Free Radical Addition to Olefins. Part XV.† Addition of Bromoform and Carbon Tetrabromide to Fluoroethylenes

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The peroxide-initiated addition of carbon tetrabromide and bromoform to ethylene, vinyl fluoride, 1,1-difluoroethylene, trifluoroethylene, and tetrafluoroethylene has been investigated in sealed tube experiments at 150°. With carbon tetrabromide the major products were adducts involving tribromomethyl radicals while in experiments with bromoform both dibromomethyl and tribromomethyl radicals were found to be important chain-carrying species. Telomers were formed, and the extent of telomer formation increased with increasing fluorine content of the alkene. The relative rates of addition of tribromomethyl and dibromomethyl radicals to the alkenes were estimated, and the orientation ratio for addition of each radical to vinyl fluoride and trifluoroethylene was obtained. The orientation ratios of radicals with any unsymmetrical alkene show significant correlations with the size and polarity of the radicals so that the orientation of radical addition appears to be governed by a complex interplay of factors in which steric and polar effects are of major importance.

THE addition of carbon tetrabromide to terminal alkenes in solution, initiated by peroxides or u.v. light, was reported to give good yields of adducts of general formula $CBr_3CH_2CH(R)Br$.[1,2] Similarly, thermolysis of carbon tetrabromide with tetrafluoroethylene gave $CBr_3CF_2CF_2Br$.[3] Bromoform was found to react much less readily with alkenes than carbon tetrabromide, and the chain-carrying radical was identified as $CHBr_2^{\bullet}$.[1,2] Bromoform also reacted with cyclodeca-1,5-diene to give the adduct of the $CHBr_2^{\bullet}$ radical.[4] It has been concluded that in bromoform and iodoform a carbon–halogen bond is broken in the initiation step, whereas in chloroform a carbon–hydrogen bond is broken.[5] If these reactions are indeed the principal chain-carrying processes in which carbon tetrabromide and bromoform take part, then this should make possible the study of the addition reactions of tribromomethyl and dibromomethyl radicals enabling their behaviour to be compared with that of other halogenoalkyl radicals.

A study of the free radical addition of carbon tetrabromide to ethylene and four fluoroethylenes, initiated by di-t-butyl peroxide (DTBP) is reported in this paper. The results of the carbon tetrabromide experiments suggested that the work be extended to bromoform, which was therefore treated under similar conditions with the same fluoroethylenes.

RESULTS AND DISCUSSION

At 150° DTBP decomposes into methyl radicals and acetone, *via* the intermediacy of t-butoxyl radicals. Methyl bromide was detected as a trace product in most of the reactions, and acetone was observed as a product in all reactions where it was not used as a solvent, hence the initiation step involves abstraction of bromine from carbon tetrabromide by methyl radicals. The main products from the carbon tetrabromide reactions, together with their relative yields, are shown in Table 1. The 1 : 1 adduct was, as expected, a major product in all the reactions, and its formation can be attributed to a straightforward chain process [equations (1)—(3) using E as the symbol for the alkene]. An interesting feature of the results was the formation, in appreciable

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† Part XIV, J. N. Cape, A. C. Greig, J. M. Tedder, and J. C. Walton, *J.C.S. Faraday I*, 1975, 592.

[1] M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Amer. Chem. Soc.*, 1946, **68**, 154.

[2] M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1100.

[3] C. G. Krespan, R. J. Harder, and J. J. Drysdale, *J. Amer. Chem. Soc.*, 1961, **83**, 3424.

[4] J. G. Traynham and H. H. Hsieh, *J. Org. Chem.*, 1973, **38**, 868.

[5] M. Weizmann, S. Israelashvili, A. Halevy, and F. Bergmann, *J. Amer. Chem. Soc.*, 1947, **69**, 2569.

yield of products such as bromoform and CBr_3EH. Hydrogen abstraction from the products and reactants

$$CH_3^\bullet + CBr_4 \longrightarrow CH_3Br + CBr_3^\bullet \qquad (1)$$

$$CBr_3^\bullet + E \longrightarrow CBr_3E^\bullet \qquad (2)$$

$$CBr_3E^\bullet + CBr_4 \longrightarrow CBr_3EBr + CBr_3^\bullet \qquad (3)$$

by $CBr_3^\bullet$ and adduct radicals is competitive with bromine abstraction from carbon tetrabromide at the reaction temperature of 150°. The product bromoform can itself take part [reactions (4) and (5)] in addition

$$CBr_3^\bullet + RH \longrightarrow CHBr_3 + R^\bullet \qquad (4)$$

$$CBr_3E^\bullet + RH \longrightarrow CBr_3EH + R^\bullet \qquad (5)$$

reactions with the alkenes, and small yields of the adducts $CHBr_2EBr$ were observed. In the run with vinyl fluoride using increased di-t-butyl peroxide hydrogen abstraction predominates, and the main products were bromoform and adducts derived therefrom. It is possible that the formation of tetrabromoethylene indicates a small participation by dibromocarbene, since di- and tri-bromomethanes are known to give carbenes in photochemical reactions.[6] However, no cyclopropane-type adducts were observed in any of the reactions, and it seems more probable that the tetrabromoethylene is formed from two tribromomethyl radicals [reaction (6)]. The extent of telomer

$$2CBr_3^\bullet \longrightarrow Br_2 + CBr_2{=}CBr_2 \qquad (6)$$

formation increased with increasing fluorine content of the alkene, becomining of major importance with tetrafluoroethylene for which telomers up to $CBr_3[CF_2CF_2]_5Br$ were identified.

