

258. *Free-radical Substitution in Aliphatic Compounds. Part V.<sup>1</sup>  
The Halogenation of 1,1,1-Trifluoropentane.*

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The chlorination and bromination of 1,1,1-trifluoropentane and 1-fluorobutane in the gas phase have been studied in a static system. The results confirm earlier work and show that the trifluoromethyl group exerts a very powerful deactivating effect on halogenation at adjacent sites. The reactions were studied at several temperatures and approximate values of the Arrhenius parameters for attack at each site have been obtained.

In the 1940's Henne and his co-workers published a series of papers describing the chlorination of alkanes containing trifluoromethyl and difluoromethylene groups.<sup>2-5</sup> The trifluoromethyl group provides an example of a substituent exerting a powerful inductive, but negligible resonance or mesomeric effects. For this reason it is a valuable group to study when directive influences are being investigated. Henne and his co-workers found that chlorination was powerfully directed away from highly fluorinated groups, and their results from the starting point of most discussions on the importance of polar effects in chlorination. The present work was aimed at repeating their work but using the much more precise analytical equipment now available, and extending the study to bromination. 1,1,1-Trifluoropentane was chosen, rather than the trifluorobutane previously studied; it was hoped that the carbon atom at the far end of the molecule would be unaffected by the substituent fluorine atoms so that the compound could be regarded as a 1-trifluoromethylbutane.

#### EXPERIMENTAL

A static system was employed similar to that previously used in the study of trichloromethyl radicals.<sup>1</sup> Analysis of the products was achieved by gas chromatography, a Griffen and George D6 apparatus being used with column packings of 10% silicone and of 10% dinonyl phthalate on Celite, and nitrogen as carrier gas. The detector was a gas density balance, and this greatly facilitated the work because it was no longer necessary to synthesise pure specimens of each of the halogenated products in order to calibrate the detector. Identification of the products was achieved by halogenating a large liquid sample (*ca.* 1 g.), and then separating the four halogenated products on a semi-preparative scale (0.5-g. samples) gas-chromatography apparatus. Carbon tetrachloride solutions of the material of each peak were then examined with an A.E.I. Ltd., RS2 n.m.r. spectrometer. Identification of the halogeno-1,1,1-trifluoropentane from n.m.r. spectra was an easy matter [*e.g.*,  $\text{CF}_3\text{-}\overset{\alpha}{\text{C}}\text{H}_2\text{-}\overset{\beta}{\text{C}}\text{H}_2\text{-}\overset{\gamma}{\text{C}}\text{H}_2\text{-}\overset{\delta}{\text{C}}\text{H}_3$   $\tau$  values:  $\alpha$  (complex) = 7.98;  $\beta$  and  $\gamma$  (complex) = 8.52;  $\delta$  (triplet) = 8.99.  $\text{CF}_3\text{-}\overset{\alpha}{\text{C}}\text{H}_2\text{-}\overset{\beta}{\text{C}}\text{HCl-}\overset{\gamma}{\text{C}}\text{H}_2\text{-}\overset{\delta}{\text{C}}\text{H}_3$ ,  $\alpha$  (double quartet) = 7.43;  $\beta$  (quartet) = 5.91;  $\gamma$  (complex) = 8.15;  $\delta$  (triplet) = 8.99.  $\text{CF}_3\text{-}\overset{\alpha}{\text{C}}\text{H}_2\text{-}\overset{\beta}{\text{C}}\text{H}_2\text{-}\overset{\gamma}{\text{C}}\text{HBr-}\overset{\delta}{\text{C}}\text{H}_3$   $\alpha$  (complex) = 7.4;  $\beta$  (complex) = 8.0;  $\gamma$  (sextet) 5.88;  $\delta$  (doublet) 8.26].

*Apparatus and Experimental Techniques.*—A conventional vacuum line was employed. The reactants were carefully "degassed" and the 286 c.c. "Pyrex" reaction vessel was filled with the halogen and the alkane at known pressures. The vessel was surrounded with a heated bath (water or liquid paraffin) and then irradiated with light from two 150-w lamps. At the end of the run, the products were condensed into a small trap from which samples could be taken for injection into the gas-chromatography apparatus.

