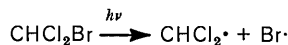


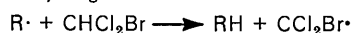
## Free Radical Addition to Olefins. Part XIII.† Photolysis of Bromodichloromethane in the Presence of Olefins

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Photolysis of bromodichloromethane alone and in the presence of ethylene and vinyl fluoride has been investigated. Although the principal photolytic step involves carbon-bromine bond fission:

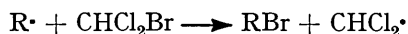


subsequent chain carrying processes involve hydrogen abstraction as much as bromine abstraction:



The almost equal importance of hydrogen and bromine abstraction from bromodichloromethane leads to a mixture of products in which both dichloromethyl ( $\text{CHCl}_2\cdot$ ) and bromodichloromethyl ( $\text{CBrCl}_2\cdot$ ) radicals are chain carrying species. In contrast to earlier reports of liquid phase studies the radical which predominates in addition to alkenes in the gas phase is the bromodichloromethyl radical.

In 1948 Kharasch, Kudema, and Urry reported the addition of bromodichloromethane to olefins by a radical process, induced by acetyl peroxide in solution.<sup>1</sup> These workers reported obtaining good yields of addition products of the general formula  $\text{BrCHRCH}_2\text{CHCl}_2$  from terminal olefins ( $\text{RCH}=\text{CH}_2$ ). Although they provided good evidence that products of this structure were present, there is no evidence that these were the only addition products they obtained, although this is what their paper implies. More recently Belyavskii and Kost have studied the addition of bromodichloromethane to ethylene, induced by benzoyl peroxide, and report 1-bromo-3,3-dichloropropane as the principal product, together with 1-bromo-5,5-dichloropentane and with 1,5-dibromo-3,3-dichloropentane as residue.<sup>2</sup> Subsequently other Russian workers studied the chain transfer efficiencies of a number of halogenoalkanes including bromodichloromethane.<sup>3</sup> They assumed, like Kharasch and his co-workers that the predominant chain transfer step involved bromine abstraction.



If this process is indeed the principal chain transfer reaction in which bromodichloromethane takes part, then it should be possible to study the chemistry of dichloromethyl radicals using the photolysis of bromodichloromethane, exactly as the reactions of trichloromethyl radicals have been studied using the photolysis of bromotrichloromethane.<sup>4,5</sup>

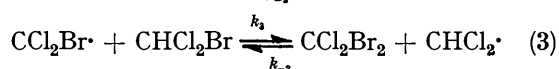
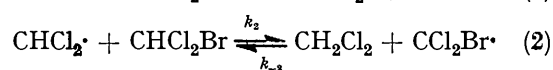
No study of the continuous photolysis of bromodichloromethane has been reported, although studies involving high energy flash photolysis are available.<sup>6</sup> In the present work light from a medium pressure mercury lamp was filtered to exclude completely the 253.7 nm line, and the main transmitted line was at 313 nm. The reaction vessel was Pyrex thus providing

an additional filter to exclude light below 290 nm. Details of the filter are described in the Experimental section. The photolysis products are summarised in Table 1, with the exception of trichloroethylene which was probably also formed but in too small a yield to be separated from the starting material.

TABLE I  
Rates of formation of products in the photolysis of bromodichloromethane in the gas phase

Temp. (°C)	Rates $\times 10^{-9}/\text{mol}^{-1}\text{s}^{-1}$			
	$\text{CH}_2\text{Cl}_2$	$\text{CCl}_2\text{Br}_2$	$\text{C}_2\text{Cl}_4$	$\text{C}_2\text{Cl}_3\text{Br}$
105	2.23	2.12	0.44	0.03
122	2.36	2.06	0.41	0.14
136	1.70	2.36	0.58	0.08
158	1.35	2.36	0.52	0.08
174	0.99	2.47	0.58	0.14

Simple homolysis of bromodichloromethane to give dichloromethyl radicals and bromine atoms which subsequently underwent no radical transfer reaction would yield tetrachloroethane and molecular bromine. In the photolysis of bromotrichloromethane, hexachloroethane and molecular bromine are indeed the principal products.<sup>7</sup> In the present work no tetrachloroethane was detected. The principal products are single carbon compounds and represent products of chain reactions (2)



and (3). Such a chain sequence requires that dichloromethane and dibromodichloromethane be formed in equal proportions; Table 1 shows that at the lower

<sup>4</sup> H. W. Melville, J. C. Robb, and R. C. Tutton, *Discuss. Faraday Soc.*, 1951, **10**, 154; 1953, **14**, 150.