TABLE 1

Relative product yields from carbon tetrabromide addition reactions at 150° [a]

Alkene E	Dibromide EBr_2	$CHBr_3$	$CBr_2{=}CBr_2$	CBr_3EH	$CHBr_2EBr$ 'normal'	$CHBr_2E'Br$ 'reverse'	$CBr_2E'Br$ 'normal'	$CBr_3E'Br$ 'reverse'	Telomer
$CH_2{=}CH_2$	34·0	26·0	1·8	40·0	3·7		220		
$CH_2{=}CHF$	8·1	17·7		12·3			59·4	2·5	
$CH_2{=}CHF$ [b]	25·6	26·3	3·6		13·2	0·83			
$CH_2{=}CF_2$	37·2	11·2	1·0	5·3			43·9		2·6
$CHF{=}CF_2$	9·3	27·0	0·4		0·13	0·046	12·6	3·0	3·5
$CF_2{=}CF_2$	5·4	13·8					20·4		14·4 [c]

[a] Yields relative to the unchanged CBr_4 as 100%. [b] Reaction with greatly increased initiator concentration, yields relative to total product as 100% (see Experimental section). [c] Indicates total telomer yield; individual telomers $CBr_3[CF_2CF_2]_nBr$, $n = 2$ (8·7%), $n = 3$ (4·1%), $n = 4$ (1·1%), $n = 5$ (0·5%).

TABLE 2

Relative yields from bromoform addition reactions at 150° [a]

Alkene E	CH_2Br_2	CBr_4	EBr_2	CBr_3EH	$CHBr_2EBr$ 'normal'	$CHBr_2E'Br$ 'reverse'	CBr_3EBr 'normal'	$CBr_3E'Br$ 'reverse'
$CH_2{=}CH_2$	11·6	0·1		1·9	11·5		14·0	
$CH_2{=}CHF$	6·8	0·0(1)		0·7	0·9		3·4(8)	0·1(4)
$CH_2{=}CF_2$	7·2	0·3		1·0	1·5		1·7	
$CHF{=}CF_2$	4·0	1·0	1·1		1·2(7)	0·3(9)	1·2(2)	0·3(4)
$CF_2{=}CF_2$	12·3	1·2	0·8		2·0		2·5 [b]	

[a] Yields based on unchanged $CHBr_3$ as 100%. [b] Yield of 2 : 1 telomer 0·1(4)%.

Bromoform reacted much less readily than carbon tetrabromide with all the alkenes under similar experimental conditions, in agreement with the earlier investigations.[1,2] Product mixtures also rapidly decomposed unless kept permanently refrigerated. The main products, together with their relative yields, are shown in Table 2. In contrast to earlier work it is apparent that both $CHBr_2^\bullet$ and $CBr_3^\bullet$ radicals act as chain carriers, and adducts derived from both these radicals were found in fair yields. Dibromomethyl radicals can abstract hydrogen [reaction (7)] from bromoform

$$CHBr_2^\bullet + CHBr_3 \longrightarrow CH_2Br_2 + CBr_3^\bullet \qquad (7)$$

giving dibromomethane, which was a major product in all the reactions. In fact step (7) is favoured over addition to the alkene by $CHBr_2^\bullet$, as is shown by the relative yields of CH_2Br_2 and the adducts $CHBr_2EBr$.

The relative yields of the adducts $CHBr_2EBr$ and CBr_3EBr suggest that $CBr_3^\bullet$ radicals add more readily to a given alkene than do $CHBr_2^\bullet$ radicals, although this conclusion cannot be fully substantiated without knowing the relative concentrations of the two radicals. This cannot be assessed from the total yield of products derived from each radical, since hydrogen abstraction by $CBr_3^\bullet$ radicals and bromine abstraction by $CHBr_2^\bullet$ radicals give bromoform which is indistinguishable from the reactant. The behaviour of bromoform parallels that of bromodichloromethane,[7] where hydrogen abstraction to give $CCl_2Br^\bullet$ radicals competes with bromine abstraction to give $CHCl_2^\bullet$ radicals.

These results reveal that bromoform is not a clean source of dibromomethyl radicals, and suggest that caution is necessary in the use of this reagent in free radical syntheses.

It was not practicable to measure the relative rate of addition of $CBr_3^\bullet$ or $CHBr_2^\bullet$ radicals to the alkenes by using a competitive technique with a standard alkene

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[6] T. Marolewski and N. C. Yang, *Chem. Comm.*, 1967, 1225.

