot} + CR_2{:}CR'_2 \longrightarrow CR_2Br{\cdot}CR'_2{\cdot}$$

$$CR_2Br{\cdot}CR'_2{\cdot} + CCl_3Br \longrightarrow Cr_2Br{\cdot}CR'_2Br + CCl_3{\cdot}$$

followed by the chain reaction

$$CCl_3{\cdot} + CR_2{:}CR'_2 \longrightarrow CCl_3{\cdot}CR_2{\cdot}CR'_2{\cdot} \xrightarrow{CCl_3Br} CCl_3{\cdot}CR_2{\cdot}CR'_2Br + CCl_3{\cdot} \longrightarrow \text{etc.}$$

so that both the CCl_3 radical and the bromine atom from the initial photochemical fission of bromotrichloromethane can be considered to initiate chain reactions in which the CCl_3 radical is the chain carrier.

Irradiation of tetrafluoroethylene and hydrogen bromide in a molar ratio *ca.* 10 : 1 enables compounds of the type $H{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}Br$ to be isolated, where $n = 1, 2, 3$, etc. The $CF_2Br{\cdot}CF_2$ radical formed initially can react with tetrafluoroethylene to propagate the chain, or with hydrogen bromide to undergo chain transfer. Despite the high concentration of tetrafluoroethylene, which is known to polymerise extremely rapidly by a free-radical mechanism, the yields of products where n = 1, 2, and 3 are 66, 12, and 0·5% respectively; this again illustrates the extreme efficiency of chain-transfer reactions involving hydrogen bromide. In all other free-radical reactions involving tetrafluoroethylene the difficulty is to suppress the propagation reaction in favour of the transfer reaction (see, *e.g.*, *J.*, 1953, 3761).

The compounds where n = 2, 3, etc., are not produced by reactions of the type

$$CHF_2{\cdot}CF_2Br \xrightarrow{h\nu} CHF_2{\cdot}CF_2{\cdot} \xrightarrow{C_2F_4} CHF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}$$

$$CHF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot} \xrightarrow{CHF_2{\cdot}CF_2Br} H{\cdot}[CF_2{\cdot}CF_2]_2{\cdot}Br + CHF_2{\cdot}CF_2{\cdot}$$

since the C–Br bond in 1-bromo-1 : 1 : 2 : 2-tetrafluoroethane is not split homolytically by light of the wave-length used.

The reaction of hydrogen bromide with chlorotrifluoroethylene was studied by Park, Sharrah, and Lacher (*J. Amer. Chem. Soc.*, 1949, **71**, 2339), but since a charcoal catalyst was used it cannot be decided whether ionic or radical intermediates were involved in the formation of the 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane isolated. The present study has shown that in absence of a catalyst there is no reaction in the dark, *i.e.*, electrophilic attack is very slow, but that ready reaction occurs on exposure to light. In Pyrex vessels only 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane (I) is produced. That the product has the constitution (I) is shown by its dehalogenation to give trifluoroethylene in high yield. The other possible product of formula $H{\cdot}[C_2ClF_3]{\cdot}Br$ which might be produced by the photochemical reaction is (II). This could not yield trifluoroethylene when treated with

$CF_2Br{\cdot}CHFCl$ (I) $\quad$ $CHF_2{\cdot}CFClBr$ (II) $\quad$ $CF_2Br{\cdot}CFCl{\cdot}CF_2{\cdot}CHFCl$ (III)

zinc and ethanol, but would yield 1-chloro-1 : 2-difluoroethylene, or, if reduction occurred initially, would give 1 : 2-difluoroethylene :

$$CHF{:}CFCl \longleftarrow CHF_2{\cdot}CFClBr \longrightarrow CHF_2{:}CHFCl \longrightarrow CHF{:}CHF$$

