0.0014 mol) was added and the solution turned a clear violet The reaction mixture was stirred at room temperature color. for 18 hr after which time the clear orange solution was diluted with water and extracted with ether. The ether layer was dried over sodium sulfate. Removal of the solvent left a pale yellow solid which was recrystallized from 95% ethanol to give 0.24 g (65%) of trans-1,2,3-triphenylcyclopropane. Mixture melting point with an authentic sample was not depressed.

A deuterium analysis by mass spectrometry of the recovered cyclopropane indicated 2.30 deuterium atom per molecule. The nmr spectrum showed that the cyclopropyl hydrogens had been exchanged.

cis-1,2,3-Triphenylcyclopropane.-This compound was synthesized in 80% yield according to the procedure of Battiste.⁴

cis-1,2,3-Triphenylcyclopropane and Potassium tert-Butoxide in DMSO-d₆.--Potassium tert-butoxide (0.69 g, 0.0062 mol) was added to DMSO- d_6 (3 ml, 0.036 mol) with stirring under nitrogen. Then cis-1,2,3-triphenylcyclopropane (0.55 g, 0.0020 mol) was added. The resulting deep blue-green solution was stirred for 18

(25) M. A. Battiste, Tetrahedron Lett., 3795 (1964).

hr at room temperature. The reaction mixture was then diluted with water and extracted with ether. The ether layer was dried over sodium sulfate. Removal of the solvent left 0.50 g (91%) of a viscous clear yellow oil which was shown by glpc (5 ft SE-30, 220°) to contain only one component having the same retention time as authentic trans-1,2,3-triphenvlcvclopropane. It should be noted that it was possible to separate an authentic mixture of cis-1,2,3-triphenylcyclopropane and trans-1,2,3-triphenylcyclopropane on the glpc column used for the crude reaction product.

A deuterium analysis by mass spectrometry of the recovered oil indicated 2.33 deuterium atom per molecule. The nmr spectrum showed that the cyclopropyl hydrogens had been exchanged.

Registry No.-3, 10539-10-3; 4, 30477-01-1; 5, 30409-61-1; 6, 30409-62-2; 13, 30409-63-3; 14, 30477-02-2; 15, 30409-64-4; 16, 30409-65-5; trans-1,2,3-triphenylpropene, 3239-33-6; cis-1,2,3-triphenylpropene, 3239-32-5; cis-3-trimethylsilyl-1,2,3-triphenylpropene, 30409-68-8.

The Copper Chloride-Ethanolamine-Catalyzed Addition of Polyhaloalkanes to Substituted Olefins¹

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The copper chloride-ethanolamine redox system initiates the addition of polyhaloalkanes to a variety of olefins. The structure of the initial olefin greatly affects both the yield and the structure of the final product. Halogenated olefins showed decreased reactivity toward radical attack. The telogen CF₂BrCFClBr gave good yields with simple α olefins, while only the more reactive CCl₃Br reacted with several halogenated olefins. This redox system of radical initiation exhibits considerable potential as a synthetic tool. The preparation and characterization of several new addition adducts are reported.

The addition of polyhalogenated alkanes to the double bond of olefins has received considerable attention in the literature.² While the usual systems for freeradical initiation give varying amounts of telomeric products, the "redox" system described by Asscher and Vofsi leads to almost exclusive formation of 1:1 adducts.^{3,4} This system utilizes iron or copper salts to catalyze the addition of carbon tetrachloride and chloroform to olefins. Reaction conditions are quite mild

$$CCl_4 + PhCH = CH_2 \xrightarrow[solvent,]{CuCl_3} PhCHClCH_2CCl_3$$

and, because telomerization reactions are minimized, the use of a large excess of alkyl polyhalide is unnecessary. Additionally, vigorous reaction conditions and the need for special apparatus can be avoided. Because of these advantages, the redox technique holds much promise for the preparation of many polyhalogenated compounds, and a study of the scope and utility of this system was of interest.

We recently reported⁵ a study of the scope of this reaction with a series of alkyl polyhalides. 1-Octene was used as the model olefin for that reactivity survey. Our initial study has now been expanded to include a variety of olefins, with the hope that the effect of olefin structure on the polyhalide additions could be ascertained.

Results and Discussion

In this study, CF₂BrCFClBr was used as a model halide. Our previous report⁵ showed it to be very reactive under redox conditions, giving a good yield of stable, 1:1 addition product with 1-octene. As previously described, the additions were carried out by refluxing the olefin, alkyl polyhalide, copper chloride, ethanolamine, and tert butyl alcohol, with stirring, for 24 hr. If no significant reaction was noted after this time, reflux was continued for at least an additional 24 The results of these addition reactions are summahr. rized in Table I.

An examination of the data in Table I reveals that this redox method successfully initiates the addition of polyhaloalkanes to both terminal and internal olefins as well as several halogen-substituted olefins.

Vpc showed that in almost every reaction, in addition to the major product, small amounts (generally less than 5% of the total product) of isomeric compounds were formed. These by-products were not identified.

The redox-initiated additions proceed in the same manner as that described for additions initiated by ordinary techniques. We have shown⁵ that addition to straight-chain, terminal olefins gives almost exclusively the simple, straight-chain 1:1 addition adduct.

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^{(1) (}a) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; (b) preliminary report in Tetrahedron Lett., 5163 (1966); (c) this investigation was supported in part by Public Health Service, Grant GM 11809.

