Experimental[15]

Disproportionation of 1,2-Dichloro-1-nitrosotrifluoroethane.—An ampoule (25-mm. o.d., 3-mm. wall, *ca.* 140-ml. volume) was charged with 1,2-dichloro-1-nitrosotrifluoroethane (9 g., 0.05 mole) and was sealed under vacuum. The tube was heated at 75° for several hours until the blue color had faded. Then the tube was cooled in liquid nitrogen and was opened into the vacuum line. The pressure rose immediately indicating the presence of nitrogen, in 20% yield. The nitrogen was swept out and a molecular weight of the most volatile gas remaining was 31.1 (calculated for NO, 30.0). In addition, this colorless gas became brown when it was exposed to the air. The tube was then immersed in Dry Ice–acetone and the volatile material was pumped off. Then, an infrared spectrum of the remaining volatile material had bands at 5.52 and 5.59 μ, indicating the presence of nitrogen dioxide. A separate run was similarly made using 1,2-dichloro-1-nitrosotrifluoroethane (30 g., 0.16 mole). From this run was obtained 2.5 g. of material, b.p. 51–53° (23 mm.).

Anal. Calcd. for $C_7Cl_3F_7NO_4$: C, 20.9; H, 0.00; Cl, 26.5; F, 33.10; N, 3.48. Found: C, 19.52; H, 0.43; Cl, 27.3; F, 32.34; N, 3.40.

The molecular weight was 416 ± 20, determined cryoscopically. The nitro and chloro compounds were determined chromatographically during the rate studies described below. They were identified by comparing their retention times by v.p.c. with known samples.

Determination of the Thermal Stabilities of the Nitroso Compounds.—The relative rates of disproportionation at 78.2° of four chlorofluoroalkyl nitroso compounds were determined with a vapor-phase chromatographic column using an internal standard.

The nitroso compounds were purified by passing each of them through a vapor-phase chromatographic column packed with material prepared from 0.6 g. of dinonyl phthalate per gram of Johns Mansville "Chromosorb," 35–80-mesh size, and were subsequently stored at −78° until they were used.

Methylene chloride was used as an internal standard for the studies of the disproportionation of I and II and methyl bromide was used as an internal standard for the studies of III and IV. Carbon tetrachloride was also used as internal standard for I.

The nitroso compound and the internal standard were mixed in the desired ratio. Aliquot portions of approximately 0.1 ml. of the mixture were then transferred to glass tubes (5-mm. o.d., *ca.* 4-cm. length) which had previously been swept out with nitrogen. The tubes were sealed and were kept in Dry Ice–acetone until they were used. For the run in which the effect of added nitric oxide was determined, the tubes were filled in the usual manner, after which nitric oxide (*ca.* 0.7 mmole) was added and they were sealed under vacuum.

The disproportionations were carried out at 78.2 ± 0.1° by placing the tubes in the vapors of refluxing 95% ethanol for the desired length of time. When each tube was removed, it was cooled in Dry Ice–acetone and opened, and a sample of its contents was introduced into the vapor-phase chromatographic column. It was necessary to maintain the column at a temperature at which the rate of disproportionation of the nitroso compound was negligible. The temperatures chosen for the individual compounds were I, 60°; II, 45°; III, 35°; and IV, 35°.

The area under each curve was computed by multiplying the height of the peak by the width at the half-height point. This method was checked by accurately weighing a sample of methylene chloride and I, mixing them, and then determining their molar ratios from both their weights and from their areas under the curve. The results were ratio of CH_2Cl_2–I from weights—2.86, 1.26; from v.p.c.—2.84, 1.30. The differences in the ratios are probably due to weighing errors. Accurate weights of these materials were difficult to obtain because of their high volatility.

The major source of error was in transferring the aliquots to the individual tubes. In the case of I and II, the errors were not large, but with III and IV, which have boiling points of −5 and −4°, errors in transferring resulted in considerable scattering of the points.

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[15] Analyses were by Galbraith Laboratories, Knoxville, Tenn.

The Addition Reaction of Bromotrichloromethane to Compounds with Vinyl and Perfluorovinyl Groups

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The light-initiated reaction of bromotrichloromethane with olefins containing vinyl and trifluorovinyl groups has been studied. In cases where both groups are present in the molecule, the attack of trichloromethyl radical occurs preferentially on the methylene carbon. 1,4-Addition takes place with 1,1,2-trifluorobutadiene. In cases where a chlorine atom was located on a carbon atom adjacent to the carbon-bearing double bond, the chief product was generally not the 1:1 adduct but an olefin containing the trichloromethyl group. Some unusual dehydrohalogenations of the adducts are noted.

