[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Influence of a CF$_3$ Group on an Adjacent Double Bond. III. Free Radical Additions[1]

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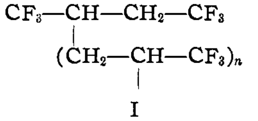
Under free radical conditions, $\mathrm{CF_3CH{=}CH_2}$ accepts HBr to yield $\mathrm{CF_3CH_2CH_2Br}$ exclusively: the direction of addition is thus the same as under polar conditions. Consistent with this trend, $\mathrm{CF_3I}$ or $\mathrm{CCl_3Br}$ are accepted to yield $\mathrm{CF_3CHICH_2\text{-}CF_3}$ or $\mathrm{CF_3CHBrCH_2CCl_3}$. All additions are slower than with propylene. The observed direction of addition is considered in terms of the currently proposed factors: (1) center of electron density, (2) stability of the intermediate radical and (3) steric considerations.

Under polar conditions $\mathrm{CF_3CH{=}CH_2}$ accepts a reagent $\mathrm{A^+B^-}$ to give $\mathrm{CF_3{-}CHA{-}CH_2B}$, exclusively; by electrophilic attack, HBr yields $\mathrm{CF_3\text{-}CH_2CH_2Br}$[2] and by nucleophilic attack an alcohol yields $\mathrm{CF_3CH_2CH_2OR}$.[3] The polarization of the double bond is thus clearly shown as $\mathrm{CF_3{-}\overset{-\delta}{C}H{=}\overset{+\delta}{C}H_2}$, and the sluggishness of addition indicates its deactivation by the $\mathrm{CF_3}$ group.

Free radical addition proceeds in the same direction. Hydrogen bromide was added in the vapor phase and with ultraviolet irradiation to yield only one product, $\mathrm{CF_3CH_2CH_2Br}$. In the absence of irradiation, no addition occurred. In ultraviolet light, the addition proceeded to quantitative completion, but was not instantaneous as the addition of HBr to propylene.[4] Addition of $\mathrm{CF_3I}$ was brought about by heat or by irradiation, to yield a mixture of products formulated as



$$\begin{array}{l}\mathrm{CF_3{-}CH{-}CH_2{-}CF_3}\\ \qquad\;|\\ \quad\mathrm{(CH_2{-}CH{-}CF_3)}_n\\ \qquad\qquad|\\ \qquad\qquad\mathrm{I}\end{array}$$

where n = 0, 1, 2, 3; the rate of addition was not improved by the presence of mercury, the catalytic effect of which had been observed in the addition of $\mathrm{CF_3I}$ to $\mathrm{CF_2{=}CF_2}$.[5] The thermal reaction gave principally a product where n = 1, while the irradiated runs gave mostly $\mathrm{CF_3{-}CHI{-}CH_2{-}CF_3}$, where n = 0. $\mathrm{CCl_3Br}$ was added with ultraviolet irradiation, and gave as main product $\mathrm{CF_3{-}CHBr{-}CH_2{-}CCl_3}$; in the absence of irradiation, no addition took place.

The reaction between HBr and $\mathrm{CF_3CH{=}CH_2}$ can be accounted for by a bromine atom attack in a chain reaction as follows

$$\mathrm{HBr} \xrightarrow{h\nu} \mathrm{H\cdot + Br\cdot}$$

$$\mathrm{Br\cdot + CF_3CH{=}CH_2 \longrightarrow CF_3{-}\dot{C}H{-}CH_2Br}$$

$$\mathrm{CF_3{-}\dot{C}H{-}CH_2Br + HBr \longrightarrow}$$

$$\mathrm{CF_3CH_2CH_2Br + Br\cdot,\ etc.\ldots}$$

Similarly, the addition of $\mathrm{CF_3I}$ or $\mathrm{CCl_3Br}$ can be represented by an attack by a $\mathrm{CF_3\cdot}$ or a $\mathrm{CCl_3\cdot}$ free radical, followed by abstraction of I· or Br· from the solvents by the intermediate free radical $\mathrm{CF_3{-}\dot{C}H{-}CH_2{-}CX_3}$.