⁽²⁾ For extensive reviews of this work, cf. (a) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, Chapter 6. (b) G. Sosnovsky, 'Free Radical Reactions in Preparative Organic Chemistry," Macmillan, New York, N. Y., 1964, Chapter 2.

M. Assoher and D. Vofsi, J. Chem. Soc., 1887 (1963).
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Allyl chloride CF ₃ BrCFCIBr 89 6 2:1 48 Allyl chloride CCl ₃ Br CCl ₃ Br CCl ₃ Br 1:1 24 74–78 (1) 1.5328 Allyl chloride CCl ₃ Br CCl ₃ Br CCl ₃ Br CCl ₃ Br 2 1:1 24 74–78 (1) 1.5328 1-Bromopentene-1 CF ₃ BrCFCIBr CHBr ₂ CH(CCl ₃)(CH ₂) ₅ CH ₃ 30428-55-2 100 88 1:1 24 74–78 (1) 1.5328 1-Bromopentene-1 CF ₃ BrCFCIBr CHBr ₂ CH(CCl ₃)(CH ₂) ₅ CH ₃ 30428-55-6 38 63 2:1 48 79–81 (0.2) 1.5396 2-Chlorobutene-2 CCl ₃ Br CH ₅ CH(CCl ₃)CCIBrCH ₃ 30428-55-6 38 63 2:1 48 79–81 (0.2) 1.5330 2-Chlorobutene-2 CCl ₃ Br CH ₅ CH(CCl ₃)CCIBrCH ₃ 30428-55-7 70 42 2:1 48 62 (0.35) 1.5330 2-Chlorobutene-2 CCl ₃ Br CCl ₃ CF CH(CH ₃) ₅ CH ₃ 30428-55-8 58 14 1:1 100 <td>Allyl chloride CF₃BrCFCIBr 89 6 2:1 48 Allyl chloride CCl₃Br CCl₃Br CCl₃Br CCl₃Br CCl₃Br C 1:1 24 74-78 (1) 1.5328 Allyl chloride CCl₃Br CCl₃Br CCl₃CH₃CHBrCH₂CH 20968-55-2 100 88 1:1 24 74-78 (1) 1.5328 1-Bromopentene-1 CF₃BrCFCIBr CHBr₂CH(CCl₃)(CH₂)₂CH₃ 30428-53-6 38 63 2:1 48 79-81 (0.2) 1.5396 2-Chlorobutene-2 CCl₃Br CH₃CH(CCl₃)(CH₂)₂CH₃ 30428-53-6 38 63 2:1 48 70-81 (0.2) 1.5396 2-Chlorobutene-2 CCl₃Br CH₃CH(CH₃)₃CH₃ 30428-55-6 38 63 0.2:1 48 70-81 (0.2) 1.5396 2-Chlorobutene-2 CCl₃Br CH₃CH(CH₃)₃CH₃ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577 BTFO CF₃BrCFCIBr CCl₃Br CCl₃Rr 20428-55-</td> <td>$\begin{array}{llllllllllllllllllllllllllllllllllll$</td> <td>Ethyl allyl ether</td> <td>CF₃BrCFCIBr</td> <td>CF2BrCFCICH2CHBrCH2OCH2CH3</td> <td>690-65-3</td> <td></td> <td>62</td> <td>2:1</td> <td>48</td> <td>78-79 (1.5)</td> <td>1.4565</td>	Allyl chloride CF ₃ BrCFCIBr 89 6 2:1 48 Allyl chloride CCl ₃ Br C 1:1 24 74-78 (1) 1.5328 Allyl chloride CCl ₃ Br CCl ₃ Br CCl ₃ CH ₃ CHBrCH ₂ CH 20968-55-2 100 88 1:1 24 74-78 (1) 1.5328 1-Bromopentene-1 CF ₃ BrCFCIBr CHBr ₂ CH(CCl ₃)(CH ₂) ₂ CH ₃ 30428-53-6 38 63 2:1 48 79-81 (0.2) 1.5396 2-Chlorobutene-2 CCl ₃ Br CH ₃ CH(CCl ₃)(CH ₂) ₂ CH ₃ 30428-53-6 38 63 2:1 48 70-81 (0.2) 1.5396 2-Chlorobutene-2 CCl ₃ Br CH ₃ CH(CH ₃) ₃ CH ₃ 30428-55-6 38 63 0.2:1 48 70-81 (0.2) 1.5396 2-Chlorobutene-2 CCl ₃ Br CH ₃ CH(CH ₃) ₃ CH ₃ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577 BTFO CF ₃ BrCFCIBr CCl ₃ Br CCl ₃ Rr 20428-55-	$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Ethyl allyl ether	CF ₃ BrCFCIBr	CF2BrCFCICH2CHBrCH2OCH2CH3	690-65-3		62	2:1	48	78-79 (1.5)	1.4565
Allyl chloride CCl ₃ Br CCl ₃ CH ₃ CHBrCH ₂ Cl 20968-55-2 100 88 1:1 24 74-78 (1) 1.5328 1-Bromopentene-1 CF ₃ BrCFClBr CCl ₃ CH ₃ CH(CCl ₃)(CH ₂) ₅ CH ₃ 30428-55-2 100 88 1:1 24 74-78 (1) 1.5328 1-Bromopentene-1 CF ₃ BrCFClBr CHBr ₂ CH(CCl ₃)(CH ₂) ₅ CH ₃ 30428-53-6 38 63 2:1 48 79-81 (0.2) 1.5396 2-Chlorobutene-2 CCl ₃ Br CH ₅ CH(CCl ₃)CClBrCH ₃ 30428-54-7 70 42 2:1 48 62 (0.35) 1.5380 2-Chlorobutene-2 CCl ₃ Br CCl ₃ Br 30428-55-8 58 14 1:1 100 80-92 (0.65) 1.4577 BTFO ⁱ CCl ₃ Br CCl ₃ Br CCl ₃ CF ₂ CFBrCH=CH(CH ₃) ₃ CH ₃ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577 BTFO ⁱ CCl ₃ Br CCl ₃ CF ₂ CFBrCH=CH(CH ₃) ₃ CH ₃ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577	Allyl chloride CCl ₃ Br CCl ₃ CH ₃ CHBrCH ₂ Cl 