A number of reports have appeared in the literature[3] on the free-radical addition reaction of halo alkanes to olefins and fluorine-containing olefins. However, very little information has been published on the relative reactivity of vinyl and perfluorovinyl groups, or allyl and perfluoroallyl groups toward free-radical addition. In order to obtain information on their relative reactivities, we have carried out the sunlight-initiated reactions of bromotrichloromethane and compounds containing a vinyl or a perfluorovinyl group, or both of them either conjugated or separated. The addition reaction to 3,3-difluoroallyl bromide was also studied to compare the reactivity of fluorine-containing unsaturated groups in allylic structure with ordinary allyl groups.

Kharasch and his co-workers[4–6] obtained predominantly 1:1 adducts, 5-bromo-1,1,1,-trichloro-3-pentene (1,4-addition) and 3-bromo-5,5,5-trichloro-1-pentene (1,2-addition), by the peroxide-induced reaction of 1,3-butadiene and bromotrichloromethane. Recently Pyne[7] reported that only the 1,4-addition product

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[3] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 249.

[4] M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947).

[5] M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949).

[6] M. S. Kharasch, E. Simon, and W. Nudenberg, *ibid.*, **18**, 328 (1953).

[7] W. J. Pyne, *ibid.*, **27**, 3483 (1962).

TABLE I

ADDITION OF CCl_3Br TO $CH_2{=}CHCFClCF_2Br$

Period of irradiation, days	Olefin		Products														
			$CF_2BrCF{=}CHCH_2CCl_3$ (I)			$CF_2BrCFClCHBr{-}CH_2Cl$ (V)			$CF_2BrCFClCHBr{-}CH_2Br$ (VI)			$CF_2BrCF{=}CHCHBrCCl_3$ (VII)			$CF_2BrCFClCHBr{-}CH_2CCl_3$ (VIII)		
	g.	mole	g.	mole	%	g.	mole	%	g.	mole	%	g.	mole	%	g.	mole	%
2	64.5	0.29	26.2	0.086	30	28.5	0.084	29	3.6	0.009	3	4.1	0.011	4	29.7	0.071	24
10	61.0	0.27	6.3	0.020	7	30.3	0.089	33	10.0	0.026	10	17.3	0.045	17	30.2	0.072	27
26	74.9	0.34	1.4	0.005	2	39.0	0.115	34	12.1	0.032	9	27.3	0.071	21	38.8	0.092	27

was obtained in 76% yield using peroxide or ultraviolet irradiation.

Although 1,3-butadiene yielded about 70% of the 1:1 adduct (only 1,4-addition product) in our laboratory in the reaction with bromotrichloromethane when initiated by sunlight, 1,1,2-trifluoro-1,3-butadiene gave mostly white polymers with small amounts of telomers. Simple adducts of bromotrichloromethane to the butadiene would be $CCl_3CH_2CH{=}CFCF_2Br$ (I), $CCl_3CF_2CF{=}CHCH_2Br$ (I), $CCl_3CH_2CHBrCF{=}CF_2$ (III), and $CCl_3CF_2CFBrCH{=}CH_2$ (IV), depending upon the preference of CCl_3 radical attack for the two kinds of vinyl groups and the types of additions (1,4-addition or 1,2-addition).

It was confirmed that no 1,2-addition occurred, since the infrared spectrum of telomers showed only one absorption of carbon–carbon double bond at 5.87 μ, attributable to $-CF{=}CH-$ bonds, and no appreciable absorptions near 5.6 and 6.1 μ, associated with $-CF{=}CF_2$ and $-CH{=}CH_2$, respectively, were noted. Further, the 1:1 adduct was isolated from the telomers and identified as I by comparison of its infrared spectrum with those of authentic samples, which were prepared as mentioned below. It seems, therefore, that the radical attacked on the $-CH{=}CH_2$ group preferentially rather than on the $-CF{=}CF_2$ group when these groups were conjugated in a substrate, and 1,4-addition prevailed as in the case of 1,3-butadiene.

To prepare the authentic samples of I and II, the addition reactions of bromotrichloromethane to 4-bromo-3-chloro-3,4,4-trifluoro-1-butene and 1,1,2-trifluoro-4-bromo-1-butene were carried out. The addition reaction of bromotrichloromethane to the former olefin, in which the molar ratio of the halomethane to olefin was about 5:1, yielded five products: $CF_2BrCF{=}CHCH_2CCl_3$ (I), $CF_2BrCFClCHBrCH_2Cl$ (V), $CF_2BrCFClCHBrCH_2Br$ (VI), $CF_2BrCF{=}CHCHBrCCl_3$ (VII), and $CF_2BrCFClCHBrCH_2CCl_3$ (VIII). Relative ratios of these products varied with the period of sunlight irradiation. The results are shown in Table I. The structures of the products were confirmed by their dehydrohalogenation or dehalogenation, infrared spectra, and analyses.