The absence of these olefins and the high yield of trifluoroethylene strongly suggest that the product $H{\cdot}[C_2ClF_3]{\cdot}Br$ is exclusively (I). Bromine atom attack is thus on the CF_2 group of chlorotrifluoroethylene :

$$Br{\cdot} + CF_2{:}CFCl \longrightarrow CF_2Br{\cdot}CFCl{\cdot}$$

$$CF_2Br{\cdot}CFCl{\cdot} + HBr \longrightarrow CF_2Br{\cdot}CHFCl + Br{\cdot} \longrightarrow \text{etc.}$$

Despite claims to the contrary (Henne and Kraus, *J. Amer. Chem. Soc.*, 1951, **73**, 1791; see, however, *idem, ibid.*, 1954, **76**, 1175) it was earlier conclusively demonstrated that attack of a trifluoromethyl radical derived from trifluoroiodomethane was exclusively on the CF_2 group of chlorotrifluoroethylene (Haszeldine and Steele, *J.*, 1953, 1592). The result obtained with hydrogen bromide thus independently establishes the direction of radical addition to chlorotrifluoroethylene and shows that, as expected, a bromine atom and a trifluoromethyl radical behave in a similar manner.

Irradiation of an approximately equimolar mixture of hydrogen bromide and chlorotrifluoroethylene in silica vessels initiates a fast reaction, and the product is again mainly (I). The use of light of shorter wave-length doubtless activates the olefin to a certain extent and also gives a more energetic bromine atom, and chain propagation therefore occurs to a small extent. Chain propagation is substantially increased when the molar ratio of chlorotrifluoroethylene to hydrogen bromide is *ca.* 6 : 1 but, as with the tetrafluoroethylene reaction, the chain-transfer step is very efficient :

$$Br{\cdot} + CF_2{:}CFCl \longrightarrow CF_2Br{\cdot}CFCl{\cdot} \xrightarrow{CF_2{:}CFCl} CF_2Br{\cdot}CFCl{\cdot}[C_2ClF_3]_m{\cdot}$$

$$CF_2Br{\cdot}CFCl{\cdot}[C_2ClF_3]_m{\cdot} \xrightarrow{HBr} CF_2Br{\cdot}CFCl{\cdot}[C_2ClF_3]_m{\cdot}H + Br{\cdot} \longrightarrow \text{etc.}$$

and the polymer isolated is of short chain length ($m = 1, 2, 3$, etc.). That the compound where $m = 1$ is 1-bromo-2 : 4-dichloro-1 : 1 : 2 : 3 : 3 : 4-hexafluorobutane (III) is shown by its reaction with zinc and dioxan to give a high yield of 4-chloro-1 : 1 : 2 : 3 : 3 : 4-hexafluorobut-1-ene (IV). The infra-red spectrum of this compound shows a C:C stretching vibration at 5·56 μ, the position shown (Haszeldine, *J.*, 1952, 4423) to be characteristic of compounds which contain the $\cdot CF{:}CF_2$ group.

$CF_2{:}CF{\cdot}CF_2{\cdot}CHFCl$ (IV) $\quad$ $CF_2Br{\cdot}CFCl{\cdot}CF_2{\cdot}CFCl{\cdot}CF_2{\cdot}CHFCl$ (V)

The compound where $m = 2$, and material of average composition $m = 5$, have infra-red spectra very similar to that of (III) and to those of the compounds $CF_3{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}I$ described earlier (*J.*, 1953, 1592). The compound where $m = 2$ thus very probably has constitution (V), and the polychlorotrifluoroethylene chain is built up by head-to-tail addition with radical attack throughout on the CF_2 group of the olefin to give $Br{\cdot}[CF_2{\cdot}CFCl]_n{\cdot}H$.

The infra-red spectrum of the 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane isolated from the photochemical experiments shows significant differences from that of the material isolated by Park *et al.* (see p. 3751), and the thermal reaction of hydrogen bromide with chlorotrifluoroethylene in presence of a charcoal catalyst was therefore studied. Only 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane was isolated, and its spectrum was identical with that of the photochemical product. It should be noted that the reaction of chlorotrifluoroethylene with a hydrogen halide, HX, by a reaction involving ionic intermediates, would yield $CF_2X\cdot CHFCl$, *i.e.*, both the free-radical and the ionic-type reaction of hydrogen bromide with chlorotrifluoroethylene yield the same product; only the free-radical reaction can yield polymeric products, however.