<sup>5</sup> B. P. McGrath and J. M. Tedder, *Bull. Soc. chim. belges*, 1962, **71**, 772; J. M. Tedder and J. C. Walton, *Trans. Faraday Soc.*, 1964, **60**, 1769.

<sup>6</sup> J. P. Simons and A. J. Yarwood, *Bull. Soc. chim. belges*, 1962, **71**, 651; *Trans. Faraday Soc.*, 1963, **59**, 90.

<sup>7</sup> H. W. Sidebottom, J. M. Tedder, and J. C. Walton, *Trans. Faraday Soc.*, 1969, **65**, 755.

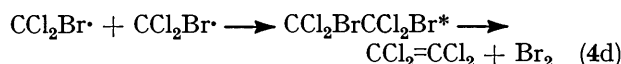
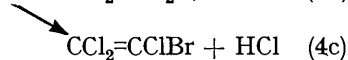
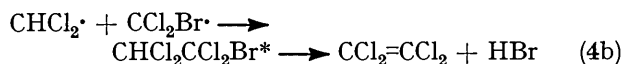
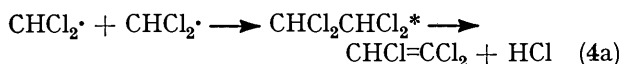
† Part XII, D. S. Ashton, J. M. Tedder, and J. C. Walton, *J.C.S. Faraday I*, 1974, **70**, 299.

<sup>1</sup> M. S. Kharasch, B. M. Kudema, and W. Urry, *J. Org. Chem.*, 1948, **13**, 895.

<sup>2</sup> A. B. Belyavskii and V. N. Kost, *Izvest. Akad. Nauk S.S.S.R. Ser. Khim.*, 1963, 1514.

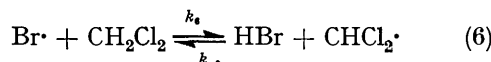
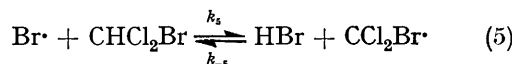
<sup>3</sup> I. B. Afanas'ev, T. N. Eryomina, S. A. Enzovatova, and N. P. Leonova, *Zhur. Org. Khim.*, 1967, **3**, 237.

temperatures studied this equality is observed. The absence of saturated C<sub>2</sub> compounds is not unexpected; the thermally excited halogenoethanes formed by the possible combination reactions eliminate hydrogen halides (4a—c) or molecular bromine (4d). Trichloroethylene, the expected product from reaction (4a) could



not be separated from the large excess of the starting bromodichloromethane. If the radicals CHCl<sub>2</sub>· and CCl<sub>2</sub>Br· have similar combination and cross combination rates then the radical chain lengths are about three cycles.

The bromine atom formed in the initiation step can abstract hydrogen either from the starting materials [reaction (5)] or from dichloromethane [reaction (6)].

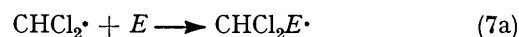
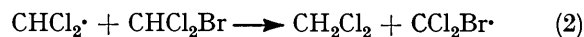
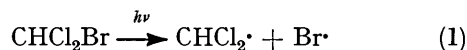


Termination by bromine atom combination is unlikely since it requires a third body, and yet with short chains the fate of the bromine is important. Reactions (5) and (6) are both endothermic and at low temperatures the reverse reactions (—5) and (—6) will be important, but as the temperature rises their significance will diminish. The effect which these changes in relative rate have on the products is clearly shown in Table 1. Increasing temperature results in a substantial decrease in the methylene dichloride, and a slight increase in the dibromodichloromethane.

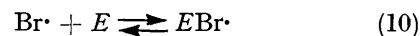
The photolysis of bromodichloromethane thus yields a mixture of products *via* a fairly complex reaction sequence. The addition of an olefin to this system would be expected to lead to an even wider range of products and not simply to the addition of the residues CHCl<sub>2</sub>— and Br— across the double bond as reported by Kharasch and his co-workers. In practice adding vinyl fluoride to the photolysis system was found to lead to the following additional products: CHCl<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>F (1—3%), BrCH<sub>2</sub>CHFBr (2—3), CHCl<sub>2</sub>CHFCH<sub>3</sub> (2—4), CCl<sub>2</sub>BrCH<sub>2</sub>CH<sub>2</sub>F (20—30), CHCl<sub>2</sub>CH<sub>2</sub>CHFBr (3—9), CHCl<sub>2</sub>CHFCH<sub>2</sub>Br (? trace only), and CCl<sub>2</sub>BrCH<sub>2</sub>CHFBr (12—20). The percentage figures represent approximate estimates (over the temperature range studied) of each product as a percentage of the *total product*. Accurate measurement of some of the components was impossible. Those components which can be estimated reasonably accurately will be discussed below. First, however,

the mechanism by which this variety of adducts are formed will be considered.