[7] J. C. Gibb, J. M. Tedder, and J. C. Walton, *J.C.S. Perkin II*, 1974, 807.

because of the complexity of the product mixtures. The addition reactions were performed using similar conditions for all the alkenes so that an estimate of the *relative overall* rate of addition of $\mathrm{CBr_3^{\bullet}}$ and $\mathrm{CHBr_2^{\bullet}}$ radicals to the alkenes can be obtained by summing the yield of $\mathrm{CBr_3}$ adducts or $\mathrm{CHBr_2}$ adducts (including the adducts from both ends of an unsymmetrical alkene) and telomers for each alkene, and comparing this with the corresponding yield from ethylene. The good agreement between the two sets of values for $\mathrm{CBr_3^{\bullet}}$ radicals shown in Table 3, calculated from the carbon tetrabromide and bromoform experiments respectively, is gratifying. The rate of addition initially decreases for both $\mathrm{CBr_3^{\bullet}}$ and $\mathrm{CHBr_2^{\bullet}}$ radicals as the number of fluorine substituents in the alkene increases, passes through a minimum, and then increases again to tetrafluoroethylene (the vinyl fluoride value for $\mathrm{CHBr_2^{\bullet}}$ radicals seems to be anomalous). This same trend has been observed with several other halogenoalkyl radicals,[8] and with hydrogen atoms [9] adding to these fluoroethylenes.

TABLE 3

Relative rate of addition of $\mathrm{CBr_3^{\bullet}}$ and $\mathrm{CHBr_2^{\bullet}}$ radicals to fluoroalkenes at 150°

Radical	$\mathrm{CH_2{=}CH_2}$	$\mathrm{CH_2{=}CHF}$	$\mathrm{CH_2{=}CF_2}$	$\mathrm{CHF{=}CF_2}$	$\mathrm{CF_2{=}CF_2}$
$\mathrm{CBr_3^{\bullet}}$ [a]	1·00	0·29	0·20	0·07	0·13
$\mathrm{CBr_3^{\bullet}}$ [b]	1·00	0·27	0·17	0·10	0·17
$\mathrm{CHBr_2^{\bullet}}$ [b]	1·00	0·08	0·13	0·14	0·17

[a] From carbon tetrabromide experiments. [b] From bromoform experiments.

Two adducts were observed from addition of each radical to vinyl fluoride and trifluoroethylene. Only one adduct was detected with 1,1-difluoroethylene, but in the light of experience with other halogenoalkyl radicals (see Table 4) it seems certain that the second adduct *is* formed, but in quantities below the limit of detection. The orientation ratio O_r can be calculated from the relative amounts of the 'normal' adduct $RE\mathrm{Br}$ (from addition to the least substituted end of the alkene) and the 'reverse' adduct $RE'\mathrm{Br}$ ($\mathrm{R} = \mathrm{CBr_3}$ or $\mathrm{CHBr_2}$) [equation (8)]. For $\mathrm{CBr_3^{\bullet}}$ radicals

$$O_r = k'_2/k_2 = [RE'\mathrm{Br}]_f/[RE\mathrm{Br}]_f \qquad (8)$$

with vinyl fluoride O_r values of $0{\cdot}042 \pm 0{\cdot}01$ and $0{\cdot}040 \pm 0{\cdot}007$ were obtained from the carbon tetrabromide and bromoform experiments respectively. The orientation ratios for trifluoroethylene and $\mathrm{CBr_3^{\bullet}}$, *i.e.* $0{\cdot}24 \pm 0{\cdot}06$ and $0{\cdot}28 \pm 0{\cdot}09$ derived from the two sets of experiments, were also in good agreement. The $\mathrm{CHBr_2^{\bullet}}$ radical is less selective with vinyl fluoride ($O_r = 0{\cdot}063 \pm 0{\cdot}005$) and with trifluoroethylene ($O_r = 0{\cdot}35 \pm 0{\cdot}04$, and from $\mathrm{CHBr_3}$ and $\mathrm{CHF{=}CF_2}$, $0{\cdot}31 \pm 0{\cdot}05$).

The orientation ratios for a number of halogenoalkyl radicals with fluoroethylenes are shown in Table 4. The present results with $\mathrm{CBr_3^{\bullet}}$ and $\mathrm{CHBr_2^{\bullet}}$ radicals are not directly comparable with the results for the other radicals, because they are derived from sealed-tube experiments in which reaction occurs mainly in the gas phase but partly in solution, whilst the O_r values of the other radicals are from homogeneous gas-phase experiments. However, O_r values for $\mathrm{CF_3^{\bullet}}$ radicals obtained from sealed tube experiments [15] are almost identical with the gas-phase values,[12] and the liquid phase O_r value for $\mathrm{CF_2Br^{\bullet}}$ with trifluoroethylene [16] is identical with the gas-phase value.[8] This suggests that changing from the gas to the liquid phase will have little effect on the O_r values of $\mathrm{CBr_3^{\bullet}}$ and $\mathrm{CHBr_2^{\bullet}}$ radicals.

