three-necked flask was added, dropwise over 30 minutes, 43 g. (0.33 mole) of *trans*-1,2-di-(hydroxymethyl)-cyclopentane (VIII) dissolved in 35 ml. of glacial acetic acid. After the mixture was heated under reflux for 14 hours, it was fractionated through a 6-inch, helix-packed column to yield 63 g. (94%) of colorless *trans*-1,2-di-(acetoxymethyl)-cyclopentane (IX), b.p. 116° (2 mm.), $n^{25}\text{D}$ 1.4471.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.11; H, 8.42. Found: C, 61.43; H, 8.48.

1,2-Dimethylenecyclopentane (I) and 1-Methylene-2-acetoxymethylcyclopentane (X).—A 25-mm. Vycor pyrolysis tube packed with Pyrex helices was externally heated with a 12-inch Hoskins furnace, as previously described,[4] and flushed out with a slow stream of oxygen-free nitrogen. Through this tube, heated at 525°, was dropped 75 g. (0.35 mole) of *trans*-1,2-di-(acetoxymethyl)-cyclopentane (IX) over a period of 65 minutes, and the pyrolysate was collected in a flask immersed in a Dry Ice–chloroform–carbon tetrachloride mixture. The pyrolysate was taken up in ether and washed several times with water to remove acetic acid, and the organic layer was dried over potassium carbonate. Titration of aliquot portions of the aqueous extracts indicated that 21 g. (0.35 mole or 50%) of acetic acid was cracked out. The ether was distilled from the organic layer, and the residue was fractionated through a 6-inch, helix-packed column to yield 5.0 g. (15%) of 1,2-dimethylenecyclopentane (I), b.p. 80–82° (130 mm.), $n^{25}\text{D}$ 1.4694, $d^4{}_{25}$ 0.8553; 10.0 g. (26%) of 1-methylene-2-acetoxymethylcyclopentane (X), b.p. 90–91° (2.5 mm.), $n^{25}\text{D}$ 1.4526; and 30 g. (40% recovery) of the diacetate IX. The yield of I, based on unrecovered IX and X, was 44%.

Anal. Calcd. for C_7H_{10}: C, 89.36; H, 10.64. Found: C, 89.35; H, 10.65. Calcd. for $C_9H_{14}O_2$: C, 70.25; H, 9.11. Found: C, 70.22; H, 9.14.

4,7-Dihydroindan-5,6-dicarboxylic Acid (XI).—In a 50-ml. flask were placed 0.5 g. (0.0053 mole) of 1,2-dimethylenecyclopentane (I), 0.6 g. (0.0052 mole) of acetylenedicarboxylic acid, and 30 ml. of dioxane, and the mixture was heated under reflux for 6 hours. The dioxane was removed under reduced pressure, and the residue was recrystallized from ether twice to yield 0.9 g. (83%) of 4,7-dihydroindan-5,6-dicarboxylic acid (XI), m.p. 146–147°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.50; H, 5.77. Found: C, 63.21; H, 6.02.

4a,5,8,8a-Tetrahydro-6,7-cyclopentano-1,4-naphthoquinone (XII).—In a 50-ml. flask were placed 0.5 g. (0.0053 mole) of 1,2-dimethylenecyclopentane (I), 0.6 g. of benzoquinone (0.0055 mole), and 30 ml. of benzene, and the reaction mixture was heated under reflux for 8 hours. The benzene was evaporated and the crystalline residue was recrystallized three times from petroleum ether (30–60°) to yield 0.8 g. (75%) of 4a,5,8,8a-tetrahydro-6,7-cyclopentano-1,4-naphthoquinone (XII), m.p. 135–136°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.22; H, 6.93. Found: C, 77.11; H, 7.17.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA]

Free Radical Additions Involving Fluorine Compounds. II. The Addition of 1-Chloro-1,2-dibromo-1,2,2-trifluorethane to Some Hydrocarbon Olefins[1,2]

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Various hydrocarbon olefins have been found to react with 1-chloro-1,2-dibromo-1,2,2-trifluoroethane to give one-to-one addition products in the presence of peroxides. These adducts may be converted to olefins or to dienes containing the perfluorovinyl group.