20968-55-2 100 88 1:1 24 74-78 (1) 1.5328 1-Bromopentene-1 CF ₃ BrCFCIBr T-Race 2:1 100 88 1:1 24 74-78 (1) 1.5328 1-Bromopentene-1 CF ₃ BrCFCIBr CHBr ₂ CH(CCl ₃)(CH ₂) ₂ CH ₃ 30428-53-6 38 63 2:1 48 79-81 (0.2) 1.5396 2-Chlorobutene-2 CCl ₃ Br CH ₃ CH(CCl ₃)(CH ₂) ₃ CH ₃ 30428-53-6 38 63 2:1 48 79-81 (0.2) 1.5380 2-Chlorobutene-2 CCl ₃ Br CH ₃ CH(CCl ₃)(CH ₂) ₃ CH ₃ 30428-55-6 38 63 2:1 48 62 (0.35) 1.5380 2-Chlorobutene-2 CCl ₃ Br CF ₃ BrCFCH ₃ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577 BTFO ⁱ CCl ₃ Br CCl ₃ CF2CFBrCH=CH(CH ₂) ₃ CH ₃ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577 Vor y analytical data were reported for all new comp	Allyl chloride CCl ₃ Br CCl ₃ CH ₃ CHBrCH ₂ Cl 20968-55-2 100 88 1:1 24 74-78 (1) 1.5328 1-Bromopentene-1 CF ₃ BrCFCIBr CHBr ₂ CH(CCl ₃)(CH ₂) ₂ CH $30428-55.2$ 100 88 1:1 24 74-78 (1) 1.5328 1-Bromopentene-1 CF ₃ BrCFCIBr CH ₃ CH(CCl ₃)(CH ₂) ₂ CH $30428-53.6$ 38 63 2:1 48 79-81 (0.2) 1.5330 2-Chlorobutene-2 CCl ₃ Br CH ₃ CH(CCl ₃)(CH ₂) ₂ CH ₃ $30428-55.4$ 70 42 2:1 48 62 (0.35) 1.5330 2-Chlorobutene-2 CCl ₃ Br CCl ₄ CrClBr $30428-55.4$ 70 42 2:1 48 62 (0.55) 1.4577 BTFO' CCl ₃ Br CCl ₄ CrCH=/CH(CH ₂) ₂ CH ₃ $30428-55.4$ 58 14 1:1 90 80-92 (0.65) 1.4577 Vor y analytical data were reported for all new compounds listed in the table. b Yield (<i>via</i> glc) = moles of adduct formed/moles of olefin charged. ^d Olefinic product. ^e Two isomers. ^J Reported for CF ₂ BrCFCICH ₂ OH ₂ O	Allyl chloride	CF ₃ BrCFCIBr			89	9	2:1	48		
1-Bromopentene-1CF_3BrCFCIBr1-Bromopentene-1CF_3BrCFCIBr1-Bromopentene-1CCl_3Br1-Bromopentene-1CCl_3Br1-Bromopentene-1CCl_3Br1-Bromopentene-1CCl_3Br1-Bromopentene-1CCl_3Br1-Bromopentene-1CCl_3Br1-Bromopentene-1CCl_3Br1-Bromopentene-1CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2CCl_3Br2-Chlorobutene-2 <td>1-Bromopentene-1CF_3BrCFCIBrTrace2:11001-Bromopentene-1CCl_3BrCHBr_3CH(CCl_3)(CH_2)_3CH_3$30428-53.6$$38$$63$$2:1$$48$$79-81$$(0.2)$$1.5396$1-Bromopentene-1CCl_3BrCH_3CH(CCl_3)(CH_2)_3CH_3$30428-53-6$$38$$63$$2:1$$48$$79-81$$(0.2)$$1.5396$2-Chlorobutene-2CCl_3BrCH_3CH(CCl_3)(CH_2)_3CH_3$30428-55-6$$38$$63$$2:1$$48$$62$$(0.35)$$1.5380$3BTFOⁱCF_3BrCFCIBrCH_3CF_3CFBrCH=CH(CH_2)_3CH_3$30428-55-8$$58$$14$$1:1$$90$$80-92$$(0.65)$$1.4577$BTFOⁱCCl_3BrCCl_3BrCCl_3Br$0404ct$$1:1$$90$$80-92$$(0.65)$$1.4577$bry analytical data were reported for all new compounds listed in the table. ^b Yield (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = 0.0000000000000000000000000000000000</td> <td>I-Bromopentene-1 CF₃BrCFCIBr Trace 2:1 100 1-Bromopentene-1 CCl₃Br CHBr₂CH(CCl₃)(CH₂)₂CH₃ $30428-53.6$ 38 63 $2:1$ 48 $79-81$ (0.2) 1.5396 1-Bromopentene-1 CCl₃Br CH₃CH(CCl₃)(CH₂)₂CH₃ $30428-53.6$ 38 63 $2:1$ 48 62 (0.35) 1.5396 2-Chlorobutene-2 CCl₃Br CH₃CH(CCl₃)CCIBrCH₃ $30428-55.4$ 70 42 $2:1$ 48 62 (0.35) 1.5380 BTFOⁱ CCl₃Br CCH₄CH(CL₃)CCH₂CH₃CH₃ $30428-55.8$ 58 14 $1:1$ 90 $80-92$ (0.65) 1.4577 Vory analytical data were reported for all new compounds listed in the table. ^b Yield (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is uned/moles of olefin charged. ^e Olefinic product. ^e Two isomers. ^f Reported for CF₃BrCFCICH₂OCH₂OH₃OH₃OH₃OH₄, bp 75^o (1.5 mm), $n^{23}0$ 1.4577 w_{a}, 26, 4646 (1961). ^e Reported for CCI₃CH₂OL₃DH₃, $n^{3}n_{2}$ 1.5337; M. S. Kharasch, O. Reinmuth, and W. H. Urry, J. Amer. Chem. Soc. 69, 1105 (1947).