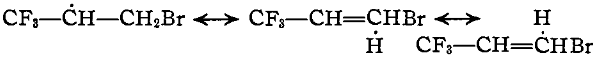
Three theories are current to account for the orientation in free radical addition to a double bond.

(I) The attacking radical is electrophilic and, therefore, moves to the carbon with the higher electron density.[6]

(II) The point of attack depends upon the relative stability of the two radicals which may be formed.[7]

(III) Steric factors, *e.g.*, accessibility, determine the point of initial attack.[8]

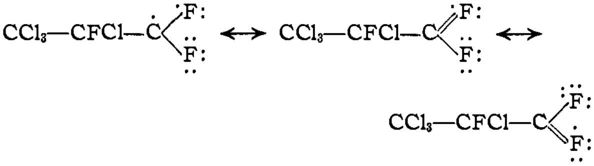
Our experimental results contradict the first theory, as an attack on the more negative of the two carbons would require the formation of a secondary bromide instead of the primary bromide actually obtained. They are acceptably accounted for by the second theory which would require the formation of an intermediate



$$\mathrm{CF_3{-}\dot{C}H{-}CH_2Br \longleftrightarrow \underset{\textstyle\dot{H}}{CF_3{-}CH{=}CHBr} \longleftrightarrow \overset{\textstyle H}{CF_3{-}CH{=}\dot{C}HBr}}$$

of lower energy level than $\mathrm{CF_3{-}CHBr{-}\dot{C}H_2} \leftrightarrow \mathrm{CF_3{-}\overset{\textstyle H}{\dot{C}}Br{=}CH_2}$. They are also acceptably explained by the third theory, as the end carbon would be more accessible than the middle carbon. We can thus reject the first theory, but cannot choose between the second and third, as both could be effective.

Mayo and Walling[8] state that in all known cases, the second and third theories operate in the same direction. In the case of additions to $\mathrm{CFCl{=}CF_2}$ however, it has recently been shown[9] that $\mathrm{CCl_3Br}$ gives $\mathrm{CCl_3{-}CFCl{-}CF_2Br}$; a $\mathrm{CCl_3\cdot}$ radical attack would be a reaction at the least accessible carbon, and the formation of an intermediate $\mathrm{CCl_3{-}CFCl{-}CF_2\cdot}$ of lower energy level than $\mathrm{CCl_3{-}CF_2{-}CFCl\cdot}$ could be considered as a more probable directing factor. Resonance in the first of these intermediates could be represented as



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[1] Presented at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1951.

[2] A. L. Henne and S. Kaye, THIS JOURNAL, **72**, 3369 (1950).

[3] A. L. Henne, M. A. Smook and R. L. Pelley, *ibid.*, **72**, 4756 (1950).

[4] W. E. Vaughan, F. E. Rust and T. W. Evans, *J. Org. Chem.*, **7**, 477 (1942).

[5] R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949). In a private communication, Haszeldine informs us that he has also found addition products with n = 0 and n = 1, in photochemical as well as thermal reactions and has proven their structure.

[6] W. A. Waters, "The Chemistry of Free Radicals," Oxford Press, New York, N. Y., 1948, p. 182.

[7] F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940). See also A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 503-506.

[8] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 261 (1950).

[9] A. L. Henne and D. W. Kraus, THIS JOURNAL, **73**, 1791 (1951).