Numerous reports have appeared in the literature on the peroxide-catalyzed addition of fluorohalomethanes to olefins[3–6] but very little information has been published on the addition to olefins of halogenated compounds containing more than one carbon atom. Feasley and Stover[7] carried out reactions of 1,1,2-trichloro-1,2,2-trifluoroethane with various straight-chain primary olefins; however, they apparently did not isolate any individual addition products.

It has been found that 1-chloro-1,2-dibromo-1,2,2-trifluoroethane, readily made by adding bromine to chlorotrifluoroethylene, reacts in the presence of benzoyl peroxide with ethylene, propylene, 2-butene, 2-methylpropene, 1-octene and 3-chloropropene to give good yields of the one-to-one addition products. The 1-chloro-1,2-dibromo-1,2,2-trifluoroethane is less reactive than bromotrichloromethane since the latter forms a one-to-one adduct with chlorotrifluoroethylene whereas the dibromide does not; however, it is more reactive than dibromodifluoromethane, which does not react to an appreciable extent with 3-chloropropene. The over-all reaction with ethylene is represented by the equation

$$CF_2BrCFClBr + CH_2{=}CH_2 \longrightarrow CF_2BrCFClCH_2CH_2Br$$

In reactions involving the homolytic scission of a carbon to bromine bond in $CF_2BrCFClBr$, it appears that either of the bromine atoms might be removed by the radical formed by the decomposition of the catalyst to give either $CF_2BrCFCl\cdot$ or $CFClBrCF_2\cdot$ and that with propylene, for example, the compound represented by either $CF_2BrCFClCH_2CHBrCH_3$ (I) or $CFClBrCF_2CH_2CHBrCH_3$ (II) might be formed. However, the carbon to bromine bond of the bromochlorofluoromethyl group is undoubtedly weaker than that of the bromodifluoromethyl group, and the compound represented by I was expected to be formed. Proof of this supposition was found in the transformation of the adduct to 1,1,2-trifluoro-1,3-pentadiene by the following reactions

$$CF_2BrCFClCH_2CHBrCH_3 \xrightarrow{\text{base}}$$

$$CF_2BrCFClCH{=}CHCH_3 \xrightarrow{\text{Zn}} CF_2{=}CFCH{=}CHCH_3$$

Had the other adduct II been obtained, the cor-

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(1) Previous paper in this series, THIS JOURNAL, **76**, 3466 (1954).

(2) The work was supported in part by the Office of Naval Research under Contract (Nonr 1017(00)).

(3) P. Tarrant and A. M. Lovelace, THIS JOURNAL, **76**, 3466 (1954).

(4) R. N. Haszeldine, *J. Chem. Soc.*, 2502 (1952).

(5) W. T. Miller, Jr., and J. M. Howald, Abstracts of Papers, p. 12K, 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

(6) A. L. Henne and M. Nager, THIS JOURNAL, **73**, 5527 (1951).

(7) C. F. Feasley and W. A. Stover, U. S. Patent 2,603,663 (July 15, (1952)).