</td> <td>Allyl chloride</td> <td>CCl₃Br</td> <td>CCl₃CH₃CHBrCH₂Cl</td> <td>20968 - 55 - 2</td> <td>100</td> <td>88</td> <td>1:1</td> <td>24</td> <td>74-78 (1)</td> <td>1.5328</td>	1-Bromopentene-1CF_3BrCFCIBrTrace2:11001-Bromopentene-1CCl_3BrCHBr_3CH(CCl_3)(CH_2)_3CH_3 $30428-53.6$ 38 63 $2:1$ 48 $79-81$ (0.2) 1.5396 1-Bromopentene-1CCl_3BrCH_3CH(CCl_3)(CH_2)_3CH_3 $30428-53-6$ 38 63 $2:1$ 48 $79-81$ (0.2) 1.5396 2-Chlorobutene-2CCl_3BrCH_3CH(CCl_3)(CH_2)_3CH_3 $30428-55-6$ 38 63 $2:1$ 48 62 (0.35) 1.5380 3BTFO ⁱ CF_3BrCFCIBrCH_3CF_3CFBrCH=CH(CH_2)_3CH_3 $30428-55-8$ 58 14 $1:1$ 90 $80-92$ (0.65) 1.4577 BTFO ⁱ CCl_3BrCCl_3BrCCl_3Br $0404ct$ $1:1$ 90 $80-92$ (0.65) 1.4577 bry analytical data were reported for all new compounds listed in the table. ^b Yield (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = 0.0000000000000000000000000000000000	I-Bromopentene-1 CF ₃ BrCFCIBr Trace 2:1 100 1-Bromopentene-1 CCl ₃ Br CHBr ₂ CH(CCl ₃)(CH ₂) ₂ CH ₃ $30428-53.6$ 38 63 $2:1$ 48 $79-81$ (0.2) 1.5396 1-Bromopentene-1 CCl ₃ Br CH ₃ CH(CCl ₃)(CH ₂) ₂ CH ₃ $30428-53.6$ 38 63 $2:1$ 48 62 (0.35) 1.5396 2-Chlorobutene-2 CCl ₃ Br CH ₃ CH(CCl ₃)CCIBrCH ₃ $30428-55.4$ 70 42 $2:1$ 48 62 (0.35) 1.5380 BTFO ⁱ CCl ₃ Br CCH ₄ CH(CL ₃)CCH ₂ CH ₃ CH ₃ $30428-55.8$ 58 14 $1:1$ 90 $80-92$ (0.65) 1.4577 Vory analytical data were reported for all new compounds listed in the table. ^b Yield (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is uned/moles of olefin charged. ^e Olefinic product. ^e Two isomers. ^f Reported for CF ₃ BrCFCICH ₂ OCH ₂ OH ₃ OH ₃ OH ₃ OH ₄ , bp 75 ^o (1.5 mm), $n^{23}0$ 1.4577 w_{a} , 26, 4646 (1961). ^e Reported for CCI ₃ CH ₂ OL ₃ DH ₃ , $n^{3}n_{2}$ 1.5337; M. S. Kharasch, O. Reinmuth, and W. H. Urry, J. Amer. Chem. Soc. 69, 1105 (1947).	Allyl chloride	CCl ₃ Br	CCl ₃ CH ₃ CHBrCH ₂ Cl	20968 - 55 - 2	100	88	1:1	24	74-78 (1)	1.5328
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$ \begin{array}{cccccc} 2 \ \ CCl_{3}Br \\ BTFO^{i} \\ CCl_{3}Br \\ $	$ \begin{array}{cccccc} 2 \text{CCl}_{3}\text{Br} & \text{CH}_{3}\text{CH}(\text{CCl}_{3}\text{)}\text{CCIBrCH}_{3} & 30428-54-7 & 70 & 42 & 2:1 & 48 & 62 & (0.35) & 1.5380 \\ \text{BTFO}^{i} & \text{CF}_{2}\text{BrCFCIBr} & \text{CH}_{3}\text{CF}_{2}\text{CFBrCH}_{-}\text{CH}(\text{CH}_{3})_{3}\text{CH}_{3} & 30428-55-8 & 58 & 14 & 1:1 & 90 & 80-92 & (0.65) & 1.4577 \\ \text{BTFO}^{i} & \text{CC}_{3}\text{Br} & \text{CC}_{3}\text{Br} & \text{CH}_{3}\text{CF}_{2}\text{CFBrCH}_{-}\text{CH}(\text{CH}_{3})_{3}\text{CH}_{3} & 30428-55-8 & 58 & 14 & 1:1 & 90 & 80-92 & (0.65) & 1.4577 \\ tory analytical data were reported for all new compounds listed in the table. b Yield (via gle) = moles of adduct formed/moles of olefin consumed. e Conversion (via gle) = moles be adduct formed/moles of olefin consumed. e Conversion (via gle) = moles be adduct formed/moles of olefin consumed. e Conversion (via gle) = moles be adduct formed/moles of olefin consumed. e Conversion (via gle) = moles be adduct formed/moles of olefin consumed. e Conversion (via gle) = moles be adduct formed/moles of olefin consumed. e Conversion (via gle) = moles be adduct formed/moles of olefin consumed. e Conversion (via gle) = moles be adduct formed/moles of olefin consumed. e Conversion (via gle) = moles be adduct formed/moles of olefin consumed. e Conversion (via gle) = moles be adduct formed/moles of olefin consumed. e Conversion (via gle) = moles be adduct formed/moles of olefin consumed. e Conversion (via gle) = moles be adduct for constanted. e Conversion (via gle) = moles be adduct for constanted. e Conversion (via gle) = moles be adduct for constanted. e Conversion (via gle) = moles be adduct for constanted. e Conversion (via gle) = moles be adduct for constanted. e Conversion (via gle) = moles be adduct for constanted. e Conversion (via gle) = moles be adduct for constanted. e Conversion (via gle) = moles be adduct for constanted. e Conversion (via gle) = moles be adduct for constanted. e Conversion (via gle) = 0 & 0.105 & 0.105 & 0.105 & 0.105 & 0.105 & 0.105 & 0.105 & 0.105 & $	$ \begin{array}{ccccc} 2\text{-Chlorobutene-2} & \text{CCl}_3\text{Br}\text{CH}(\text{CCl}_3)\text{CCIBrCH}_3 & 30428-54-7 & 70 & 42 & 2:1 & 48 & 62 (0.35) & 1.5380 \\ \text{BTFO} & \text{CF}_3\text{Br}\text{CFCIBr} & \text{CH}_3\text{CH}(\text{CCl}_3)\text{CCIBrCH}_3 & 30428-55-8 & 58 & 14 & 1:1 & 90 & 80-92 (0.65) & 1.4577 \\ \text{OC}_3\text{Br} & \text{CC}_3\text{Br} & \text{CC}_3\text{Br} & \text{CH}_3\text{CH}(\text{CH}_3), \text{CH}_3 & 30428-55-8 & 58 & 14 & 1:1 & 90 & 80-92 (0.65) & 1.4577 \\ \text{lory analytical data were reported for all new compounds listed in the table. } Yield (via glc) = moles of adduct formed/moles of olefin consumed. ° Conversion (via glc) = moles \\ \text{lorw mod/moles of olefin charged. } dolefinic product. ° Two isomers. ' Reported for CF_3BrCFICICH_5CHBrCH_5OCH_5OH_5, bp 75° (1.5 mm), n^{23}0 1.4534: P. Tarrant and E. C. Stump, \\ m', 26, 4646 (1961). \\ \circ \text{ Reported for CCl_5CH_5CHBrCH_2CH, bp 59-60° (0.6 mm), n^{30}D 1.5337: M. S. Kharasch, O. Reinmuth, and W. H. Urry, J. Amer. Chem. Soc. 69, 1105 (1947). \\ \end{array}$	1-Bromopentene-1	CCI _a Br	CHBr ₂ CH(CCl ₃)(CH ₂) ₂ CH ₃	30428-53-6	38	63	2:1	48	79-81 (0.2)	1.5396
BTFO ⁱ CF ₂ BrCFCIBr CGl ₃ CF ₂ CFBrCH—CH(CH ₂) ₃ CH ₃ ⁱ $30428-55-8$ 58 14 1:1 100 CCl ₃ Br CCl ₃ CF ₂ CFBrCH—CH(CH ₂) ₃ CH ₃ ⁱ $30428-55-8$ 58 14 1:1 90 80-92 (0.65) 1.4577 tory analytical data were reported for all new compounds listed in the table. ^b Yield (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> gle) = moles of adduct formed/moles of formed/moles of adduct formed/moles of adduct formed/moles of adduct formed/moles of adduct formed/moles of formed/moles of adduct formed/moles of adduct formed/moles of adduct formed/moles of adduct formed/moles of fo	BTFO ⁱ CF ₂ BrCFCIBr BTFO ⁱ CC ₃ BrCFCIBr BTFO ⁱ CC ₃ Br CC ₃ BrCFCIBr BTFO ⁱ CC ₃ Br CC ₃ Br CC ₃ CF ₂ CFBrCH=CH(CH ₂) ₃ CH ₃ ⁱ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577 tory analytical data were reported for all new compounds listed in the table. ^b Yield (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> glc) = moles sumed/moles of olefin charged. ^e Olefinic product. ^e Two isomers. ^J Reported for CF ₂ BrCFCICH ₂ OCH ₅ OCH ₅ OCH ₅ , bp 75 ^o (1.5 mm), n^{23} D 1.4534: P. Tarrant and E. C. Stump, ^{end} Content of the context of the construction (<i>via</i> glc) = moles of adduct formed/moles of formed. ⁿ Conversion (<i>via</i> glc) = moles ^{end} CH ₂ OCH ₅ OCH	BTFO ⁱ CF ₂ BrCFClBr CCl ₃ CFCFBrCH=CH(CH ₂),CH ₃ ⁱ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577 BTFO ⁱ CCl ₃ Br CCl ₃ Br CCl ₃ CF ₂ CFBrCH=CH(CH ₂),CH ₃ ⁱ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577 tory analytical data were reported for all new compounds listed in the table. ^b Yield (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> glc) = moles sumed/moles of olefin charged. ^d Olefinic product. ^e Two isomers. ^J Reported for CF ₃ BrCFCICH ₃ CHBrCH ₃ OCH ₃ , bp 75 ^o (1.5 mm), n^{33} D 1.4534: P. Tarrant and E. C. Stump, m, 26, 4646 (1961). ^e Reported for CCl ₃ CH ₂ CHBrCH ₂ CI, bp 59-60 ^o (0.6 mm), n^{30} D 1.5337: M. S. Kharasch, O. Reinmuth, and W. H. Urry, J. Amer. Chem. Soc. 69, 1105 (1947).	