EXPERIMENTAL

Hydrogen bromide, prepared by Duncan's method (*Inorg. Synth.*, **1**, 151) was freed from traces of bromine, dried (P_2O_5), and carefully purified by fractionation *in vacuo* (Found : *M*, 81·0; Calc. for HBr : *M*, 81·0). Chlorotrifluoroethylene (Found : *M*, 116·5. Calc. for C_2ClF_3 : *M*, 116·5) and tetrafluoroethylene (Found : *M*, 100. Calc. for C_2F_4 : *M*, 100) were commercial samples, purified by repeated distillation, and shown by infra-red spectroscopic examination to be free from impurities. Irradiation experiments were carried out in sealed Pyrex or silica tubes, with rigid exclusion of air, moisture, etc. A Hanovia lamp was used without the Wood's filter as a source of ultra-violet radiation. Liquid products were distilled through specially designed columns which have a minimum hold-up. Hydrogen was not formed during the photochemical reactions described below; its presence in even small amount would have been readily detected by the sensitive vacuum techniques used.

Reaction of Hydrogen Bromide with Tetrafluoroethylene.—The olefin and hydrogen bromide did not react when kept for 14 days in a sealed tube in the dark. Tetrafluoroethylene (8·50 g., 0·085 mole) and hydrogen bromide (0·76 g., 0·0094 mole) were sealed in a Pyrex vessel (300 ml.) and irradiated for 2 days. A small amount of solid polymer was formed on the side of the tube. The unchanged olefin was separated from the reaction products and was resealed with hydrogen bromide (0·95 g.) and again irradiated (2 days). The unchanged olefin was combined with fresh tetrafluoroethylene (2·5 g.) and hydrogen bromide (0·75 g.) and exposed to light again (2 days). The combined products (from 11·00 g., 0·11 mole, of C_2F_4, and 2·46 g., 0·03 mole, of HBr) were distilled to give unchanged tetrafluoroethylene (7·00 g., 64%) and liquid products (5·25 g.). These were distilled to give 1-bromo-1 : 1 : 2 : 2-tetrafluoroethane (3·64 g., 66% based on hydrogen bromide), b. p. 12·5° (Found : C, 13·6; H, 0·7%; *M*, 182. Calc. for C_2HBrF_4 : C, 13·3; H, 0·6%; *M*, 181), 1-*bromo*-1 : 1 : 2 : 2 : 3 : 3 : 4 : 4-*octafluorobutane* (1·0 g., 12%), b. p. 66°, n_D^{20} 1·309 (Found : C, 16·8; H, 0·7%; *M*, 280. C_4HBrF_8 requires C, 17·1; H, 0·4%; *M*, 281), and a residual fraction of 1-*bromo*-1 : 1 : 2 : 2 : 3 : 3 : 4 : 4 : 5 : 5 : 6 : 6-*dodecafluorohexane* (0·3 g., 0·5%) (Found : C, 18·8; H, 0·4. C_6HBrF_{12} requires C, 18·9; H, 0·3. Calc. for C_8HBrF_{16} : C, 20·0%). Park *et al.* (*loc. cit.*) report b. p. −3·5°/626 mm. for 1-bromo-1 : 1 : 2 : 2-tetrafluoroethane.

Reaction of Hydrogen Bromide with Chlorotrifluoroethylene.—(a) *In the dark.* There was no reaction when hydrogen bromide (6·5 g., 0·080 mole) and chlorotrifluoroethylene (9·4 g., 0·082 mole) were sealed in a 300-ml. Pyrex vessel and kept in the dark for 3 days.