TABLE I

ADDITION PRODUCTS FROM 2-CHLORO-1,2-DIBROMO-1,1,2-TRIFLUOROETHANE AND OLEFINS

Olefin	Adduct	Yield, %	B.p. °C.	B.p. Mm.	t, °C.	n^t_D	d^t_4	MR_D Calcd.	MR_D Found	Analyses silver equiv. Calcd.	Analyses silver equiv. Found
$CH_2{=}CH_2$	$CF_2BrCFClCH_2CH_2Br$	58	67	20	25	1.4563	2.035	40.77	40.69	101.5	101.9
$CH_2{=}CHCH_3$	$CF_2BrCFClCH_2CHBrCH_3$	83	66	11	27	1.4560	1.890	45.86	46.34	106.2	105.0
$CH_2{=}CHCH_2Cl$	$CF_2BrCFClCH_2CHBrCH_2Cl$	45	90	6	27	1.4762	1.9953	50.25	49.86	88.2	87.9
$CH_2{=}\overset{\overset{CH_3}{\vert}}{C}{-}CH_3$	$CF_2BrCFClCH_2\overset{\overset{CH_3}{\vert}}{C}BrCH_3$	43	43–45	2	25	1.4590	1.8003	60.28	49.36	110.8	108.7
$CH_3CH{=}CHCH_3$	$CF_2BrCFCl\overset{\overset{CH_3}{\vert}}{C}HCHBrCH_3$	35	49	2.5	24	1.4592	1.8180	50.24	50.20	110.8	109.7
$CH_2{=}CHC_6H_{13}$	$CF_2BrCFClCH_2CHBrC_6H_{13}$	34	84	0.3	24	1.4612	1.5580	68.77	68.47	129.5	129.3

responding olefin, $CFClBrCF_2CH{=}CHCH_3$, would no doubt have been formed but it is unlikely that it would react with zinc under the conditions employed to give a diene. Furthermore, if such a dehalogenation occurred, the resulting diene would contain either bromine or chlorine. It is therefore clear that the addition products from $CF_2BrCFClBr$ contain the $CF_2BrCFCl$-group.

In order to complete the proof of the course of the addition reaction, it is necessary to establish the point of attack of the bromochlorotrifluoroethyl radical on the olefin. A relatively simple proof that this attacking radical adds to the terminal methylene group of unsaturated hydrocarbons is afforded by the reaction product from 3-chloropropene. Since the addition product could be converted in a one-step reaction to a trifluoropentadiene, it is evident that the adduct had the structure $CF_2BrCFClCH_2CHBrCH_2Cl$ rather than $CF_2BrCFClCH(CH_2Cl)CH_2Br$. The latter would give a cyclopropane derivative upon treatment with zinc and the infrared spectrum shows no absorption peaks at the frequencies associated with cyclopropane derivatives; however, the vibration frequencies of the perfluorovinyl and vinyl groups appeared at 5.55 and 6.07 μ, respectively. It is thus clear that the 1-chloro-1,2-dibromo-1,2,2-trifluoroethane adds preferentially to the methylene end of a terminal double bond and thus follows the same course as has been shown to take place with halomethanes.

The reaction of $CF_2BrCFClBr$ with ethylene, in contrast to the reaction of dibromodifluoromethane,[3] took place smoothly and gave the one-to-one addition product in good yields. It was also found that 2-butene readily accepted the ethane derivative across the double bond to give a branched-chain adduct isomeric with that obtained from 2-methylpropylene. The physical properties of the addition products are shown in Table I.

The adducts, except that from allyl chloride, reacted with alcoholic potassium hydroxide to give olefins of the type $CF_2BrCFClCH{=}CHR$. Since no fluorine is present on the double-bonded carbon atoms, side reactions such as the formation of ethers are minimized and good yields of olefins are obtained. These olefins were readily converted into the corresponding dienes by treatment with zinc and alcohol. It was also found that an olefin containing the perfluorovinyl group could be obtained by treating the adduct with zinc. For example, $CF_2BrCFClCH(CH_3)CHBrCH_3$ gave $CF_2{=}CFC(CH_3)CHBrCH_3$, the infrared spectrum of which clearly shows the presence of the perfluorovinyl group at 5.55 μ.

Undoubtedly the adduct from allyl chloride also underwent dehydrohalogenation but it was not possible to obtain a pure sample of $CF_2BrCFClCH{=}CHCH_2Cl$, probably because of the increased reactivity of the chlorine atom of the chloromethyl group due to its allylic nature.