It is interesting that I was the chief product rather than adduct VIII using mild conditions. A few cases have been reported[8] of a loss of a neighboring halogen during free-radical additions to halo allyl compounds. Nesmeyanov and his co-worker[9] reported that the addition of bromotrichloromethane to 3,3,3-trichloropropene gave, instead of the expected $CCl_3CH_2CHBrCCl_3$, a mixture of $CCl_3CH_2CHClCCl_2Br$ and $CCl_3CH_2CH{=}CCl_2$. The olefin can presumably be formed by loss of chlorine from the radical $CCl_3\dot{C}HCH_2CCl_3$ and the bromide by attack on this olefin of the chlorine atom to give $CCl_3CH_2CHClCCl_2\cdot$ which abstracts bromine from bromotrichloromethane. Kharasch and Sage[5] obtained $CCl_3CH_2CHBrCH_2CCl_3$ and $CH_2BrCHBrCH_2Br$ in the addition of bromotrichloromethane to allyl bromide. The formation of the former product was explained on the basis of β-elimination of bromine from an intermediate radical $CCl_3CH_2\dot{C}HCH_2Br$ to form $CCl_3CH_2CH{=}CH_2$, which was actually isolated in a run carried out in excess allyl bromide.

The mechanism suggested by Kharasch, *et al.*, for the addition of bromotrichloromethane to allyl bromide may be applied to the formation of five products mentioned above as follows.

$$\mathrm{CCl_3Br} \xrightarrow{h\nu} \mathrm{CCl_3\cdot} + \mathrm{Br\cdot}. \tag{1}$$

$$\mathrm{CF_2BrCFClCH{=}CH_2} + \mathrm{CCl_3\cdot} \longrightarrow \mathrm{CF_2BrCFCl\dot{C}HCH_2CCl_3} \tag{2}$$

$$\mathrm{CF_2BrCFCl\dot{C}HCH_2CCl_3} \longrightarrow \mathrm{CF_2BrCF{=}CHCH_2CCl_3\ (I)} + \mathrm{Cl\cdot} \tag{3}$$

$$\mathrm{CF_2BrCFClCH{=}CH_2} + \mathrm{Cl\cdot} \longrightarrow \mathrm{CF_2BrCFCl\dot{C}HCH_2Cl} \tag{4}$$

$$\mathrm{CF_2BrCFCl\dot{C}HCH_2Cl} + \mathrm{CCl_3Br} \longrightarrow \mathrm{CF_2BrCFClCHBrCH_2Cl\ (V)} + \mathrm{CCl_3\cdot} \tag{5}$$

$$\mathrm{CF_2BrCFCl\dot{C}HCH_2CCl_3} + \mathrm{CCl_3Br} \longrightarrow \mathrm{CF_2BrCFClCHBrCH_2CCl_3\ (VIII)} + \mathrm{CCl_3\cdot} \tag{6}$$

$$\mathrm{CF_2BrCFClCH{=}CH_2} + \mathrm{Br\cdot} \longrightarrow \mathrm{CF_2BrCFCl\dot{C}HCH_2Br} \tag{7}$$

$$\mathrm{CF_2BrCFCl\dot{C}HCH_2Br} + \mathrm{CCl_3Br} \longrightarrow \mathrm{CF_2BrCFClCHBrCH_2Br\ (VI)} + \mathrm{CCl_3\cdot} \tag{8}$$

$$\mathrm{CF_2BrCF{=}CHCH_2CCl_3} + \mathrm{Br\cdot} \longrightarrow \mathrm{CF_2BrCF{=}CH\dot{C}HCCl_3} + \mathrm{HBr} \tag{9}$$

$$\mathrm{CF_2BrCF{=}CH\dot{C}HCCl_3} + \mathrm{CCl_3Br} \longrightarrow \mathrm{CF_2BrCF{=}CHCHBrCCl_3\ (VII)} + \mathrm{CCl_3\cdot} \tag{10}$$

The data presented in Table I indicate that VII is formed at the expense of I and eq. 9 and 10 are consistent with this fact.

In supporting the above mechanisms, the addition of bromotrichloromethane to 1,1,2-trifluoro-4-bromo-1-butene, in which an intermediate radical formed has no neighboring chlorine or bromine atoms, yielded only a 1:1 adduct, $CH_2BrCH_2CFBrCF_2CCl_3$ (IX) in good yield with small amounts of $CH_2BrCH_2CFBrCF_2Br$ (X) and hexachloroethane, and no halo-2-pentene. An authentic sample of II was prepared by

$$\mathrm{CH_2BrCH_2CF{=}CF_2} + \mathrm{CCl_3\cdot} \longrightarrow \mathrm{CH_2BrCH_2\dot{C}FCF_2CCl_3} \xrightarrow{\mathrm{CCl_3Br}} \mathrm{CH_2BrCH_2CFBrCF_2CCl_3\ (IX)} + \mathrm{CCl_3:} \longrightarrow \mathrm{CCl_3CCl_3}$$

dehydrohalogenation of IX using potassium hydroxide in ethanol.