2-Chlorobutene-2	CClaBr	CH ₃ CH(CCl ₃)CClBrCH ₃	30428 - 54 - 7	20	42	2:1	48	62 (0.35)	1.5380
BTFO ⁱ CCl ₃ Br CCl ₃ Br CCl ₃ CF ₂ CFBrCH=CH(CH ₂) ₃ CH ₃ ⁱ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577 tory analytical data were reported for all new compounds listed in the table. ^b Yield (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (<i>via</i> glc) = moles of adduct formed/moles	BTFO ⁱ CCl ₃ Br CCl ₃ Br CCl ₃ CFBrCH=CH(CH ₃) ₃ CH ₃ ⁱ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577 tory analytical data were reported for all new compounds listed in the table. ^b Yield (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is a difference of the construction (<i>via</i> gle) = moles is adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> gle) = moles is a distributed of the constant is addict formed/moles of olefin constant is addict formed/moles of olefin constant is addict formed of the constant is addicted of the constant is addicted of	BTFO ¹ CCl ₃ Br CCl ₃ Br CCl ₃ CF ₂ CFBrCH=CH(CH ₂) ₃ CH ₃ ⁱ 30428-55-8 58 14 1:1 90 80-92 (0.65) 1.4577 tory analytical data were reported for all new compounds listed in the table. ^b Yield (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> glc) = moles sumed/moles of olefin charged. ^d Olefinic product. ^e Two isomers. ^J Reported for CF ₂ BrCFCICH ₃ CHBrCH ₅ OCH ₅ CH ₅ , bp 75 ^o (1.5 mm), n^{33} D 1.4534: P. Tarrant and E. C. Stump, m_{2} , 26, 4646 (1961). ^e Reported for CCl ₃ CHBrCH ₂ CH, me, N. S. Kharasch, O. Reinmuth, and W. H. Urry, J. Amer. Soc. 69, 1105 (1947).	BTFO ¹	CF ₂ BrCFCIBr				Trace	1:1	100		
tory analytical data were reported for all new compounds listed in the table. ^b Yield (via glc) = moles of adduct formed/moles of olefin consumed. ^c Conversion (via glc) = moles	the provide the state of a second state of the second	tory analytical data were reported for all new compounds listed in the table. ^b Yield (<i>via</i> glc) = moles of adduct formed/moles of olefin consumed. ^e Conversion (<i>via</i> glc) = moles is unded/moles of olefin charged. ^d Olefinic product. ^e Two isomers. ^J Reported for CF ₃ BrCFCICH ₃ CHBrCH ₃ OCH ₂ CH ₃ , bp 75° (1.5 mm), n^{33} D 1.4534: P. Tarrant and E. C. Stump, m_{2} , 26, 4646 (1961). ^e Reported for CCl ₃ CHBrCH ₂ CH, bp 75° (1.6 mm), n^{30} D 1.5337: M. S. Kharasch, O. Reinmuth, and W. H. Urry, J. Amer. Soc., 69, 1105 (1947).	BTFO	CCl _a Br	CCl ₃ CF ₂ CFBrCH=CH(CH ₂) ₃ CH ₃ ^j	30428 - 55 - 8	58	14	1:1	0 6	80-92 (0.65)	1.4577
	with the construction of the function of the construction of the const	Burned/moles of olefin charged. ^a Olefinic product. ^a Two isomers. ^b Reported for CF ₃ BTCFUCUCH ₃ CHBFUF ₃ CHBFUF ₃ of the transmerter of	 ory analytical data we	re reported for all r	new compounds listed in the table. ^b Yield (i a g	glc) = moles of	adduct for	med/mol	es of olefin c	onsumed.	^e Conversion (via	glc) = moles