(b) *In Pyrex vessels.* When the reaction mixture of (a) was exposed to ultra-violet light, an immediate reaction was observed and gave, after 2 days, unchanged reactants (1·2 g.) (*M*, 100) and 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane (14·7 g., 93% conversion), b. p. 52·5°, n_D^{20} 1·3705, n_D^{25} 1·368 (Found : C, 12·1; H, 0·7%; *M*, 197·5. Calc. for $C_2HBrClF_3$: C, 12·1; H, 0·5%; *M*, 197·5). Park *et al.* (*loc. cit.*) report b. p. 46·02°/615 mm., n_D^{25} 1·3685.

(c) *In silica vessels.* Hydrogen bromide (2·9 g., 0·036 mole) and chlorotrifluoroethylene (3·1 g., 0·027 mole), sealed in a silica tube and irradiated for 2 hr., gave unchanged hydrogen bromide (0·7 g., 24%) (Found : *M*, 81) and 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane (4·5 g., 88%), b. p. 52·5—53°, n_D^{20} 1·371, shown by infra-red spectroscopic examination to be identical with the compound obtained in (b) above. A small amount (0·5 g.) of a liquid with a higher b. p. remained.

(d) *With an activated charcoal catalyst.* Activated charcoal (3 g.) was heated at 250° for 2 hr. *in vacuo* to remove adsorbed gases and was then sealed with chlorotrifluoroethylene (2·8 g., 0·024 mole) and hydrogen bromide (1·9 g., 0·024 mole). After 24 hours' heating at 90°, the products were distilled to give unchanged reactants (1·1 g.) and 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane (3·6 g., 76%), b. p. 51·5—51·9°, n_D^{20} 1·3705, identical (infra-red spectrum) with the earlier specimens.

(e) *In silica with an excess of olefin.* The olefin (7·60 g., 0·065 mole) and hydrogen bromide (0·89 g., 0·011 mole) were exposed to ultra-violet light for 2 hr. A small amount of solid polymer was formed on the side of the tube nearer the lamp. Distillation gave unchanged chlorotrifluoroethylene, 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane (1·85 g., 85% based on hydrogen bromide), and a residue (0·4 g.). The combined residues from several such experiments were distilled to give 1-*bromo*-2 : 4-*dichloro*-1 : 1 : 2 : 3 : 3 : 4-*hexafluorobutane* (4% based on hydrogen bromide), b. p. 130° (micro), n_D^{20} 1·386 (Found : C, 15·2; H, 0·5. $C_4HBrCl_2F_6$ requires C, 15·3; H, 0·3%), 1-*bromo*-2 : 4 : 6-*trichloro*-1 : 1 : 2 : 3 : 3 : 4 : 5 : 5 : 6-*nonafluorohexane* (0·5% based on hydrogen bromide), b. p. 140°/100 mm. (micro), n_D^{20} 1·405 (Found : C, 16·3; H, 0·8. $C_6HBrCl_3F_9$ requires C, 16·7; H, 0·2%), and a glass-like residue of average composition $Br{\cdot}[CF_2{\cdot}CFCl]_6{\cdot}H$ (Found : C, 18·5; H, 0·1. Calc. for $C_{12}HBrCl_6F_{18}$: C, 18·4; H, 0·1%).

Dehalogenation of 1-*Bromo*-2-*chloro*-1 : 1 : 2-*trifluoroethane*.—A solution of the compound (7·0 g.) in ethanol (15 ml.) was added to a well-stirred mixture of zinc dust (40 g.) and refluxing ethanol (100 ml.). After 8 hr. the gaseous product was washed with water and distilled *in vacuo* to give trifluoroethylene (2·5 g., 85%) (Found : *M*, 82. Calc. for C_2HF_3 : *M*, 82), identified by means of its infra-red spectrum. 1-Chloro-1 : 2-difluoroethylene was not produced.