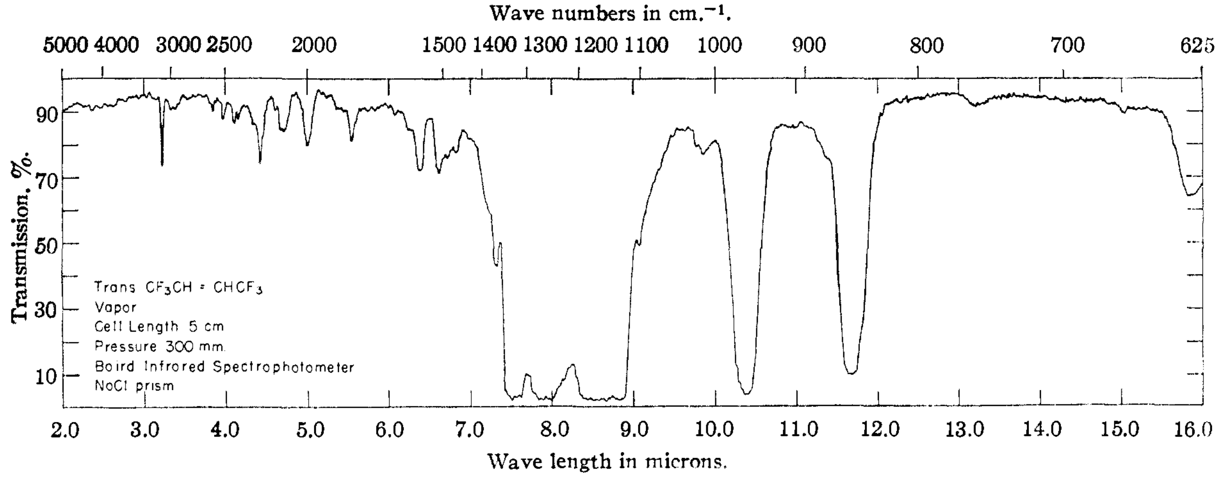
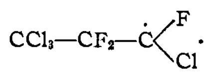


Fig. 1.

which would have more importance than the corresponding forms for



$$CCl_3-CF_2-\overset{F}{\underset{Cl}{\dot{C}}}\cdot$$

Experimental

Trifluoropropylene.—$CF_3CH=CH_2$ was prepared from $CCl_3CH_2CH_2Cl$, as previously shown[10]; before use, it was dried by passage through a tower of anhydrous calcium chloride.

Addition of HBr.—A quartz ampule one inch in diameter and 12 inches long was cleaned and dried by flaming. It was loaded under anhydrous conditions with $CF_3CH=CH_2$ (12 g. or 0.12 mole) and HBr (25 g. or 0.31 mole) by liquefying them in the ampule cooled with Dry Ice; after further cooling in liquid air, the ampule was evacuated, sealed, clamped in a vertical position and allowed to warm up to room temperature. The vapor phase was then irradiated with a Westinghouse EH-4 mercury flood lamp, while the liquid phase was shielded. Soon after irradiation was applied, small droplets formed on the wall and ran down into the liquid phase; the droplet formation stopped when the lamp was turned off and was soon resumed after it was turned on again. After 24 hours, the ampule was opened, the excess HBr vented off, and the remaining liquid distilled. One product only was present, b.p. 60.5–62.5°, n^{20}D 1.3603, d^{25}_4 1.654; this is $CF_3CH_2CH_2Br$ (16 g. or 0.11 mole) in 90% yield. Assignment of the structure was based on agreement with the reported properties for $CF_3CH_2CH_2Br$, b.p. 62.0–62.5°,[11,2] n^{20}D 1.3602,[2] d^{25}_4 1.653[11] and contrast with those reported for the isomer $CF_3CHBrCH_3$, b.p. 48.6°,[12,13] d^{15}_4 1.633.[13] A control reaction held for 168 hours at room temperature, without irradiation failed to yield any addition product.

Addition of CF_3I.—A steel container was loaded with $CF_3CH=CH_2$ (21 g. or 0.22 mole), CF_3I[14] (38 g. or 0.19 mole) and mercury (0.5 g.); this was held at a temperature of 215° for 122 hours; between 48 and 72 hours the pressure dropped steadily from 115 to 75 p.s.i. after which it slowly drifted to about 65 p.s.i. At the end of the heating period, the unreacted material (16.5 g.) was collected, and a residual liquid (40 g.) poured off. Distillation failed to yield any distinct cut from 80 to 160°. The iodine content of various fractions was found to be 40.6, 39.3, 36.8 and 26.4%; a 1 to 1 condensation product would require 43.5%, and a product made of two moles of $CF_3CH=CH_2$ and one of CF_3I would call for 32.7%.