A uniform decrease in O_r, for the vinyl fluoride and trifluoroethylene results, is revealed in Table 4 for the series of radicals $\mathrm{CF_3^{\bullet}}$, $\mathrm{CCl_3^{\bullet}}$, $\mathrm{CBr_3^{\bullet}}$ and a similar uniform decrease occurs along the series $\mathrm{CF_3^{\bullet}}$, $\mathrm{CF_2Br^{\bullet}}$, $\mathrm{CFBr_2^{\bullet}}$, $\mathrm{CBr_3^{\bullet}}$; suggesting that the size of the radical is an important factor in determining the orientation ratio. The diameters of the radicals were estimated from the covalent atomic radii,[17] by finding the smallest circle, perpendicular to the three-fold axis, which could contain the three substituents attached to the central carbon. All the radicals were considered as

TABLE 4

Orientation of addition of halogenoalkyl radicals to fluoroethylenes at 150°

Radical	No.	Diam. d_c/Å	$\mathrm{CH_2{=}CHF}$ O_r	$\mathrm{CH_2{=}CF_2}$ O_r	$\mathrm{CHF{=}CF_2}$ O_r	Ref.
$\mathrm{CH_3^{\bullet}}$	1	2·58	0·59	0·18	7·26	10
$\mathrm{CH_2F^{\bullet}}$	2	3·16	0·29	0·45	2·04	11
$\mathrm{CHF_2^{\bullet}}$	3	3·63	0·19	0·18	0·95	11
$\mathrm{CF_3^{\bullet}}$	4	3·92	0·094	0·032	0·50	12
$\mathrm{CF_2Br^{\bullet}}$	5	4·45	0·089	0·029	0·47	8
$\mathrm{CF_3CF_2^{\bullet}}$	6	5·16	0·054	0·011	0·29	12
$\mathrm{CCl_3^{\bullet}}$	7	5·26	0·070	0·012	0·29	13
$\mathrm{CFBr_2^{\bullet}}$	8	5·41	0·085	0·019	0·36	14
$\mathrm{CHBr_2^{\bullet}}$	9	5·41	0·063		0·31	This work
$\mathrm{CF_3(CF_2)_2^{\bullet}}$	10	5·42	0·050	0·009	0·25	12
$\mathrm{CBr_3^{\bullet}}$	11	5·84	0·040		0·24	This work
$\mathrm{(CF_3)_2CF^{\bullet}}$	12	6·62	0·020	0·001	0·062	12

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[8] J. M. Tedder and J. C. Walton, *J.C.S. Faraday I*, 1974, 308.

[9] J. P. Kilcoyne and K. R. Jennings, *J.C.S. Faraday I*, 1974, 379.

[10] J. M. Tedder, J. C. Walton, and K. D. R. Winton, *J.C.S. Faraday I*, 1972, 1866.

[11] J. P. Sloan, unpublished work.

[12] D. S. Ashton, A. F. Mackay, J. M. Tedder, D. C. Tipney, and J. C. Walton, *J.C.S. Chem. Comm.*, 1973, 496; J. N. Cape, A. C. Greig, J. M. Tedder, and J. C. Walton, *J.C.S. Faraday I*, 1975, 592.

[13] J. M. Tedder and J. C. Walton, *Trans. Faraday Soc.*, 1966, **62**, 1859.

[14] J. P. Sloan, J. M. Tedder, and J. C. Walton, *J.C.S. Faraday I*, 1973, 1143.

[15] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1954, 923; 1957, 2800; R. N. Haszeldine, D. W. Keen, and A. E. Tipping, *J. Chem. Soc.* (*C*), 1970, 414.

[16] A. T. Cosia, *J. Org. Chem.*, 1961, **26**, 2995.

[17] J. A. A. Ketelaar, 'Chemical Constitution,' Elsevier, Amsterdam, 1958, 2nd edn., p. 199.

pyramidal, and regular tetrahedral bond angles were assumed, since even those radicals which are planar in their ground state probably become pyramidal in the transition state of the addition reaction. Only atoms α- and β- to the radical centre were taken into account. This means that the calculated radii of radicals having n-perfluoroalkyl chains are the same for C_3 and upward. It would be predicted on this basis that the orientation ratios of radicals n-C_nF_{2n+1} with $n \geqslant 3$ should all be the same. That this is a reasonable approximation is shown by the experimental orientation ratios of n-perfluoroalkyl radicals [12] which exhibit little variation up to C_8.