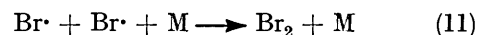
Using the symbol *E* for the alkene the reaction products can be rationalised by the following overall scheme.



Termination processes probably include reactions (4a—c), but the reaction chains are sufficiently long to make detection of these termination products extremely difficult. The bromine atoms can take part in reactions (5) and (6); addition to an olefin (10) is reversible and



some of the EBr<sub>2</sub> detected at the end of the reaction probably comes from addition of molecular bromine to unchanged olefin when the products are condensed out [(11) and (12)].



The approximate percentage yields of products listed above show that adducts derived from the addition of CCl<sub>2</sub>Br· radicals are present in far greater concentration than adducts from CHCl<sub>2</sub> addition. Although accurate measurement of all the wide variety of products was impossible estimates could be made of the ratios of *some* of the more important products. These are listed in Table 2. The ratio [CH<sub>2</sub>Cl<sub>2</sub>]<sub>f</sub> : [CCl<sub>2</sub>Br<sub>2</sub>]<sub>f</sub> is greater than

TABLE 2

Temp. (°C)	Product ratios * from the photolysis of bromodichloromethane in the presence of vinyl fluoride		
	$\frac{[\text{CH}_2\text{Cl}_2]_f}{[\text{CCl}_2\text{Br}_2]_f}$	$\frac{[\text{CCl}_2\text{BrCH}_2\text{CHFBr}]_f}{[\text{CHCl}_2\text{CH}_2\text{CHFBr}]_f}$	$\frac{[\text{CCl}_2\text{BrCH}_2\text{CH}_2\text{F}]_f}{[\text{CCl}_2\text{BrCH}_2\text{CHFBr}]_f}$
114	1.70	5.32	1.38
122	2.36	3.70	2.30
134	2.14	3.89	2.09
150	2.57	3.63	1.24
180	2.53	2.22	1.04
190	3.31	2.08	1.13

\* Subscript f represents final concentration.

unity and increases with temperature. In the photolysis of bromodichloromethane by itself the ratio was never greater than unity and decreased with temperature. The rates of formation of methylene dichloride and dibromodichloromethane are directly

proportional to the steady state concentrations of the  $\text{CHCl}_2\cdot$  and  $\text{CCl}_2\text{Br}\cdot$  radicals respectively:

$$R_{\text{CH}_2\text{Cl}_2} = k_2[\text{CHCl}_2\cdot][\text{CHCl}_2\text{Br}]$$

$$R_{\text{CCl}_2\text{Br}_2} = k_3[\text{CCl}_2\text{Br}\cdot][\text{CHCl}_2\text{Br}]$$

The effect which the addition of vinyl fluoride has on the system is thus relatively to decrease the steady state concentration of  $\text{CCl}_2\text{Br}\cdot$  radicals. This implies  $k_{7b} > k_{7a}$  which is in accord with expectation; the rate of addition of trichloromethyl radicals to vinyl fluoride is considerably faster than the addition of methyl radicals at the same temperature.<sup>8,9</sup> In general the successive replacement of hydrogen by halogen in the methyl radical appears to lower the activation energy for its addition to ethylene. The magnitude of the ratio  $[\text{CCl}_2\text{BrCH}_2\text{CHFBr}]_f : [\text{CHCl}_2\text{CH}_2\text{CHFBr}]_f$  and its decrease with temperature is in part a measure of the inequality  $E_{7b} < E_{7a}$ , since the rate constants  $k_{8a}$  and  $k_{8b}$  will be almost identical.