Easy loss of the neighboring halogen atom from the intermediate radical could be partly due to the steric effect, because both β-carbons have such bulky groups as $-CF_2Br$ and $-CCl_3$, and partly due to the more stable

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[8] For example, C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y. 1957, p. 268.

[9] A. N. Nesmeyanov, R. K. Freidlina, and L. I. Zakharin, *Dokl. Akad. Nauk SSSR*, **81**, 199 (1951).

TABLE II

HALO HYDROCARBONS[a]

Compounds	B.p. (mm.), °C.	n^{28}_D	d^{28}_4	MD		C, %		H, %		F, %		Halogen, %[b]	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
XII, $CCl_3CF_2CFBrCH_2CHBrCH_2CCl_3$	117–118 (1)	1.5200	2.002	79.0	78.8	16.21	16.27	0.97	1.18	11.18	11.19	54.69	54.84
VIII, $CF_2BrCFClCHBrCH_2CCl_3$	106–107 (7)	1.4950	2.046	60.0	60.1	14.24	14.27	0.72	0.93	13.52	13.54	50.45	50.54
XIX, $CF_2BrCFClCClBrCH_2CCl_3$	91–92 (1)	1.5195	2.172	64.9	63.8	13.16	13.40	0.44	0.68	12.49	12.15	54.41	54.07
IX, $CH_2BrCH_2CFBrCF_2CCl_3$	109–109.5 (7)	1.4990	2.065	55.7	56.4	15.50	15.75	1.04	1.12	14.72	14.91	45.80	45.92
VI, $CF_2BrCFClCHBrCH_2Br$	93 (12.5)	1.4970	2.332	48.5	48.2	12.53	12.44	0.79	0.85	14.87	15.04	37.01	37.29
X, $CF_2BrCFBrCH_2CH_2Br$	72.5–73 (12.5)	1.4794	2.265	43.7	43.7	13.76	13.89	1.16	1.22	16.34	16.17	68.74	68.88
V, $CF_2BrCFClCHBrCH_2Cl$	85–86 (15)	1.4780	2.097	45.6	44.6	14.17	14.22	0.89	0.95	16.82	18.75	41.86	42.17
XVI, $CF_3CBr_2CH_2CBr(CF_3)CH_2CCl_3$	88–89 (1)	1.4816	2.150	72.9	72.8	15.31	16.15	0.74	0.90	20.40	21.03	38.81	38.81
XV, $CF_3CBr_2CH_2CCl_3$	80 (9)	1.4860	2.136	50.5	50.2	12.86	12.79	0.54	0.63	15.27	15.54	47.50	47.26

[a] Analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. [b] Calculated as Cl.

allylic structure of the product. Since the dehalogenation on the β-carbon of the intermediate radical was observed only in the CCl_3 radical attack on the olefin and not in chlorine radical attack (eq. 4), the steric effect would probably be the chief cause of radical dehalogenation. Additional evidence supporting the steric effect is that, in the addition of bromotrichloromethane to a more crowded olefin, $CF_2BrCFClCCl{=}CH_2$, predominant products were the unsaturated compound and $CF_2BrCFClCClBrCH_2Cl$ with a small amount of 1:1 adduct.

In the addition reaction of bromotrichloromethane to 1,1,2-trifluoro-1,4-pentadiene, it was observed that the CCl_3 radical attacked the vinyl group first, then the perfluorovinyl group. Thus, a mixture of bromotrichloromethane and 1,1,2-trifluoro-1,4-pentadiene gave, in good yield, predominantly $CF_2{=}CFCH_2CHBrCH_2CCl_3$ (XI) with $CCl_3CF_2CFBrCH_2CHBrCH_2CCl_3$ (XII) under sunlight irradiation for 6 days. Irradiation for 11 days produced the latter adduct predominantly and in 25 days of irradiation XII was the only adduct obtained. The vinyl group seems also to be more reactive than the perfluorovinyl group for free-radical addition in an unsaturated compound with the two kinds of vinyl groups isolated from each other by a methylene group.

Another example which showed the lessened reactivity of the perfluorovinyl group toward free-radical addition is the addition of bromotrichloromethane to 3,3-difluoroallyl bromide. As is mentioned above, Kharasch and co-worker[3] obtained the product, $CCl_3CH_2CHBrCH_2CCl_3$, from allyl bromide. In the case of 3,3-difluoroallyl bromide, however, the main products were $CF_2{=}CHCBr_3$ (XIII) and $CF_2{=}CHCBrCCl_3$ (XIV), the $CF_2{=}CH-$ group being intact after reaction. The formation of these products could be explained by preferential dissociation[10] of C–Br bond of 3,3-difluoroallyl bromide under sunlight irradiation, or by debromination with CCl_3 radical to give the 3,3-difluoroallyl radical. The allyl radical formed, then, would attack bromotrichloromethane. Since allylic hydrogens of the 1,1-difluoro-4,4,4-trichloro-1-butene formed are rather reactive, the free-radical displacement of hydrogen by bromine atom would follow to yield XIV.

$$CF_2{=}CHCH_2\cdot + CCl_3Br \longrightarrow CF_2{=}CHCH_2CCl_3 + Br\cdot$$

The addition reaction of bromotrichloromethane and 2-bromo-3,3,3-trifluoro-1-propene gave mainly the expected 1:1 adduct (XV) with small amounts of 2:1 adduct (XVI).