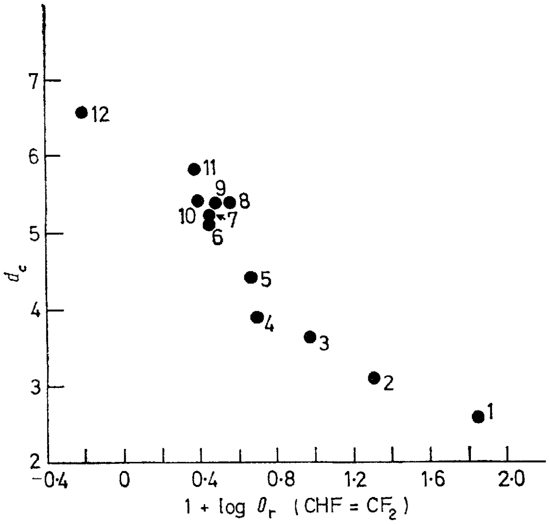

FIGURE 1 Correlation between radical diameter d_c and log O_r. For key see Table 4

Significant correlations are found between the radical diameters d_c, given in Table 4, and the logarithms of the orientation ratios frim the vinyl fluoride (r 0·95), 1,1-difluoroethylene (r 0·95, excluding the methyl point) and trifluoroethylene (r 0·94) results. The correlation is shown in Figure 1 for the trifluoroethylene results. Taft steric substituent constants, E_s, are not available for many of the radicals,[18] but it is noteworthy that log O_r correlates very well with E_s for the few that are known. The deviations from linearity observed in all three correlations of log O_r against d_c might be attributed to conformational effects. A radical containing one or two bulky substituents CX_2Y could rotate in such a way as to place the bulky substituents away from the site of steric interaction. The radical diameter d_c, calculated as above, would then overestimate the effect of size for the radical $^{\bullet}CX_2Y$. If effects such as this were important the symmetrical radicals $^{\bullet}CX_3$ would be expected to define a straight line (or uniform curve), and the experimental O_r values for $^{\bullet}CX_2Y$ radicals would be greater (*i.e.* lie to the right of this line in Figure 1) than those from the defined line. The symmetrical radicals do not however define a straight line, and even if the $CH_3^{\bullet}$ result is ignored and the line through the $CF_3^{\bullet}$, $CCl_3^{\bullet}$, and $CBr_3^{\bullet}$ radicals (points 4, 7, and 11 in Figure 1) is taken as definitive, the points for $^{\bullet}CF_2Br$, $^{\bullet}CFBr_2$, and $^{\bullet}CHBr_2$ lie to the right, but the result for $(CF_3)_2CF^{\bullet}$ lies to the left of this line.

It is notable that the orientation ratios of methyl and the mono- and di-fluoromethyl radicals are too high in comparison with those of the fully halogenated radicals. The points for $CH_3^{\bullet}$, $CH_2F^{\bullet}$, and $CHF_2^{\bullet}$ lie well to the right of the line defined by $CF_3^{\bullet}$, $CCl_3^{\bullet}$, and $CBr_3^{\bullet}$ in Figure 1. This might indicate that polar effects are important. To test this hypothesis we sought to correlate the O_r values with the electronegativities of the radicals. Empirical group electronegativities are known for only three of the radicals,[19] and although group electronegativities can usually be approximated by the method of Gordy, as modified by Wilmshurst,[19] this method leads to unreasonable electronegativities for the fluorine-substituted methyl radicals. The radical electronegativites, as measured by the sum of the electronegativities of the atoms or groups α to the radical centre, show a very poor correlation with the orientation ratios. An alternative approach is to consider the σ_I (aliphatic) substituent constants (proportional to σ^*) of the groups attached to the radical centre.[20] The correlation between the sum of the σ_I constants of the α-substituents ($\sum_{\alpha}\sigma_I$) and log O_r is poor for all three alkenes, but an expression of the type (9) where a is a constant determined empirically

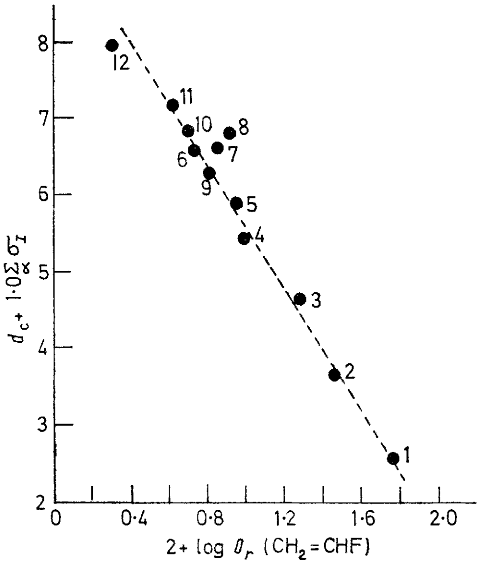

FIGURE 2 Correlation between $d_c + \sum_{\alpha}\sigma_I$ and log O_r. For key see Table 4

$$\log O_r \propto d_c + a\sum_{\alpha}\sigma_I \qquad (9)$$

from the results does lead to an improved overall correlation. The optimum value of a is found to be the same, *i.e.* 1·0, for the all three alkenes, and the correlation

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[18] M. Charton, *Progr. Phys. Org. Chem.*, 1971, **8**, 235.

[19] P. R. Wells, *Progr. Phys. Org. Chem.*, 1968, **6**, 111.

[20] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.

coefficients are then 0·98, 0·97, and 0·97 for the vinyl fluoride, 1,1-difluoroethylene, and trifluoroethylene series respectively. The final correlation is shown in Figure 2 for the vinyl fluoride series. These satisfactory correlations suggest that the orientation of addition of halogenoalkyl radicals to unsymmetrical olefins is governed by a complex interplay of factors in which polar and steric effects are of major importance.