TABLE

Thus, attack by the $CF_2BrCFCl$ radical occurs preferentially at the 1 carbon to form a secondary radical rather than at the 2 carbon to give a less stable primary radical. When attempting to predict the orientation of radical attack in substituted olefins, however, several directive effects (*e.g.*, steric factors, electronic effects, and radical stabilization effects) must be considered.

It was anticipated that addition to an internal olefin would give rise to two isomeric products, since attack by the CF₂BrCFCl· radical at either of the two olefinic carbons would give rise to secondary radicals. This was indeed found to be the case. With 2-octene, two products were formed: CH₃CHBrCH(CFClCF₂Br)CH₂-(CH₂)₃CH₃ and CH₃CH(CFClCF₂Br)CHBrCH₂(CH₂)₃-CH₃. A vpc indicated that the ratio of these two isomers in the reaction mixture was 2:1. No attempt was made to determine the structure of the predominant isomer.

The accessibility of the double bond to attack by a bulky polyhaloalkane radical was a major factor in determining the reactivity of an olefin. For example, the reaction of CF₂BrCFClBr with 1-octene⁵ gave a 96% conversion of olefin, while with 2-octene, even after 79 hr, 62% of the initial olefin was recovered unreacted. For the purpose of simplification, 2-octene can be considered a terminal olefin with a methyl group substituted for one of the hydrogens on the 1 carbon. Apparently, the increased bulk of the CH₃ group compared to hydrogen is enough to inhibit attack by the CF_2Br -CFCl radical. However, if the methyl group is substituted for hydrogen on the 2 carbon no decrease in reactivity is noted. The reaction of 2-methylpentene-1 gave complete conversion to product after only 24 hr, for in this case there was no hindrance to attack by the $CF_2BrCFCl$ · radical at the 1 carbon. However, the yield of 1:1 adduct dropped to 17%. The major product in the reaction was CF₂BrCFClCH=C(CH₃)CH₂- CH_2CH_3 , formed by the loss of a hydrogen atom from the incipient radical CF₂BrCFClCH₂C(CH₃)CH₂CH- CH_3 . This olefin formation was not unexpected, as Lovelace⁶ has described the formation of CCl₃CH=C- $(CH_3)_2$ from the reaction of CCl_4 with isobutylene, an olefin which also has a methyl group attached to the 2 carbon. Tarrant and Tandon⁷ have recently reported formation of the terminal olefins CF₂ClCF₂- $CCl_2CH_2C(CH_3) = CH_2$ and $CF_3CF_2CCl_2CH_2C(CH_3) =$ CH_2 from the peroxide-initiated reaction of isobutylene with $CF_2ClCF_2CCl_3$ and $CF_3CF_2CCl_3$, respectively. No explanation was given for this phenomenon.

The especially low yield of the 1:1 cyclohexene adduct (60%) is reasonable, as Huyser⁸ has reported an exceptional amount of allylic attack by radicals on cyclohexene.

The styrene adducts were thermally unstable and in our hands could not be isolated in pure form by distillation or preparative vpc. This instability can be attributed to the presence of an extremely labile benzylic bromine or chlorine atom on the expected adducts, and to the increased acidity of hydrogen on carbon adjacent to a CFClCF₂X group.

The additions to halo olefins constitute a special series of their own. Allyl chloride, for example, was

- (7) P. Tarrant and J. P. Tandon, J. Org. Chem., 34, 864 (1969).
- (8) E. S. Huyser, ibid., 26, 3261 (1961).

⁽⁶⁾ A. M. Lovelace, M.S. Thesis, University of Florida, 1952.

found to be reactive under redox conditions, but apparently underwent attack on the reactive chlorine atom more rapidly than addition of CF₂BrCFClBr could occur. This behavior was surprising, as Tarrant and Gillman⁹ reported a 45% yield of 1:1 adduct from this reaction utilizing peroxide initiation. There are other indications, however, that allyl chloride is less reactive to polyhaloalkane additions than are hydrocarbon olefins. Tarrant and Tandon⁷ report that neither CF₃-CF₂CCl₈ nor CF₂ClCF₂CCl₄ reacted with allyl chloride (peroxide initiation), while both of these telogens were reactive with propylene. When we repeated the allyl chloride reaction with the more reactive CCl₃Br, under redox conditions, a good yield of 1:1 adduct was obtained.

Tarrant¹⁰ has reported other examples of decreased reactivity of bromo and chloro olefins to radical attack when compared to ordinary hydrocarbons, and the data in Table I lend support to this contention. For example, even after 100 hr, CF₂BrCFClBr gave only traces of adduct with 1-bromopentene and 4-bromo-1,1,2-trifluorooctene-1. By again selecting a more reactive polyhalide, CCl₃Br, the desired adducts were obtained. In these last additions the halogen atoms exerted quite interesting directive effects, and apparently, consideration of steric interactions is not the entire story. For example, a CCl_{a} radical has little to choose between attack at the 1 or the 2 carbon of 1-bromopentene if only steric interactions are considered. However, reaction with CCl₃Br gave almost exclusively one product, CHBr₂CH(CCl₃)CH₂CH₂CH₃. A vpc of the reaction mixture indicated that the product was approximately 90% one compound, with possibly 10% of another isomer. The isolated product gave a pmr spectrum with two methine proton signals, the first, a doublet centered at δ 6.5, and the second, an unresolved multiplet centered around δ 3.2. If the addition adduct was the CCl₃CHBrCHBrCH₂CH₂CH₃ isomer (A), a signal corresponding to the methine proton on the 3 carbon would be expected in the δ 4.2 region. Furthermore, an attempted dehalogenation procedure gave only unreacted starting material. If the product was A, loss of Br_2 to give an olefin would be expected.