In order to prove the assigned structures of addition products, dehydrohalogenation and dehalogenation were carried out using ethanolic potassium hydroxide and zinc dust in ethanol, respectively. The dehydrohalogenation of $CH_2BrCH_2CFBrCF_2CCl_3$ (IX) can give two olefins, $CH_2BrCH{=}CFCF_2CCl_3$ (II) and $CH_2{=}CHCFBrCF_2CCl_3$. Actually the halo-2-pentene was obtained almost exclusively, the infrared spectrum of which exhibited a sharp absorption band at 5.93 μ, attributable to $-CF{=}CH-$ bond. When the reaction was carried out with excess potassium hydroxide, the predominant product was $C_2H_5OCH_2CH{=}CFCF_2CCl_3$ (XVII) which showed an absorption band at 5.91 μ for the $-CF{=}CH-$ group. The dehydrohalogenation of $CH_2BrCH_2CFBrCF_2Br$ (X) also yielded mainly $CH_2BrCH{=}CFCF_2Br$ (XVIII) with small amounts of $CH_2{=}CHCFBrCF_2Br$.

The formation of halo-2-pentene rather than halo-1-pentene could be explained by the steric effect of bulky groups and the stable allylic structure formation. In connection with the latter reasoning, the dehydrohalogenation of $CF_2BrCH_2CH_2Br$ was found to yield $CF_2{=}CHCH_2Br$ predominantly.[11]

An attempt to dehydrohalogenate $CF_2{=}CFCH_2CHBrCH_2CCl_3$ (XI) to get the halohexadiene or halohexatriene failed. The attack of ethoxide seemed to occur on the $-CF{=}CF_2$ group preferentially rather than

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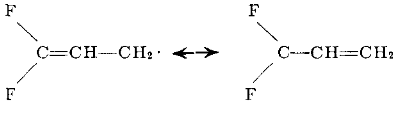
[10] The following resonance would stabilize the radical formed.



$$F_2C{=}CH{-}CH_2\cdot \longleftrightarrow F_2\dot{C}{-}CH{=}CH_2$$

[11] P. Tarrant, A. M. Lovelace, and M. R. Lilyquist [*J. Am. Chem. Soc.*, **77**, 2783 (1955)] reported that dehydrohalogenation of $CF_2BrCH_2CH_2Br$ with aqueous potassium hydroxide gave mainly $CF_2BrCH{=}CH_2$. Therefore, the choice of solvent seems to be an important factor.

TABLE III

HALO OLEFINS[a]

	B.p.			MD		C, %		H, %		F, %		Halogen, %[b]	
Compounds	(mm.), °C.	n^{28}_D	d^{28}_4	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
XI, $CF_2{=}CFCH_2CHBrCH_2CCl_3$	96–97 (15)	1.4720	1.726	52.1	52.0	22.49	22.21	1.57	1.66	17.79	17.83	44.25	44.50
I, $CF_2BrCF{=}CHCH_2CCl_3$	77–78 (15)	1.4592	1.740	47.4	48.1	19.60	20.07	0.99	1.35	18.61	18.82	46.30	46.55
XX, $CF_2BrCF{=}CClCH_2CCl_3$	102–103 (14)	1.4887	1.917	51.9	51.3	17.62	16.24	0.59	0.68	16.73	17.09	52.02	50.39
II, $CH_2BrCH{=}CFCF_2CCl_3$	88–89 (14)	1.4720	1.767	47.4	48.4	19.60	19.49	0.99	1.18	18.61	19.50	46.30	45.63
VII, $CF_2BrCF{=}CHCHBrCCl_3$	102–103 (15)	1.4971	2.025	55.2	55.7	15.58	15.71	0.52	0.69	14.80	15.11	46.02	46.21
XVIII, $CF_2BrCF{=}CHCH_2Br$	132 (760)	1.4596	1.999	36.0	36.6	17.92	18.17	1.13	1.12	21.28	21.15	59.67	59.35
XVII, $C_2H_5OCH_2CH{=}CFCF_2CCl_3$	93–94 (16)	1.4345	1.402	50.5	50.4	30.95	30.72	2.97	2.87	21.00	21.39	39.19	39.47
XIV, $CF_2{=}CHCBr_2CCl_3$	109 (25)	1.4958	2.039	50.5	50.6	13.59	13.92	0.29	0.50	10.76	11.00	50.19	49.89
XIII, $CF_2{=}CHCBr_3$	77–78 (27)	1.5010	2.343	39.0	39.6	11.44	11.79	0.32	0.97	12.07	11.02	76.16	79.28

[a] Analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. [b] Calculated as Cl.

on the hydrogen of the adjacent carbon, yielding high boiling viscous liquid products which were not identified.