EXPERIMENTAL

Materials.—Carbon tetrabromide was recrystallized three times from ethanol giving material *ca.* 99·0% pure by g.l.c. Bromoform was redistilled, trap-to-trap distilled, and degassed, giving material *ca.* 99·0% pure by g.l.c. Di-t-butyl peroxide, ethylene, vinyl fluoride, 1,1-difluoroethylene trifluoroethylene, and tetrafluoroethylene were commercial materials, trap-to-trap distilled, and degassed before use; g.l.c. showed no impurities.

Method.—Materials were handled on a conventional vacuum line. Measured amounts of carbon tetrabromide (or bromoform), di-t-butyl peroxide, and the appropriate alkene were distilled into a thick Pyrex tube (*ca.* 100 ml) and thoroughly degassed. The tube was then sealed under vacuum and transferred to a furnace at 150 ± 4° where reaction occurred for a timed interval. The reaction was quenched in liquid nitrogen, the tube was opened, and the contents were dissolved in carbon tetrachloride or acetone (the product acetone could not be measured in this case).

Analysis.—Product identification was achieved by coupled g.l.c.–mass spectrometry (m.s.) of the reaction mixtures using a Pye 104 gas chromatograph, with a 7 ft 10% w/w Embaphase silicone oil on silanized Chromosorb G column, coupled *via* a single stage Bieman separator to an A.E.I. MS902 mass spectrometer.* Wherever possible products were then separated by preparative g.l.c. on a Pye 105 instrument. ^1H and ^{19}F n.m.r. spectra were recorded on the products at room temperature on CCl_4 solutions containing traces of Me_4Si and CCl_3F as internal standards. A Varian HA-100 instrument was employed.

Quantitative analysis was performed by a g.l.c. on a modified Griffin and George gas density balance chromatograph using the same column as in the g.l.c.–mass spectral analyses. Peak areas were measured with a DuPont 310 curve resolver. Each reaction was run twice in the carbon tetrabromide series to check the consistency of the results, and each mixture was analysed several times, figures given in the tables being average values.

Reaction of Carbon Tetrabromide with Ethylene.—Carbon tetrabromide (3·0 mmol), ethylene (3·6 mmol), and DTBP (0·077 mmol) reacted at 150° for 15 h. Six main products were observed on the g.l.c. trace: peak 1, $BrCH_2CH_2Br$ (structures established by m.s., R_t, and n.m.r.); peak 2, $CHBr_3$ (m.s. R_t, n.m.r.); peak 3, $CBr_3CH_2CH_3$ (m.s.); peak 4, $CBr_2{=}CBr_2$ (m.s.); peak 5, $CHBr_2CH_2CH_2Br$ (m.s.); peak 6, $CBr_3CH_2CH_2Br$ (m.s. and n.m.r.). The n.m.r. spectrum confirmed this structure. Thus the ^1H n.m.r. spectrum showed an A_2B_2 multiplet at δ 4·4. The relative yields of these products are given in Table 1. Traces (<1·0% based on unchanged CBr_4) of MeBr, EtBr, and Bu^tBr were also detected.

Reaction of Carbon Tetrabromide with Vinyl Fluoride.—Carbon tetrabromide (3·0 mmol), vinyl fluoride (3·6 mmol), and DTBP (0·077 mmol) reacted at 150° for 18 h. Five products were observed on the g.l.c. traces: peak 1, $BrCH_2CHFBr$ (m.s. and n.m.r.); peak 2, $CHBr_3$ (m.s., n.m.r., and R_t); peak 3, $CBr_3CH_2CH_2F$ (m.s.); peak 4, CBr_3CH_2CHFBr (m.s. and n.m.r.). The n.m.r. spectra confirmed the structure $CBr_3CH_bH_cCH_aFBr$, δ 4·0 (H_b and H_c, complex) and 7·2 (J_{H_aF} 51·5, $J_{H_aH_b}$ 7·0, $J_{H_aH_c}$ 3·5 Hz). The ^{19}F n.m.r. spectrum showed Φ 133 (J_{FH_a} 51·5, J_{FH_b} 24·5, J_{FH_c} 17·0 Hz). Peak 5 was shown to arise from CBr_3CHFCH_2Br (m.s.). The relative yields of these products are given in Table 1.

In a second run the extent of reaction was greatly increased by using an increased DTBP concentration (1·3 mmol). Virtually all the CBr_4 was consumed in this reaction, making it impossible to compute the yields of the products relative to the unchanged CBr_4. Product yields are, therefore, given relative to the total product. Nine products were observed: peak 1, CH_3Br (5·9%); peaks 2 and 3 CH_2BrCH_2F and CH_3CHFBr (21·3%); peak 4, CH_2Br_2 (3·1%); peak 5, $CH_2BrCHFBr$ (25·6%); peak 6, $CHBr_3$ (26·3%); peak 7, $CHBr_2CH_2CHFBr$ (13·2%) (m.s.); peak 8, $CBr_2{=}CBr_2$ (3·6%); peak 9, $CHBr_2CHFCH_2Br$ (0·83%) (m.s.).