Although the results have considerable scatter the ratio  $[\text{CCl}_2\text{BrCH}_2\text{CH}_2\text{F}]_f : [\text{CCl}_2\text{BrCH}_2\text{CHFBr}]_f$  shows that hydrogen abstraction (8b) is faster than bromine abstraction (9b). In Table 2 this ratio appears to change little with temperature but in the analogous reaction with ethylene (see Table 3 below) the corresponding ratio decreases with rising temperature. In other words the preference for hydrogen abstraction is at least in part due to a lower activation energy. This means that as the temperature rises reactions (9a) and (9b) become increasingly important, thus increasing the

amplify some of the conclusions drawn above. In addition to the products described for the photolysis of bromodichloromethane above and in the presence of vinyl fluoride the analogous adducts to ethylene were detected. Because of the complexity of the mixture accurate estimation of all the peaks was not possible, the principle adducts being:

Vinyl fluoride adducts	Ethylene adducts
$\text{CHCl}_2\text{CH}_2\text{CH}_2\text{F}$	$\text{CHCl}_2\text{CH}_2\text{CH}_3$ (6—8%)
$\text{CHCl}_2\text{CH}_2\text{CHFBr}$ ( $\sim 2\%$ )	$\text{CCl}_2\text{BrCH}_2\text{CH}_3$ (30—40%)
$\text{CHCl}_2\text{CH}_2\text{CHFBr}$ (1—4%)	(coincident with $\text{CH}_2\text{BrCH}_2\text{Br}$ )
$\text{CCl}_2\text{BrCH}_2\text{CH}_2\text{F}$ (7—10%)	$\text{CHCl}_2\text{CH}_2\text{CH}_2\text{Br}$ (2—5%)
$\text{CCl}_2\text{BrCH}_2\text{CHFBr}$ (4—7%)	$\text{CCl}_2\text{BrCH}_2\text{CH}_2\text{Br}$ (4—7%)

The percentage figures represent estimates (over the temperature range studied) of each adduct as a percentage of the *total product*. Again the propanes formed by addition of  $\text{CCl}_2\text{Br}\cdot$  radicals predominate over the propanes derived from  $\text{CHCl}_2\cdot$  addition. No new steps are required to account for the additional products, which can all be accommodated in the reaction sequence described above. As before some of the product ratios can be estimated quantitatively.

The two last columns in Table 3 represent the same ratios as the third and fourth columns in Table 2. Although the actual amounts of these products will differ, it is satisfying to find that the product ratios are almost the same in both Tables. The ratio  $[\text{CHCl}_2\text{CH}_2\text{CH}_3]_f : [\text{CHCl}_2\text{CH}_2\text{CH}_2\text{Br}]_f$  shows that  $\text{CHCl}_2\text{CH}_2\text{CH}_2\cdot$  radicals abstract hydrogen in preference to bromine atoms and the change of this ratio with

TABLE 3

Product ratios from the photolysis of bromodichloromethane in the presence of ethylene and vinyl fluoride

Temp. (°C)	$\frac{[\text{CHCl}_2\text{CH}_2\text{CH}_2\text{Br}]_f}{[\text{CHCl}_2\text{CH}_2\text{CHFBr}]_f}$	$\frac{[\text{CHCl}_2\text{CH}_2\text{CH}_3]_f}{[\text{CHCl}_2\text{CH}_2\text{CH}_2\text{Br}]_f}$	$\frac{[\text{CCl}_2\text{BrCH}_2\text{CHFBr}]_f}{[\text{CHCl}_2\text{CH}_2\text{CHFBr}]_f}$	$\frac{[\text{CCl}_2\text{BrCH}_2\text{CH}_2\text{F}]_f}{[\text{CCl}_2\text{BrCH}_2\text{CHFBr}]_f}$
116	2.25	3.56	6.63	1.43
130	2.10	3.05	3.30	2.48
150	2.00	2.85	3.00	2.28
164	1.21	2.21	2.00	1.67
177	1.35	2.07	1.39	1.58
184	1.37	1.73	1.07	2.88
198	1.35	1.62	1.24	1.31

steady state concentration of  $\text{CHCl}_2\cdot$  radicals. This is reflected in the increase in the  $[\text{CH}_2\text{Cl}_2]_f : [\text{CCl}_2\text{Br}_2]_f$  ratio with rising temperature.

The products include both possible isomers for the addition of  $\text{CHCl}_2\cdot$  radicals to vinyl fluoride but only one of the isomers for the addition of  $\text{CCl}_2\text{Br}\cdot$  radicals. The reverse adduct for the latter radical is undoubtedly present but the yields are likely to be too small for their detection. The ratio of the two adducts when methyl radicals add to vinyl fluoride<sup>9</sup> at 160° is 1.5 : 1 whereas for trichloromethyl radicals<sup>8</sup> the ratio is 10 : 1.