Reaction of 1-*Bromo*-2 : 4-*dichloro*-1 : 1 : 2 : 3 : 3 : 4-*hexafluorobutane with Zinc and Dioxan*.—The compound (0·89 g.) was sealed in a Pyrex tube with zinc dust (2 g.) and dioxan (5 ml.) and heated to 100° for 24 hr. in a rocking furnace. The volatile products were washed with water, dried (P_2O_5), and distilled *in vacuo* to give 4-*chloro*-1 : 1 : 2 : 3 : 3 : 4-*hexafluorobut*-1-*ene* (0·42 g., 75%), b. p. 56° (isoteniscope) (Found : C, 24·3%; *M*, 197. C_4HClF_6 requires C, 24·2%; *M*, 198·5).

Infra-red Spectra.—These were recorded on a Perkin–Elmer Model 21 instrument with sodium chloride optics. Values are in μ (m = medium, s = strong, vs = very strong, w = weak).

$CHF_2{\cdot}CF_2Br$ (vapour) : 3·36 (m), 4·40, 4·51 (m, doublet), 7·20 (s), 7·40 (s), 7·67 (w), 8·03 (vs), 8·34 (w), 8·57 (vs), 8·81 (vs), 9·33 (s), 10·32 (vs), 11·15 (m), 12·14 (vs), 13·45 (m), 15·05, 15·17 (m, doublet).

$H{\cdot}[C_2F_4]_2{\cdot}Br$ (vapour) : 3·36 (w), 4·41 (w), 7·12 (m), 7·35 (m), 7·66 (s), 7·85 (s), 8·14 (s), 8·35 (vs), 8·73 (vs), 9·05 (s), 9·30 (m), 9·70 (w), 9·90 (w), 10·15 (m), 11·05 (m), 11·36 (m), 11·86 (s), 12·15 (s), 12·45 (s), 12·80 (s), 13·45 (vs), 14·33 (w).

$CF_2{:}CF{\cdot}CF_2{\cdot}CHFCl$ (vapour) : 3·35 (w), 4·64 (w), 5·56 (s), 7·25 (m), 7·50 (m), 7·64 (m), 8·16 (m), 8·30 (m), 8·45 (vs), 8·60 (vs), 8·78 (s), 8·96 (s), 9·17 (s), 9·77 (s), 10·15 (m), 10·36 (m), 11·85 (s), 12·25 (s), 12·80 (s).

$CF_2Br{\cdot}CHFCl$ (vapour) : 3·35 (w), 4·56 (w), 7·47 (m), 7·87 (m), 8·15 (s), 8·67 (vs), 9·05 (vs), 9·52 (vs), 10·3 (vs), 11·0 (w), 11·7 (vs), 12·5 (s), 13·1 (m).

$Br{\cdot}[CF_2{\cdot}CFCl]_2{\cdot}H$ (liquid) : 3·34 (w), 7·43 (m), 7·48 (m), 8·01 (s), 8·42 (vs), 8·65 (vs), 8·99 (vs), 9·64 (s), 9·78 (s), 10·02 (w), 10·50 (s), 11·37 (m), 11·75 (m), 12·15 (m), 12·63 (w), 13·25 (w), 13·65 (m), 14·25 (w).

$Br{\cdot}[CF_2{\cdot}CFCl]_3{\cdot}H$ (liquid) : 3·3 (w), 7·42 (w), 7·90 (m), 8·45 (broad, vs), 8·7 (vs), 8·93 (vs), 9·07 (s), 9·77 (s), 10·34 (s), 11·25 (m), 11·77 (m), 12·50 (m), 13·65 (m), 14·45 (m).

Lacher, Lea, Walden, Olson, and Park (*J. Amer. Chem. Soc.*, 1950, **72**, 3231) assumed that in the charcoal-catalysed reaction of hydrogen bromide with chlorotrifluoroethylene the bromine became attached to the CF_2 group, and concluded that there was less than 0·2% of side reaction. Their infra-red spectrum of 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane shows bands at 12·6 (s), 13·8 (m) and 14·4 (w) μ, however, which are not present in the spectrum of 1-bromo-2-chloro-1 : 1 : 2-trifluoroethane prepared photochemically.

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