Reaction of Carbon Tetrabromide with 1,1-*Difluoroethylene.*—Carbon tetrabromide (3·0 mmol), 1,1-difluoroethylene (3·6 mmol), and DTBP (0·077 mmol) reacted at 150° for 16 h. Seven main products were observed on the g.l.c. trace: peak 1, CH_2BrCF_2Br (m.s.); peak 2, $CHBr_3$ (m.s., R_t); peak 3, $CBr_3CH_2CF_2H$ (m.s.); peak 4, $CBr_2{=}CBr_2$ (m.s.); peak 5, $CBr_3CH_2CF_2Br$ (m.s.). Confirmation of this structure was provided by the ^1H n.m.r. spectrum, δ 4·4 (t, J_{HF} 12·5 Hz) and by the ^{19}F n.m.r. spectrum, Φ 46·6 (t, J_{FH} 12·5 Hz). Peaks 6 and 7 were shown from their mass spectra to be 2 : 1 telomers $C_5H_4F_4Br_4$. The ^1H n.m.r. spectrum of peak 6 showed δ 3·3 (t, J_{HF} 13·0 Hz) and 3·9 (t, J_{HF} 12·5 Hz) indicating the structure $CBr_3CH_2CF_2CF_2CH_2Br$. Peak 7 was too small for collection but the probable structure is $CBr_3CH_2CF_2CH_2$-CF_2Br. The relative yields of these products are shown in Table 1. Traces of MeBr and Bu^tBr were identified in addition to the above compounds.

Reaction of Carbon Tetrabromide with Trifluorethylene.—Carbon tetrabromide (3·0 mmol), trifluoroethylene (3·6 mmol), and DTBP (0·077 mmol) reacted at 150° for 17 h. Eight main products were identified: peak 1, $CHFBr$-CF_2Br (m.s.); peak 2, $CHBr_3$ (m.s., R_t); peak 3, $CHBr_2$-$CHFCF_2Br$ (m.s.); peak 4 $CHBr_2CF_2CHFBr$ (m.s.); peak 5, $CBr_2{=}CBr_2$ (m.s.); peak 6 CBr_3CHFCF_2Br (m.s. and n.m.r.). The structure $CBr_3CHF_aCF_bF_cBr$ was confirmed by the ^1H n.m.r. spectrum, δ 5·2 (8 lines, J_{HF_a} 42·0, J_{HF_b} 3·0, J_{HF_c} 13·5 Hz) and by the ^{19}F spectrum, Φ 48·1 (F_b, 8 lines, $J_{F_bF_c}$ 167·0, $J_{F_bF_a}$ 16·5, J_{F_bH} 3·0 Hz), 59·2 (F_c, 8 lines, $J_{F_cF_b}$ 167·0, $J_{F_cF_a}$ 16·5, J_{F_cH} 13·5 Hz), and 155·1 (F_a, 8 lines, J_{F_aH} 42·0, $J_{F_aF_b} = J_{F_aF_c} =$ 16·5 Hz). Peak 7 was shown to arise from CBr_3CF_2CHFBr (m.s. and n.m.r.). The structure $CBr_3CF_bF_cCHF_aBr$ was confirmed by the ^1H n.m.r. spectrum, δ 7·2 (4 lines, J_{HF_a} 47·5, J_{HF_b} 0, J_{HF_c} 15·5 Hz), and by the ^{19}F n.m.r. spectrum, Φ 94·2 (F_b, 4 lines, $J_{F_bF_c}$ 247, $J_{F_bF_a}$ 18·5, J_{F_bH} 0 Hz), 114·7 (F_c, dt, $J_{F_cF_b}$ 247, $J_{F_cF_a} = J_{F_cH} =$ 15·5 Hz) and 144·5 (F_a, 8 lines, J_{F_aH} 47·5, $J_{F_aF_b}$ 18·5, $J_{F_aF_c}$ 15·5 Hz). Peak 7 was followed by a group of overlapping peaks which were shown by mass spectrometry to be 2 : 1 telomers $C_5H_2F_6Br_4$. Individual

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* Mass spectral data are given in Supplementary Publication No. SUP 21226 (10 pp., 1 microfiche). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

structures could not be determined. The relative yields of these products are given in Table 1. Trace products found were MeBr and Bu^tBr.