However, it was possible to remove all of the halogen atoms other than fluorine by treatment of the 3-chloropropene addition product with zinc and as a result 1,1,2-trifluoro-1,4-pentadiene was obtained. The isomeric compound, 1,1,2-trifluoro-1,3-pentadiene was obtained from the propylene adduct. The infrared spectra of these two dienes show distinct absorption bands in regions which are probably due to the stretching of the carbon–carbon double bond. The characteristic stretching band of the C=C of an isolated perfluorovinyl group, based on $CF_2{=}CFCH(CH_3)CHBrCH_3$ and $CF_2{=}CFCH_2CH{=}CH_2$, seems to occur at 5.55 μ. In the conjugated dienes this band has shifted to 5.65 μ, as noted in the spectrum of $CF_2{=}CFCH{=}CHCH_3$. The C=C stretching band associated with propylene, about 6.07 μ, also appears in the unconjugated diene; a slight shift to 6.02 μ appears in the conjugated diene but this may be due to the $-CH{=}CHCH_3$ group since 2-butene has a peak at this point. In none of the cases studied were absorption maxima observed around 6.25 μ which appears to be the region in which conjugated dienes show carbon–carbon stretching. It thus appears from the infrared spectra of these compounds that the presence of the fluorine atoms may interfere with the resonance effect in some way to reduce the conjugation. It has previously been observed that 1,1-difluoro-1,3-butadienes do not form maleic anhydride adducts. The physical properties of the olefins and dienes derived from the addition products of 1-chloro-1,2-dibromo-1,2,2-trifluoroethane and the hydrocarbon olefins are given in Table II.

Experimental[8]

1,4-Dibromo-2,5-dichloro-1,1,2-trifluoropentane.—In a flask heated on a steam-cone and equipped with a stirrer, reflux condenser and addition funnel was placed 1656 g. (6 moles) of 1-chloro-1,2-dibromo-1,2,2-trifluoroethane. A solution of 36 g. (0.14 mole) of benzoyl peroxide in 152 g. (2 moles) of allyl chloride was added as rapidly as reflux permitted. After the addition was completed, the mixture was heated an additional seven hours. After removal of the

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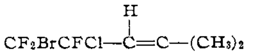
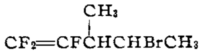
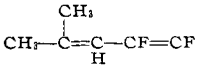
[8] Analyses by Peninsular Chem. Research, Inc., Gainesville, Florida.

TABLE II

OLEFINS AND DIENES OBTAINED FROM THE ADDITION PRODUCTS

Compound	Yield, %	B.p. °C.	B.p. Mm.	t, °C.	n^t_D	d^t_4	MR_D Calcd.	MR_D Found	Analyses Calcd. C	Analyses Calcd. H	Analyses Found C	Analyses Found H
$CF_2BrCFCl{-}CH{=}CH{-}CH_3$	45	74–75	93	26	1.4100	1.5684	37.14	38.44	118.5[a]		121.2[b]	
 $CF_2BrCFCl{-}\overset{H}{C}{=}C{-}(CH_3)_2$	50	42	39	24	1.4423	1.5274	41.77	41.90	126.0[a]		125.9[b]	
$CF_2BrCFCl{-}CH{=}CH{-}(CH_2)_5{-}CH_3$	70	62	0.5	24	1.4410	1.329	60.23	61.08	154.0[a]		152.6[b]	
$CF_2{=}CF{-}CH{=}CH{-}CH_3$	60	44–45	760	24	1.3689	0.9974	27.85	26.95	49.20	4.09	49.16	4.13
 $CF_2{=}CF\overset{CH_3}{C}HCHBrCH_3$		79	65	22	1.4160	1.442	37.20	37.67	36.8[c]		36.5[d]	
 $CH_3{-}\overset{CH_3}{C}{=}\underset{H}{C}{-}CF{=}CF$	42	52–54	760	24	1.3606	0.8538	28.45	27.74	52.90	5.19	53.0	5.09
$CF_2{=}CFCH_2{-}CH{=}CH_2$	65.3	38	870	27	1.3435	1.0324	24.05	24.96	49.25	4.09	49.34	4.02
$CF_2{=}CF{-}CH{=}CH{-}(CH_2)_5{-}CH_3$	72	25	35	24	1.3810	.838	49.04	49.69	62.65	7.82	62.20	7.92

[a] Calculated for silver equivalent. [b] Found for silver equivalent. [c] Calculated for bromine. [d] Found for bromine.

excess chlorodibromotrifluorethane, the addition product was obtained in 45% yield. Its properties are given in the table.