The addition of ethylene as well as vinyl fluoride to the reaction vessel in which bromodichloromethane was photolysed had the effect of making the separation and quantitative analysis of the products even more difficult. However the results obtained helped to confirm and to

<sup>8</sup> H. W. Sidebottom, J. M. Tedder, and J. C. Walton, *Internat. J. Chem. Kinetics*, 1972, **4**, 249.

temperature indicates that the activation energy for hydrogen abstraction is less (*i.e.*  $E_{8a} < E_{9a}$ ). Although ethylene and vinyl fluoride compete for the two radicals  $\text{CHCl}_2\cdot$  and  $\text{CCl}_2\text{Br}\cdot$  it is impossible to obtain the relative rates of addition without knowing the rates of formation of both  $\text{CHCl}_2\text{EH}$  and  $\text{CHCl}_2\text{EBr}$ , and of  $\text{CCl}_2\text{BrEH}$  and  $\text{CCl}_2\text{BrEBr}$  when  $E$  is ethylene and vinyl fluoride. Unfortunately neither  $[\text{CHCl}_2\text{CH}_2\text{CH}_2\text{F}]_f$  nor  $[\text{CCl}_2\text{BrCH}_2\text{CH}_3]_f$  are available in sufficient accuracy. Qualitatively, adducts of both radicals to ethylene predominate, the predominance being more substantial for  $\text{CCl}_2\text{Br}\cdot$  radicals. This is in accord with expectation, as trichloromethyl radicals add four times faster to ethylene than to vinyl fluoride. The temperature dependence of the ratio  $[\text{CHCl}_2\text{CH}_2\text{CH}_2\text{Br}]_f : [\text{CHCl}_2\text{CH}_2\text{CHFBr}]_f$  may in part be due to a lower activation energy

<sup>9</sup> J. M. Tedder, J. C. Walton, and K. D. R. Winton, *J.C.S. Faraday I*, 1972, **68**, 1866.

for the addition of  $\text{CHCl}_2\cdot$  radicals to ethylene compared with vinyl fluoride.

The important conclusion from this work is that while it is true that bromodichloromethane will take part in a radical chain reaction with olefins,  $\text{CCl}_2\text{Br}\cdot$  radicals are more important chain carriers than  $\text{CHCl}_2\cdot$  radicals. The reason for this is that  $\text{CCl}_2\text{Br}\cdot$  radicals add faster to olefins than  $\text{CHCl}_2\cdot$  radicals ( $k_{7b} > k_{7a}$ ) and hydrogen abstraction by alkyl radicals from bromodichloromethane is faster than bromine abstraction ( $k_8 > k_9$ ). The fact that hydrogen atom abstraction is competitive with bromine atom abstraction from bromodichloromethane was unexpected in view of the large difference in the bond dissociation energies. Similar effects have however been observed before. Whittle and his co-workers showed that hydrogen abstraction from chloromethane by trifluoromethyl radicals was faster than chlorine abstraction, in spite of the fact that the carbon-hydrogen bond strengths are greater than the carbon-chlorine bond strengths.<sup>10</sup> Szwarc and his co-workers found hydrogen abstraction to be competitive with bromine and iodine abstraction from alkyl bromides and iodides by methyl radicals.<sup>11</sup> Although this work has been restricted to two olefins the strong presumption must be that similar behaviour will be found for other hydrocarbon olefins. Previous work in the liquid phase has assumed that  $\text{CHCl}_2\cdot$  radicals are the exclusive chain carriers in analogous reactions. In view of the present results this assumption must be treated with reserve. The results also show that it is not possible to use bromodichloromethane as a source of dichloromethyl radicals, at least not in a system in which a radical chain reaction is involved.

#### EXPERIMENTAL

**Materials.**—Bromodichloromethane (Aldrich Chemical Co.) was purified by preparative g.l.c. to give material of at least 99.5% purity. Ethylene and vinyl fluoride were commercial materials purified by trap to trap distillation and degassing before use. 1,2-Dibromoethane and 1,2-dibromo-1-fluoroethane were prepared as described previously<sup>5</sup> and used for identification purposes only.