Dehalogenation of $CF_2BrCFClCHBrCH_2CCl_3$ (VIII), which could possibly give the halo-1-pentene and halo-2-pentene (I), gave predominantly halo-2-pentene. This result may be also explained by the same reasoning as the case of dehydrohalogenation.

The physical properties and results of analyses of the new compounds are listed in Tables II and III.

Experimental[12]

Materials.—1,1,2-Trifluoro-1,3-butadiene and 1,1,2-trifluoro-1,4-pentadiene were prepared by dehalogenation of 4-bromo-3-chloro-3,4,4-trifluoro-1-butene and 1,4-dibromo-2,5-dichloro-1,1,2 trifluoropentane with zinc dust in ethanol.[13] 4-Bromo-3-chloro-3,4,4-trifluoro-1-butene and 1,1,2-trifluoro-4-bromo-1-butene were obtained from Peninsular ChemResearch, Inc. 3,3-Difluoroallyl bromide was made by dehydrohalogenation of 1,3-dibromo-1,1-difluoropropane[14] with ethanolic potassium hydroxide.

Addition Reactions of Bromotrichloromethane to 1,1,2-Trifluoro-1,3-butadiene.—A mixture of 68 g. (0.34 mole) of bromotrichloromethane and 8 g. (0.07 mole) of 1,1,2-trifluoro-1,3-butadiene was sealed in a glass tube and irradiated by sunlight for 2 days. The white polymer which formed during the irradiation was filtered and washed with methanol in a Soxhlet extractor for 15 hr. and dried. Five grams of polymer was obtained. Distillation of the filtrate at reduced pressure gave 0.5 g. of 1:1 adduct (b.p. 77–85° at 12 mm.) and 3.5 g. of higher telomers (viscous liquid). The infrared spectrum of the 1:1 adduct (I) was superimposable with that of 1-bromo-1,1,2-trifluoro-5,5,5-trichloro-2-penene, prepared from other methods such as dehalogenation of 1,3-dibromo-1,1,2-trifluoro-2,5,5,5-tetrachloropentane (VIII) or addition of bromotrichloromethane to 4-bromo-3-chloro-3,4,4-trifluoro-1-butene.

Addition Reactions of Bromotrichloromethane to 4-Bromo-3-chloro-3,4,4-trifluoro-1-butene.—A mixture of 291 g. (1.47 moles) of bromotrichloromethane and 64.5 g. (0.29 mole) of 4-bromo-3-chloro-3,4,4-trifluoro-1-butene was added to a 200-ml. flask with a stopper and put under sunlight irradiation for 2 days. Fractional distillation of the irradiation products at reduced pressure, after the removal of unchanged bromotrichloromethane and olefin, gave five main products. From the gas chromatograms of each fraction, the yields of products were calculated. The results were shown in Table I. Additional runs were made by the same procedure.

Addition Reaction of Bromotrichloromethane to 4-Bromo-2,3-dichloro-3,4,4-trifluoro-1-butene.—Irradiation of a mixture of 236 g. (1.19 moles) of bromotrichloromethane and 49 g. (0.19 mole) of 4-bromo-2,3-dichloro-3,4,4-trifluoro-1-butene for 26 days yielded 34.7 g. (0.10 mole, 53% yield) of $CF_2BrCF{=}CClCH_2CCl_3$ (XX), b.p. 101–103° (12 mm.), 24 g. (0.06 mole, 34% yield) of $CF_2BrCFClCClBrCH_2Cl$, b.p. 93–97 (6 mm.), and 3.5 g. (0.008 mole, 4% yield) of $CF_2BrCFClCClBrCH_2CCl_3$ (XIX), b.p. 90–92° (1 mm.).

Addition Reaction of Bromotrichloromethane to 1,1,2-Trifluoro-4-bromo-1-butene.—A mixture of 199 g. (1.00 mole) of bromotrichloromethane and 33 g. (0.17 mole) of 1,1,2-trifluoro-4-bromo-1-butene was added to a 200-ml. flask and irradiated by sunlight for 22 days. After the removal of unchanged bromotrichloromethane and olefin, fractional distillation of products gave about 3 g. of hexachloroethane which sublimed on a condenser, 6.4 g. (0.018 mole, 11% yield) of 1,2,4-tribromo-1,1,2-trifluorobutane (X), b.p. 68° (11 mm.), 53.4 g. (0.14 mole, 81% yield) of 3,5-dibromo-1,1,1-trichloro-2,2,3-trifluoropentane, b.p. 109–109.5° (7 mm.), and 2.4 g. of viscous liquid residue. The structure of 1,2,4-tribromo-1,1,2-trifluorobutane was confirmed by comparison of its infrared spectrum with that of an authentic sample prepared by bromine addition to 1,1,2-trifluoro-4-bromo-1-butene.