Reaction of Carbon Tetrabromide with Tetrafluoroethylene.—Carbon tetrabromide (3·0 mmol), tetrafluoroethylene (3·6 mmol), and DTBP (0·077 mmol) reacted at 150° for 15 h. Seven main products were identified: peak 1, CF_2BrCF_2Br (m.s.); peak 2, $CHBr_3$ (m.s., R_t); peak 3, $CBr_3CF_2CF_2Br$ (m.s. and n.m.r.). This structure was confirmed by the ^{19}F n.m.r. spectrum, Φ 98·1 (s) and 53·5 (s). Peak 4 arises from $CBr_3[CF_2CF_2]_2Br$; m.s. showed strong peaks for $(M - Br)^+$, CF_2Br^+, and for breakdown of the chain. The structure was confirmed by the ^{19}F n.m.r. spectrum which showed signals at Φ 63·4, 103·1, 112·8, and 117·7 (all complex). Peak 5 arises from $CBr_3[CF_2CF_2]_3Br$; m.s. showed $(M - Br)^+$ and a lengthy series of peaks corresponding to break-up of the chain. The ^{19}F n.m.r. spectrum showed six complex signals at Φ 63·9, 103·0, 113·4, 117·9, 121·3, and 122·2. Peaks 6 and 7 were telomers $CBr_3[CF_2CF_2]_4Br$ and $CBr_3[CF_2CF_2]_5Br$ as shown by their mass spectra. The relative yields of these products are given in Table 1. The trace products MeBr, Bu^tBr, and Me_2CO were also detected.

Reaction of Bromoform with Ethylene.—Bromoform (4·3 mmol), ethylene, (4·0 mmol), and DTBP (0·086 mmol) reacted for 17 h at 150°. Seven major products were identified: peak 1, Me_2CO (m.s., R_t); peak 2, CH_2Br_2 (m.s., R_t); peak 3, CH_2BrCH_2Br (m.s., R_t); peak 4, CBr_4 (m.s., R_t); peak 5, $CBr_3CH_2CH_3$; peak 6, $CHBr_2CH_2CH_2Br$; and peak 7, $CBr_3CH_2CH_2Br$. For these last three peaks the m.s. and R_t were identical with those of the compounds reported above. The relative yields of these products are given in Table 2, except for CH_2BrCH_2Br which was obscured on the chromatogram by the bromoform peak. Traces of MeBr were also identified.

Reaction of Bromoform with Vinyl Fluoride.—Bromoform (7·1 mmol), ethylene (4·0 mmol), and DTBP (0·086 mmol) reacted at 150° for 17 h. Seven major products were identified: peak 1, Me_2CO (m.s., R_t); peak 2 CH_2Br_2 (m.s., R_t); peak 3, CBr_4 (m.s., R_t); peak 4, $CHBr_2CH_2CHFBr$; peak 5, $CBr_3CH_2CH_2F$; peak 6, CBr_3CH_2CHFBr; peak 7, CBr_3CHFCH_2Br. The mass spectra and relative retention times of the last four peaks were the same as those of the compounds given above in the $CBr_4 + CH_2{=}CHF$ reactions. The relative yields of these products are given in Table 2. Traces of MeBr and $CHBr_2CHBr_2$ were also detected.

Reaction of Bromoform with 1,1-*Difluoroethylene.*—Bromoform (5·1 mmol), 1,1-difluoroethylene (4·0 mmol), and DTBP (0·086 mmol) reacted for 17 h at 150°. Six main products were identified: peak 1, Me_2CO (m.s., R_t); peak 2, CH_2Br_2 (m.s., R_t); peak 3, CBr_4 (m.s., R_t); peak 4, $CHBr_2CH_2CF_2Br$ (m.s.); peak 5, $CBr_3CH_2CF_2H$; peak 6, $CBr_3CF_2CH_2Br$. The mass spectra and relative retention times of these last two peaks were the same as those of the compounds reported in the $CBr_4 + CH_2{=}CF_2$ reaction. The relative yields are reported in Table 2. Traces of MeBr were also observed.

Reaction of Bromoform with Trifluoroethylene.—Bromoform (7·7 mmol), trifluoroethylene (4·0 mmol), and DTBP (0·086 mmol) reacted at 150° for 17 h. Seven products were identified: peak 1, $CHFBrCF_2Br$ (m.s., R_t); peak 2, CH_2Br_2 (m.s., R_t); peak 3, CBr_4 (m.s., R_t); peak 4, $CHBr_2CHFCF_2Br$, peak 5, $CHBr_2CF_2CHFBr$; peak 6, CBr_3CHFCF_2Br; peak 7, CBr_3CF_2CHFBr. The mass spectra and relative retention times of the last four peaks were the same as those of the compounds reported in the $CBr_4 + CHF{=}CF_2$ reaction. The relative yields of the products are given in Table 2.

Reaction of Bromoform with Tetrafluoroethylene.—Bromoform (5·1 mmol), tetrafluoroethylene (4·0 mmol), and DTBP (0·086 mmol) reacted for 17 h at 150°. Seven products were identified: peak 1, CF_2BrCF_2Br (m.s., R_t); peak 2, CH_3COCH_3 (m.s., R_t); peak 3, CH_2Br_2 (m.s., R_t); peak 4, $CHBr_2CF_2CF_2Br$ (m.s.); peak 5, CBr_4 (m.s., R_t); peak 6, $CBr_3CF_2CF_2Br$; peak 7, $CBr_3(CF_2CF_2)_2Br$. The mass spectra and relative retention times of last two peaks were the same as those of the compounds reported in the $CBr_4 + CF_2{=}CF_2$ reaction. The relative yields of the products are given in Table 2. Traces of MeBr were also observed.

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