**Method.** The technique was similar to that described previously.<sup>5</sup> Materials were handled on a conventional vacuum line. The light source was a Hanovia UVS 220 medium pressure mercury arc filtered by a solution transmitting between 260 and 370 nm.<sup>12</sup> The photolyses of  $\text{CHCl}_2\text{Br}$  alone were performed in a Pyrex vessel. All other photolyses were carried out in a cylindrical quartz cell (140 ml).

**Analysis.**—Product identification was achieved by coupled g.l.c.–mass spectrometry of the reaction mixtures using a Pye 104 gas chromatograph with a 20% w/w D.N.P./Chromosorb G column coupled to an A.E.I. MS902C mass spectrometer. In the experiments with  $\text{CHCl}_2\text{Br}$  and  $\text{CH}_2=\text{CHF}^{19}\text{F}$  and  $^1\text{H}$  n.m.r. spectra were recorded on some of the products. Since the percentage conversion in the photolyses was low, a larger number of runs were carried out and the accumulated products separated by preparative g.l.c. The n.m.r. spectra were recorded at

<sup>10</sup> W. G. Alcock and E. Whittle, *Trans. Faraday Soc.*, 1965, **61**, 244; 1966, **62**, 134.

room temperature on  $\text{CCl}_4$  solutions of the separated products containing traces of  $\text{Me}_4\text{Si}$  and  $\text{CCl}_3\text{F}$  as internal standards on a Varian HA-100 instrument.

Quantitative analysis was by g.l.c. on a Griffin and George D6 gas density balance chromatograph using 6 ft  $\times$  3/16 in columns packed with 20% DNP or 20% 'Embaphase' Silicone oil on Chromosorb G. Peak areas were measured with a DuPont 310 resolver. Each reaction mixture was analysed 3–4 times and the figures in the text are average values.

**Photolysis of Bromodichloromethane.**—Six products were formed in the preparative runs (lasting 19 h) on bromodichloromethane (0.54 mmol) by itself. G.l.c.–m.s. enabled the following identifications to be made: peak 1,  $\text{CH}_2\text{Cl}_2$ ; peak 2,  $\text{CHCl}_3$ ; peak 3,  $\text{CHClBr}_2$ ; peak 4,  $\text{CCl}_2=\text{CCl}_2$ ; peak 5,  $\text{CCl}_2\text{Br}_2$ ; and peak 6,  $\text{CCl}_2=\text{CClBr}$ . The identities of peaks 1, 2, 4, and 5 were confirmed by comparison of their retention times with those of authentic materials run under the same conditions. A series of photolyses, each lasting 17 h, was carried out with bromodichloromethane at various temperatures. No  $\text{CHCl}_3$  or  $\text{CHClBr}_2$  was detected in those runs. The rates of formation of the products are given in Table 1.