Addition Reactions of Bromotrichloromethane to 1,1,2-Trifluoro-1,4-pentadiene.—In a glass tube were sealed 112 g. (0.57 mole) of bromotrichloromethane and 11.7 g. (0.10 mole) of 1,1,2-trifluoro-1,4-pentadiene. The contents of the tube were irradiated by sunlight for 6 days. Fractional distillation of the reaction mixture under reduced pressure yielded 13.2 g. (0.041 mole, 43% yield) of 1,1,2-trifluoro-4-bromo-6,6,6-trichloro-1-hexane (XI), b.p. 96–97° (15 mm.), 17.8 g. (0.034 mole, 35% yield) of 1,1,1,7,7,7-hexachloro-2,2,3-trifluoro-3,5-dibromoheptane (XII), b.p. 117–118° (1 mm.), and 2 g. of residue. Using the same procedure, a mixture of 123 g. (0.62 mole) of bromotrichloromethane and 21.7 g. (0.18 mole) of 1,1,2-trifluoro-1,4-pentadiene under irradiation for 11 days gave 18.5 g. (0.058 mole, 32% yield) of the halohexene (XI) and 35.4 g. (0.068 mole, 38% yield) of the haloheptane (XII). Irradiation of a mixture of 54.8 g. (0.28 mole) of bromotrichloromethane and 7.5 g. (0.06 mole) of 1,1,2-trifluoro-1,4-pentadiene for 25 days gave exclusively XII, 27.6 g. (0.05 mole, 86% yield).

Addition Reaction of Bromotrichloromethane to 3,3-Difluoroallyl Bromide.—A mixture of 361 g. (1.82 moles) of bromotrichloromethane and 56 g. (0.36 mole) of 3-bromo-1,1-difluoropropene in a 200-ml. flask was irradiated for 10 days. Fractional distillation of products gave 48.4 g. (0.15 mole, 43% yield) of 1,1-difluoro-3,3,3-tribromo-2-propene (XIII), b.p. 76–78° (29 mm.), and 20 g. (0.06 mole, 16% yield) of 1,1-difluoro-3,3-dibromo-4,4,4-trichloro-1-butene (XIV), b.p. 109° (25 mm.), and 7 g. of residue.

Addition Reaction of Bromotrichloromethane to 2-Bromo-3,3,3-trifluoro-1-propene.—Irradiation of a mixture of 302 g. (1.52 moles) of bromotrichloromethane and 64.5 g. (0.37 mole) of 2-

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[12] All temperature readings are uncorrected. Analyses were by Galbraith Laboratories, Knoxville, Tenn.

[13] P. Tarrant and E. G. Gilman, *J. Am. Chem. Soc.*, **76**, 5423 (1954).

[14] P. Tarrant and A. M. Lovelace, *ibid.*, **76**, 3466 (1954).

bromo-3,3,3-trifluoro-1-propene for 13 days gave 52.3 g. (0.14 mole, 38% yield) of 1:1 adduct (XV), b.p. 86–88° (12 mm.), and 19.4 g. (0.035 mole, 10% yield) of 1:2 adduct (XVI), b.p. 86–89° (1 mm.).

Dehydrobromination of 1,3-Dibromo-5,5,5-trichloro-3,4,4-trifluoropentane (IX).—In a 300-ml. three-necked flask with a stirrer and reflux condenser was placed 81.5 g. (0.21 mole) of the halopentane. A solution of 34 g. (0.61 mole) of potassium hydroxide in 150 ml. of absolute ethanol was added dropwise for 40 min. and kept stirring for an additional 10 min. The cooled reaction mixture was suction filtered to remove the potassium bromide and water was added to the solution. The organic layer was separated, dried, and distilled to give 11 g. (0.036 mole, 17% yield) of a mixture of $CH_2BrCH{=}CHCF_2CCl_3$ (II) and $CH_2{=}CHCFBrCF_2CCl_3$, b.p. 88–90° (17 mm.), and 27.6 g. (0.10 mole, 48% yield) of $C_2H_5OCH_2CH{=}CFCF_2CCl_3$ (XVII), b.p. 93–94° (16 mm.), and viscous liquid residue, 9.8 g.

In the same procedure, a reaction of 99 g. (0.26 mole) of the halopentane with 21 g. (0.37 mole) of potassium hydroxide in 60 ml. of absolute ethanol gave 3.7 g. (0.01 mole, 5% yield) of $CH_2{=}CHCFBrCF_2CCl_3$, 37.4 g. (0.12 mole, 47% yield) of II, 6.3 g. (0.02 mole, 9% yield) of XVII, and 20.5 g. of unchanged halopentane.