The whole mixture was treated with alcoholic alkali to yield a small amount of an olefin boiling between 5 and 10°, the infrared spectrum of which (Fig. 1) was found identical to that of *trans*-$CF_3CH=CHCF_3$.[15] The alcoholic solution was then poured into ice-water and the organic layer separated; the material thus recovered did not decolorize permanganate and boiled over a range only slightly higher than before, 100–160°.

The addition of CF_3I (40 g.) to $CF_3CH=CH_2$ (20 g.) refluxing in a quartz flask at atmospheric pressure under ultraviolet conditions yielded only small amounts of condensed material after one week of irradiation. After recovery of the unreacted portion the product consisted in part (4 g.) of material boiling at 25°, presumably $CF_3-CH_2-CH_2-CF_3$ (b.p. 24.6°)[16] formed by reduction of $CF_3-CHI-CH_2-CF_3$. The remainder of the material (16 g.) proved to be mainly a 1:1 adduct b.p. 80–80.5°, n^{20}D 1.3617 (analysis for C, 16.89; H, 1.28; calcd. C, 16.45; H, 1.03); it underwent dehydroiodination with alcoholic alkali to yield an olefin b.p. 8–9° the spectrum of which proved to be identical with that of *trans*-$CF_3CH=CHCF_3$.

Both the thermal and the ultraviolet experiments yielded some iodine and some gas presumably CF_3-CF_3 not condensable at −78°.

Addition of CCl_3Br.—The experimental procedure was the same as above. The ampule was charged with $CF_3-CH=CH_2$ (32 g. or 0.33 mole) and CCl_3Br (130 g. or 0.65 mole), evacuated at liquid air temperature and sealed. It was then held horizontally, to permit irradiation of both liquid and vapor phases for 24 hours. The excess CCl_3Br was distilled off, a fraction (69 g.) then obtained b.p. 76–77° at 36–37 mm., n^{20}D 1.4415 and a higher residue (15 g.) left behind. Computing the main addition product as $CF_3CHBrCH_2CCl_3$ shows a 76% yield; analysis of 0.2178 g. of this material would require the formation of 0.4579 g. of insoluble silver halide, and 0.4636 g. (an excess of about 1%) was actually obtained. A control test held for 168 hours without irradiation showed no addition.

For structure assignment, the addition compound was chlorinated at high temperature and in intense radiation, drastic conditions which proved needed and caused much decomposition. A sample of $C_4F_3Cl_7$ was obtained by sublimation which melted at 167–169° in sealed tube. It has been reported[17] that $CF_3CCl_2CCl_2CCl_3$ melts at 165–167° while its isomer $CF_3CCl(CCl_3)_2$ melts at 183–189°; a previous report[18] that $CF_3CCl_2CCl_2CCl_3$ melts at 67–69° should have read 167–169° and is a misprint carried over from the thesis of Thomas Newby.

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(10) A. L. Henne and M. Nager, THIS JOURNAL, **73**, 1042 (1951).

(11) E. T. McBee, *et al.*, *Ind. Eng. Chem.*, **39**, 420 (1947).

(12) B. H. Robbins, *J. Pharmacol. Exptl. Therap.*, **86**, 197 (1946).

(13) F. Swarts, *Bull. soc. chim. Belg.*, **38**, 99 (1929).

(14) A. L. Henne and W. G. Finnegan, THIS JOURNAL, **72**, 3806 (1950).

(15) W. G. Finnegan, Ph.D. Thesis, The Ohio State University, 1949.

(16) A. L. Henne and W. G. Finnegan, THIS JOURNAL, **71**, 298 (1949).

(17) E. R. Purchase, Ph.D. Dissertation, The Ohio State University, 1948.

(18) A. L. Henne and T. H. Newby, THIS JOURNAL, **70**, 130 (1948).