**Photolysis of Bromodichloromethane with Vinyl Fluoride.**—Bromodichloromethane (0.27 mmol) was irradiated with vinyl fluoride (0.27 mmol) at various temperatures in the range 387–463 K for 3 h. Eight products were observed on the g.l.c. trace: peak 1,  $\text{CH}_2\text{Cl}_2$ ; peak 2 (poorly resolved from  $\text{CHCl}_2\text{Br}$ ),  $\text{CHCl}_2\text{CH}_2\text{CH}_2\text{F}$ ,  $m/e$  111/109 (3%, 3%,  $M - \text{HCl}^+$ ), 87/85/83 (16, 66, 100,  $\text{CHCl}_2^+$ ), 77/75 (4, 11,  $\text{C}_3\text{H}_4\text{Cl}^+$ ), 59 (20,  $\text{C}_3\text{H}_4\text{F}^+$ ), and 33 (4,  $\text{CH}_2\text{F}^+$ ); peak 3,  $\text{BrCH}_2\text{CHFBr}$  (m.s. and  $R_t$ ); peak 4,  $\text{CCl}_2\text{Br}_2$  (m.s. and  $R_t$ ); peak 5 (poorly resolved from neighbouring peaks)  $\text{CHCl}_2\text{CHFCH}_3$ ,  $m/e$  134/132/130 (13, 40, 67,  $M^+$ ), 113/111/109 (12, 5, 1,  $\text{C}_3\text{H}_3\text{Cl}_2^+$ ), 95/93 (40, 100,  $\text{C}_3\text{H}_3\text{FCl}^+$ ), 87/85/83 (3, 7, 10,  $\text{CHCl}_2^+$ ), and 59 (34,  $\text{C}_3\text{H}_4\text{F}^+$ ); peak 6,  $\text{CCl}_2\text{BrCH}_2\text{CH}_2\text{F}$ ,  $m/e$  176/174/172 (3, 6, 5,  $M - \text{HCl}^+$ ), 165/163/161 (2, 3, 2,  $\text{CCl}_2\text{Br}^+$ ), 133/131/129 (30, 70, 100,  $\text{C}_3\text{H}_4\text{Cl}_2\text{F}^+$ ), 113/111/109 (5, 18, 24,  $\text{C}_3\text{H}_3\text{Cl}_2^+$ ), 95/93 (23, 59,  $\text{C}_3\text{H}_3\text{FCl}^+$ ), 86/84/82 (7, 24, 35,  $\text{CCl}_2^+$ ), and 33 (24,  $\text{CH}_2\text{F}^+$ ); peak 7,  $\text{CHCl}_2\text{CH}_2\text{CHFBr}$ ,  $m/e$  177/175/173 (2, 6, 4,  $M - \text{Cl}^+$ ), 133/131/129 (11, 61, 100,  $M - \text{Br}^+$ ), 113/111 (9, 9,  $\text{CHFBr}^+$ ), 95/93 (19, 56,  $\text{C}_3\text{H}_3\text{FCl}^+$ ), 87/85/83 (6, 22, 33,  $\text{CHCl}_2^+$ ), and 57 (16,  $\text{C}_3\text{H}_2\text{F}^+$ ); peak 8,  $\text{CCl}_2\text{BrCH}_2\text{CHFBr}$ ,  $m/e$  213/211/209/207 (8, 50, 100, 71,  $M - \text{Br}^+$ ), 175/173/171 (4, 15, 12,  $\text{C}_3\text{H}_2\text{FClBr}$ ), 167/165/163/161 (3, 13, 14, 10,  $\text{CCl}_2\text{Br}$ ), 139/137 (14, 14,  $\text{C}_3\text{H}_3\text{FBr}^+$ ), 131/129/127 (14, 57, 71,  $\text{C}_3\text{H}_2\text{FCl}_2^+$ ), 113/111 (57, 57,  $\text{CHFBr}^+$ ), 95/93 (30, 71,  $\text{C}_3\text{H}_3\text{FCl}^+$ ), and 57 (36,  $\text{C}_3\text{H}_2\text{F}$ ). The n.m.r. spectra of peak 7 confirmed it as the adduct  $\text{Cl}_2\text{CH}_c\text{-CH}_a\text{H}_b\text{-CH}_d\text{BrF}$ . Thus the  $^1\text{H}$  n.m.r. spectrum showed four multiplets at  $\tau$  7.07 ( $\text{H}_a$ ,  $J_{\text{H}_a\text{H}_b}$  15.5,  $J_{\text{H}_a\text{H}_c}$  7.7,  $J_{\text{H}_a\text{H}_d}$  5.0, and  $J_{\text{H}_a\text{F}}$  22.7 Hz), 6.84 ( $\text{H}_b$ ,  $J_{\text{H}_b\text{H}_c}$  6.0,  $J_{\text{H}_b\text{H}_d}$  6.7, and  $J_{\text{H}_b\text{F}}$  9.9 Hz), 4.23 ( $\text{H}_c$ ,  $J_{\text{H}_c\text{H}_d}$  0.0 and  $J_{\text{H}_c\text{F}}$  0.5 Hz), and 3.50 ( $\text{H}_d$ ,  $J_{\text{H}_d\text{F}}$  49.5 Hz). The  $^{19}\text{F}$  n.m.r. spectrum showed a single multiplet at  $\delta$  140. The n.m.r. spectra of peak 8 confirmed it as  $\text{BrCl}_3\text{C-CH}_a\text{H}_b\text{-CH}_c\text{BrF}$ . Thus the  $^1\text{H}$  n.m.r. spectrum showed three multiplets at  $\tau$  6.4 ( $\text{H}_a$ ), 6.2 ( $\text{H}_b$ ), and 3.2 ( $\text{H}_c$ ) and the  $^{19}\text{F}$  n.m.r. spectrum showed a single multiplet at  $\delta$  134. The n.m.r. spectra were computed using the LAOCOON III program. Good agreement between the calculated and observed frequencies

<sup>11</sup> M. Szwarc and F. W. Evans, *Trans. Faraday Soc.*, 1961, **57**, 1905; R. J. Fox, F. W. Evans, and M. Szwarc, *ibid.*, p. 1915.