Dehydrobromination of 1,2,4-Tribromo-1,1,2-trifluorobutane.—A reaction of 92 g. (0.26 mole) of the halobutane with 19 g. (0.34 mole) of potassium hydroxide in 100 ml. of absolute ethanol gave 31.6 g. (0.12 mole, 46% yield) of $CH_2BrCH{=}CFCF_2Br$, b.p. 51–52° (70 mm.), 10.6 g. of a mixture of two compounds, b.p. 70–72° (67 mm.), and 8 g. of unchanged halobutane.

Dehalogenation of 1,3-Dibromo-2,5,5,5-tetrachloro-1,1,2-trifluoropentane.—To 15 g. (0.23 mole) of zinc dust in 100 ml. ethanol was added dropwise 49 g. (0.12 mole) of the halopentane for 1 hr. The reaction mixture was filtered and diluted hydrochloric acid was added to the filtrate. The organic layer was separated and dried. Fractionation gave 4 g. (0.013 mole, 11% yield) of $CF_2{=}CFCHBrCH_2CCl_3$, 9.4 g. (0.031 mole, 26% yield) of $CF_2BrCF{=}CHCH_2CCl_3$, b.p. 74–78° (14 mm.), and 14.6 g. of unchanged halopentane.

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The Synthesis and Reactions of β-Chloroacrylonitrile

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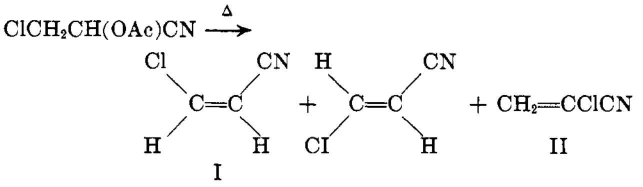
A mixture of *cis* and *trans* isomers of β-chloroacrylonitrile and α-chloroacrylonitrile is obtained by the pyrolysis of α-acetoxy-β-chloropropionitrile. The chlorine of β-chloroacrylonitrile is easily displaced by nucleophilic reagents enabling the compound to be used successfully as a cyanovinylating reagent. Reactions involving compounds containing nitrogen, sulfur, phosphorus, and carbon as the nucleophilic ceuters are described. Ethoxide ion and *p*-toluene sulfide ion react with *cis*- or *trans*-β-chloroacrylonitrile to give products of the same steric configuration as the starting material. In contrast, only one product, the *trans*-β-cyanovinylpiperidine, is obtained on cyanovinylation of piperidine with either the *cis*- or *trans*-β-chloroacrylonitrile. The mechanism of the cyanovinylation reaction is discussed.

In the last few years several investigators have shown increasing interest in the reactivity of vinyl halides both from a mechanistic and practical synthetic point of view. Vinyl halides which have β-electron-attracting substituents have been of particular interest because of the ease of replacement of the halogen atom by nucleophilic reagents.[1] The reactions of β-chloroacrylonitrile (I), a material of this structural type, have not been described in the literature.

Two methods for the preparation of I have been published. Dutcher[2] reported its synthesis by the addition of cyanogen chloride to acetylene; however, no physical or chemical properties were described. Gryszkiewicz-Trochimowski[3] described the synthesis of the *trans* isomer from the corresponding *trans* amide. A brief investigation of Dutcher's procedure revealed that only a very low yield of the hitherto unknown *cis* isomer was produced. We have found that I can be conveniently obtained by the pyrolysis of α-acetoxy-β-chloropropionitrile at 535°. Fractionation of the



pyrolysate gave equivalent amounts of the *cis* (b.p. 145–146°) and *trans* (b.p. 118°) isomers in 33% total yield along with a 28% yield of α-chloroacrylonitrile (II). The large amount of II obtained in the reaction is surprising. Acetate pyrolyses of this type are generally considered to proceed through an uncharged cyclic transition state; the chlorine rearrangement observed here suggests a unique mechanism involving charged species in the vapor phase.

The physical properties of *trans*-I obtained by pyrolysis were identical with those previously reported.[3] The *cis*-I obtained by the pyrolysis route was identical with the product of the cyanogen chloride–acetylene reaction.[2] In addition, the above assignments of configuration were substantiated by both infrared and nuclear magnetic resonance spectra (Table VI). The *trans* isomer exhibits a band at 935 cm.$^{-1}$ in the infrared which has been assigned to the *trans* in-phase, out-of-plane, carbon–hydrogen bending vibration.[4] The isomer to which we assign the *cis* configuration exhibits this vibrational band at 740 cm.$^{-1}$ as expected. The hydrogen–hydrogen coupling constants, 7.7 c.p.s.

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