*Reactants.*—1,1,1-Trifluoropentane was prepared from n-valeric acid by treatment with sulphur tetrafluoride according to the directions of Hasek, Smith, and Engelhardt.<sup>6</sup> The compound had b. p. 39°,  $n_D^{25}$  1.3101, and was shown by gas chromatography to contain a trace

<sup>1</sup> Part IV, McGrath and Tedder, *Bull. Soc. Chim. belges*, 1962, **71**, 772.

<sup>2</sup> Henne and Whaley, *J. Amer. Chem. Soc.*, 1942, **64**, 1157.

<sup>3</sup> Henne and Hinkamp, *J. Amer. Chem. Soc.*, 1945, **67**, 1194.

<sup>4</sup> Henne and Hinkamp, *J. Amer. Chem. Soc.*, 1945, **67**, 1197.

<sup>5</sup> Henne and Dewitt, *J. Amer. Chem. Soc.*, 1948, **70**, 1548.

<sup>6</sup> Hasek, Smith, and Engelhardt, *J. Amer. Chem. Soc.*, 1960, **82**, 543.

(2%) of some low-boiling material as the only impurity. 1-Fluorobutane was prepared from 1-bromobutane by treatment with potassium fluoride in ethylene glycol<sup>7</sup> and had b. p. 32—33°.

*Chlorination of 1,1,1-Trifluoropentane.*—The vessel was charged with the pentane (*ca.* 6 vol.) and chlorine (*ca.* 1 vol.) at a total pressure of 250 mm. Experiments were carried out at 4 temperatures, and the proportions of the chlorinated products are tabulated as relative selectivities ( $RS_4^*$ ).

Temp.	No. of runs	CF <sub>3</sub> ·CH <sub>2</sub> —	CH <sub>2</sub> —	CH <sub>2</sub> —	CH <sub>3</sub> —	CH <sub>3</sub>
0°	5	0·03 ± 0·01	1·07 ± 0·07	4·46 ± 0·10	1	1
20	9	0·03 ± 0·004	1·11 ± 0·16	4·55 ± 0·11	1	1
60	7	0·04 ± 0·01	1·21 ± 0·03	4·38 ± 0·05	1	1
230	4	0·06 ± 0·01	1·29 ± 0·11	4·01 ± 0·16	1	1

There were three principal peaks besides that of starting material, on the gas chromatograms. About 2 c.c. of the trifluoropentane was chlorinated in the liquid phase and approximately 0·7-c.c. samples were injected into a large-scale gas-chromatography apparatus. From this apparatus it was possible to obtain on elution, specimens of the products of the three large peaks. They were readily identified by n.m.r. spectra as 3-chloro-, 4-chloro-, and 5-chloro-1,1,1-trifluoropentane, eluted in that order. Besides these main products, there was a very small peak on the analytical chromatograms between the starting material and the 3-chloro-isomer. The quantity of this material was too small for collection to be practical, but it was assumed to be 2-chloro-1,1,1-trifluoropentane.

*Bromination of 1,1,1-Trifluoropentane.*—The vessel was charged with the pentane (*ca.* 20 vol.) and bromine (*ca.* 1 vol.) at a total pressure of *ca.* 200 mm. The products are listed as selectivities relative to carbon atom 3 ( $RE_3^*$ ) because the relative rate of attack on carbon atom 4 was very small and hence the analysis of the rate of attack on this site by far the least accurate.