<sup>12</sup> W. W. Wladimiroff, *Photochem. and Photobiol.*, 1966, **5**, 243.

and intensities was achieved with the following constants:  $J_{\text{H}_a\text{H}_b}$  15.7,  $J_{\text{H}_a\text{H}_c}$  1.9,  $J_{\text{H}_a\text{F}}$  25.9,  $J_{\text{H}_b\text{H}_c}$  7.5,  $J_{\text{H}_b\text{F}}$  13.9, and  $J_{\text{H}_c\text{F}}$  50.8 Hz.

*Photolysis of Bromodichloromethane with Ethylene.*—Bromodichloromethane (1.1 mmol) was irradiated with ethylene (0.55 mmol) at 483 K for 3 h. Eight products were observed on the g.l.c. trace: peak 1,  $\text{C}_2\text{H}_5\text{Br}$  (3.3%) (m.s.,  $R_t$ ); peak 2,  $\text{CH}_2\text{Cl}_2$  (21.9%) (m.s.,  $R_t$ ); peak 3,  $\text{CHCl}_2\text{CH}_2\text{CH}_3$  (13.0%),  $m/e$  85/83 (5%, 10%,  $\text{CHCl}_2^+$ ), 79/77 (23, 73,  $M - \text{Cl}^+$ ), 62/60 (5, 13,  $\text{C}_2\text{HCl}^+$ ), 42 (5,  $\text{C}_3\text{H}_6^+$ ), 41 (81,  $\text{C}_3\text{H}_5^+$ ), and 40 (100,  $\text{C}_3\text{H}_4^+$ ); peak 4,  $\text{CCl}_2\text{BrCH}_2\text{CH}_3$  (34.3%),  $m/e$  165/163/161 (3, 6, 4,  $\text{CCl}_2\text{Br}^+$ ), 115/113/111 (10, 64, 100,  $\text{C}_3\text{H}_5\text{Cl}_2^+$ ), 110/108 (32, 35,  $\text{C}_2\text{H}_5\text{Br}^+$ ), 77/75 (36, 100,  $\text{C}_3\text{H}_4\text{Cl}^+$ ), and 39 (79,  $\text{C}_3\text{H}_3^+$ ); peak 5,  $\text{CCl}_2\text{Br}_2$  (3.8%) (m.s.,  $R_t$ ); peak 6,  $\text{CH}_2\text{BrCH}_2\text{Br}$  (1.0%) (m.s.,  $R_t$ ); peak 7,  $\text{CHCl}_2\text{CH}_2\text{CH}_2\text{Br}$  (7.2%),  $m/e$  194/192/190 (6, 16, 8,  $M^+$ ), 159/157/155 (1, 4, 3,  $\text{C}_3\text{H}_5\text{ClBr}^+$ ), 121/119 (3, 3,  $\text{C}_3\text{H}_4\text{Br}^+$ ), 114/112/110 (3, 21, 33,  $\text{C}_3\text{H}_4\text{Cl}_2^+$ ),

109/107 (17, 17,  $\text{C}_2\text{H}_4\text{Br}^+$ ), 95/93 (8, 8,  $\text{CH}_2\text{Br}^+$ ), 87/85/83 (2, 8, 15,  $\text{CHCl}_2^+$ ), and 77/75 (35, 100,  $\text{C}_3\text{H}_4\text{Cl}^+$ ); peak 8,  $\text{CCl}_2\text{BrCH}_2\text{CH}_2\text{Br}$  (14.1%),  $m/e$  195/193/191/189 (6, 43, 90, 61,  $M - \text{Br}^+$ ), 157/155/153 (5, 15, 11,  $\text{C}_3\text{H}_3\text{ClBr}^+$ ), 113/111/109 (6, 33, 59,  $\text{C}_3\text{H}_3\text{Cl}_2^+$ ), 95/93 (20, 22,  $\text{CH}_2\text{Br}^+$ ), and 39 (100,  $\text{C}_3\text{H}_3^+$ ).

*Competitive Photolyses with Vinyl Fluoride and Ethylene.*—Bromodichloromethane (0.54 mmol) was irradiated with vinyl fluoride (0.27 mmol) and ethylene (0.27 mmol) at various temperatures in the range 389–471 K for 3 h. The product chromatogram was compared with the chromatogram of the combined mixtures from the runs with each separate alkene. No new products were observed, but as a cross-check, mass spectra were run on each peak in the competitive chromatogram. The mass spectra were essentially the same as those obtained in the previous experiments.

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