2-Chloro-1,4-dibromo-1,2-trifluorodecane.—Using the procedure described above, 828 g. (3 moles) of 1-chloro-1,2-dibromo-1,2,2-trifluoroethane, 10 g. (0.04 mole) of benzoyl peroxide and 110 g. (0.9 mole) of octene were allowed to react. The addition product was isolated by distillation and had the properties shown in Table I.

2-Chloro-1,4-dibromo-1,1,2-trifluorobutane.—A 1.4-l. stainless steel autoclave was charged with 1125 g. (4.0 moles) of 1-chloro-1,2-dibromo-1,2,2-trifluoroethane and 15 g. (0.06 mole) of benzoyl peroxide, sealed and the air removed by a vacuum pump. Ethylene was introduced until the gage pressure was approximately 27 atmospheres; 51 g. was thus introduced. The reaction vessel was then rocked for four hours at 100°. The vessel was cooled in ice-water and the unreacted ethylene discharged. The crude product was distilled through a fractionating column to give 319 g. of one-to-one addition product. Additional runs were made using the same procedure and in no case was any material boiling higher than the simple addition product obtained.

2-Chloro-1,4-dibromo-1,1,2-trifluoropentane.—The autoclave was cooled in Dry Ice and acetone and loaded with 1656 g. (6 moles) of 1-chloro-1,2-dibromo-1,2,2-trifluoroethane, 22 g. (0.09 mole) of benzoyl peroxide and 88 g. (2 moles) of propylene. The reaction was carried out at 80° for four hours. The vessel was cooled, opened and the excess haloethane removed by distillation. The addition product was obtained in a yield of 83%.

2-Chloro-1,4-dibromo-3-methyl-1,1,2-trifluoropentane.—Using the procedure described above, 6 moles of the haloethane, 2 moles of 2-butene and 0.09 mole of benzoyl peroxide gave a 35% yield of one-to-one adduct.

2-Chloro-1,4-dibromo-4-methyl-1,1,2-trifluoropentane.—Substituting 1.8 moles of isobutylene in the procedure above gave a 43% yield of the 4-methylpentane derivative.

Dehydrobromination of the Adducts to Olefins.—In general all reactions were carried out in a three-neck flask of suitable size fitted with a stirrer, reflux condenser and addition funnel with a pressure equalizing side tube. A saturated solution of potassium hydroxide in ethanol was added dropwise to the compound to be dehydrohalogenated. Whenever heat was required to start a reaction, a steam-bath was used. The cooled reaction mixture was suction filtered to remove the potassium bromide, water was added to the solution, and the organic layer was separated. The product was dried and distilled through a 48-cm. column packed with glass helices. The properties of the various olefins obtained in this manner are given in Table II.

In addition to the compounds listed in the table, one run on the dehydrohalogenation of the addition product from allyl chloride, $CF_2BrCFClCH_2CHBrCH_2Cl$, gave a 50% yield of material which had the following properties: b.p. 52–55° at 93 mm., $n^{24}D$ 1.4513, d^{24}_4 1.7423, MR_D (calculated for $C_5H_4BrClF_3$) 41.01, MR_D (found) 42.28. Infrared spectra indicate that this olefin was contaminated by a small amount of other substances.

Dehalogenation Reactions.—The dehalogenation reactions were carried out with zinc dust and 2-propanol in the apparatus described above. It was found necessary to heat all the reaction mixtures to initiate the reaction but, once started, the reactions were exothermic and caution had to be exercised to control the dehalogenation. In cases where the diene boiled low enough, the product was allowed to pass through the reflux condenser and was caught in traps immersed in Dry Ice. A 10% molar excess of zinc dust was used and it was found helpful to add a small amount of zinc chloride to initiate reaction. The dienes which were prepared by this method are shown in Table II.

Acknowledgment.—We wish to express our appreciation to Mr. M. R. Lilyquist for carrying out the reaction of 1-chloro-1,2-dibromo-1,2,2-trifluoroethane with ethylene.

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