Temp.	No. of runs	CF <sub>3</sub> ·CH <sub>2</sub> —	CH <sub>2</sub> —	CH <sub>2</sub> —	CH <sub>3</sub>
40°	15	—	0·118 ± 0·008	1	0·005 ± 0·002
76	13	—	0·132 ± 0·007	1	0·005 ± 0·002
155	5	—	0·148 ± 0·007	1	0·011 ± 0·002
200	5	—	0·160 ± 0·004	1	0·015 ± 0·001
230	7	—	0·204 ± 0·020	1	0·019 ± 0·001

There were three principal products, their peaks being followed on the analytical gas chromatograms, by two much smaller peaks in addition to unchanged material. On the large-scale gas chromatograph it was possible to obtain specimens corresponding to the three principal peaks and to measure their n.m.r. spectra. The second and third peaks were unambiguously identified as due to 3-bromo- and 4-bromo-1,1,1-trifluoropentane. The very small fourth peak was assumed to be due to 5-bromo-1,1,1-trifluoropentane. The first peak could not be identified from its n.m.r. or infrared spectra. Its elution time corresponded with that expected for 2-bromo-1,1,1-trifluoropentane but the spectra showed that it did not have this structure (in fact the n.m.r. spectrum showed it was not a trifluoropentane; changing the carrier gas showed it had a smaller molecular weight than the bromotrifluoropentanes). The amount of this product never represented more than 7% of the brominated product (at 40°) and it was present in very much smaller concentrations (< 0·5%) in the high-temperature runs. This unidentified peak may have masked traces of the expected 2-bromo-1,1,1-trifluoropentane, but if so the amount of the latter was very small indeed. The remaining peak on the gas chromatograms was very small and of very high boiling material. It may have been a dibromotrifluoropentane but the quantity was too small to permit isolation and to have any appreciable effect on the results.

*Bromination of 1-Fluorobutane.*—The vessel was charged with 1-fluorobutane (10 vols.) and bromine (1 vol.) at a total pressure of *ca.* 150 mm. Experiments were carried out at 4 temperatures and the results are tabulated as relative selectivities ( $RS_4^*$ ). The identification of the bromofluorobutanes has been described previously.<sup>8</sup>

<sup>7</sup> Hoffmann, *J. Amer. Chem. Soc.*, 1948, **70**, 2596.

<sup>8</sup> Fredricks and Tedder, *J.*, 1960, **144**; 1961, 3520; *Chem. and Ind.*, 1959, 490.

Temp.	No. of runs	FCH <sub>2</sub> —	—CH <sub>2</sub> —	—CH <sub>2</sub> —	—CH <sub>3</sub>
62°	10	11.3 ± 1.4	9.5 ± 1.0	146 ± 13	1
107	8	15.5 ± 1.6	14.4 ± 1.3	201 ± 17	1
160	7	6.7 ± 1.5	4.7 ± 0.9	63 ± 8	1
185	7	8.7 ± 0.6	7.3 ± 0.5	81 ± 8	1

## DISCUSSION

Following the practice of previous papers of this series the relative rates of halogenation at each site, or "relative selectivities," are compared (Table 1).

TABLE 1.

The halogenation of 1-fluorobutane and 1,1,1-trifluoropentane, expressed <sup>8</sup> as relative selectivities,  $RS_p^x$ .

	X	Chlorination at 75°			Bromination at 150°		
		H	F	CF <sub>3</sub>	H	F	CF <sub>3</sub>
α	XCH <sub>2</sub>	1	0.9	0.04	1	9	<1
β	CH <sub>2</sub>	3.6	1.7	1.2	80	7	7
γ	CH <sub>2</sub>	3.6	3.7	4.3	80	90	90
δ	CH <sub>3</sub>	1	1	1	1	1	1

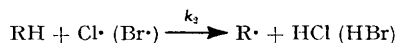
The chlorination results confirm the earlier qualitative work of Henne and his co-workers. The present work utilised the comparatively easy one-step synthesis of 1,1,1-trifluoropentane from valeric acid and sulphur tetrafluoride followed by the quantitative separation of the products by using gas chromatography and their identification by n.m.r. spectroscopy.

Table 1 shows, as expected that a trifluoromethyl group exerts a deactivating effect on chlorination and bromination at a β-carbon atom. This deactivation is of the same order as that exerted by a fluorine atom. The inductive effect ( $-I_o$ ) of a trifluoromethyl group and a fluorine atom are of the same order (cf. the dissociation constants of fluoroacetic acid,  $pK$  3.3, and 3,3,3-trifluoropropionic acid,  $pK$  3.1). Halogenation is almost completely inhibited at the carbon atom α to the trifluoromethyl group, in marked contrast to halogenation at the carbon atom α to a fluorine atom. The relatively high reactivity

TABLE 2.

Approximate values for the Arrhenius parameters for the chlorination and bromination of 1-fluorobutane and 1,1,1-trifluoropentane.

( $\log A_2$  in mole<sup>-1</sup> cm.<sup>3</sup> sec.<sup>-1</sup>;  $E_2$  in kcal. mole<sup>-1</sup>)



## Chlorination

	α-CH <sub>2</sub>		β-CH <sub>2</sub>		γ-CH <sub>2</sub>		δ-CH <sub>3</sub>	
	$\log A_2$	$E_2$	$\log A_2$	$E_2$	$\log A_2$	$E_2$	$\log A_2$	$E_2$
X = H .....	13.2	0.8	13.3	0.3	13.3	0.3	13.2	0.8
X = F .....	13.0	0.8	13.1	0.6	13.3	0.3	13.1	0.8
X = CF <sub>3</sub> .....	12.2	2.0	13.0	0.6	13.3	0.3	12.8	0.5

## Bromination

X = H .....	13.1	13.4	13.6	10.2	13.6	10.2	13.1	13.4
X = F .....	13.2	11.6	13.1	11.5	13.6	10.2	13.0	13.0
X = CF <sub>3</sub> .....	—	—	13.2	11.0	13.6	10.2	13.1	13.0

of hydrogen atoms attached to the same carbon atom as a halogen has been attributed to the ability of the halogen to conjugate with the incipient trivalent carbon atom and has been discussed at length in previous papers.<sup>8</sup> The trifluoromethyl group exerts about the same inductive effect as a fluorine atom but it is unable to stabilise the incipient radical by conjugation.

The relative selectivities listed in Table 1 are in good accord with the predictions made in Part II<sup>8</sup> and with the subsequent, more comprehensive discussion.<sup>9</sup> Greater weight could be placed on these arguments if the changes in activation energy brought about by a substituent could be measured. The present work has been carried out over a fairly wide temperature range and it is possible to calculate very approximate values for the Arrhenius parameters for chlorination and bromination at each site of these molecules (Table 2).

On the basis of the relative selectivities it appeared that the fluorine atom or the trifluoromethyl group have no effect on the rate of halogenation at the terminal  $\delta$  carbon atom and very little influence at the  $\gamma$  position. In order to calculate absolute values of the reaction rates at each site it was necessary to assume that the rate of halogenation at either the  $\delta$  or the  $\gamma$  position was the same as that for the primary or secondary positions in n-butane. By taking the values for the chlorination from the data of Knox and Nelson<sup>10</sup> and for the bromination from the data of Fettis, Knox, and Trotman-Dickenson<sup>11</sup> it was possible to calculate very approximate values for the other sites in 1-fluorobutane and 1,1,1-trifluoropentane (in Table 2 the figures in italics represent the assumed values). The values in Table 2 are very approximate because of the large scatter in the experimental results and because the differences in the relative rates over the temperature ranges studied are comparatively small. Nonetheless Table 2 forms a very consistent overall picture and provides strong confirmatory evidence for the theoretical ideas developed previously. The bromination data for the  $\gamma$  and  $\delta$  positions in butyl fluoride and 1,1,1-trifluoropentane represent the first time the relative rates of attack at primary and secondary hydrogen atoms in the same molecule have been obtained over a temperature range (the values in italics in Table 2 come from ethane and the secondary position in n-butane). It is very satisfactory to find that the present results are so close to the previous interpolated figures.

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<sup>9</sup> Tedder, *Quart. Rev.*, 1960, **14**, 336.

<sup>10</sup> Knox and Nelson, *Trans. Faraday Soc.*, 1959, **55**, 937.

<sup>11</sup> Fettis, Knox, and Trotman-Dickenson, *J.*, 4177, 1960.

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