Chlorine is electron attracting and a trichloromethyl radical is therefore quite electrophilic. The 1 carbon of 1-bromopentene-1 is relatively electron-poor, and the CCl_3 radical is thus more inclined to attack at the 2 carbon than at the 1 position. A similar argument has been used by Stacey and Harris to explain radical addition of thiols¹¹ and HBr¹² to fluoro olefins, and by Davies and Rowley¹³ to explain exo attack of CCl_3 radicals on 1,4,7,7-tetrachloronorborn-2-ene. An alternative explanation is the possibility of stabilization of the $\dot{CHBrCH(CCl_3)CH_2CH_2CH_3$ radical by the bromine atom.

The addition of CCl₃Br to 2-chlorobutene-2 showed similar directive effects, but steric interactions cannot be ruled out in this case. As with the 1-bromopentene-1 reaction, the product appeared to contain a small amount ($\sim 10\%$) of a second isomeric product. Adduct XII is the same product that was obtained by Tarrant 10 from the peroxide-initiated reaction of CCl₃Br with 2-chlorobutene-2.

A final example of the decreased reactivity of halogenated olefins is apparent in the reactions of 4-bromo-1,1,2-trifluorooctene-1. Even bromotrichloromethane gave a poor olefin conversion, a result that could hardly be ascribed to steric hindrance. Most probably, the decreased reactivity of the electron-poor fluoro olefin to attack by the electrophilic CCl_3 radical is the important factor. The formation of what appeared to be the olefin $CCl_3CF_2CFBrCH=CH(CH_2)_3CH_3$ must be ascribed to the unusual acidity of hydrogen on the carbon adjacent to the CFBr group.

The adducts from 1-octene, 1-hexene, and 2-octene reacted with alcoholic KOH, giving ready dehydrohalogenation. The adduct from allyl chloride also underwent dehydrohalogenation, but we obtained a mixture of products, probably due to the reactivity of the allylic chlorine atoms on the expected product, CCl₃ CH=CHCH₂Cl. Similarly, adduct XI gave a mixture of products, undoubtedly for the same reason.

Some preliminary attempts to carry out these redoxcatalyzed additions with simple acetylenes gave no addition adducts.

Experimental Section

The elemental analyses and spectral data of all the compounds that were identified were consistent with the given structures. Boiling points are uncorrected. Elemental analyses were performed by personnel in this laboratory. Infrared spectra were obtained on a Perkin-Elmer Model 21 double-beam recording spectrophotometer. The pmr spectra (Table II) (neat, internal TMS) were recorded on a Varian A-60 instrument with tetramethylsilane as an internal standard. Vpc analyses were obtained with a F & M Model 720 gas chromatograph, and peak areas were used to calculate the yield of addition adducts.

Copper chloride was purified via the method of Keller and Wycoff.¹⁴ Bromotrichloromethane and styrene were distilled before use. The CF₂BrCFClBr⁹ and 1-bromopentene-1¹⁵ were prepared by the reported methods. The 2-chlorobutene-2 was prepared by the dehydrohalogenation of 2,3-dichlorobutane, which was prepared by the dehydrohalogenation of 2,3-dichlorobutane, which with alcoholic KOH (bp 62-64°). Synthesis of CF₂=CF-CH₂CHBr(CH₂)₃CH₃ is detailed below. All other materials were best commercial grade, used without further purification.

Addition of Perhaloalkanes to Olefins.—The experimental data for these addition reactions are compiled in Table I. A typical reaction procedure has been detailed previously.⁶

Initial reactions were catalyzed by freshly prepared copper(I) chloride. The copper(I) chloride is slowly oxidized by moist air to yield a green compound, $CuCl_2 \cdot 3Cu(OH)_2$. However, it was found that this partially oxidized mixture of Cu(I) and Cu(II) was an effective catalyst for these additions, and the *mixture* was therefore used to initiate subsequent addition reactions.

Dehydrohalogenation of CF₂BrCFClCH₂CHBr(CH₂)₃CH₃ (II). —A mixture of KOH (7.2 g) in ethanol (100 ml) was dripped slowly into 44.2 g of II at 100°. After refluxing for 1 hr the reaction mixture was poured into water and the organic layer was separated, washed, and dried. Distillation gave 14.9 g of product, bp 56-58° (1 mm), identified as CF₂BrCFClCH==CH(CH₂)₃-CH₃. Anal. Calcd for C₈H₁₁F₃ClBr: C, 34.4; H, 3.94. Found: C, 34.30; H, 3.87. The pmr and ir spectra were consistent with the above structure.

Dehydrohalogenation of CF₂BrCFClBr-2-Octene Adduct (IV). —A mixture of KOH (6.6 g) in ethanol (150 ml) was dripped slowly into 34.1 g of IV at 100°. After refluxing for 4 hr the reaction mixture was poured into water and the organic layer was separated, washed, and dried. Distillation gave 16.5 g of product, bp 52-55° (0.25 mm), identified as a mixture of CH₃-CH=C(CFClCF₂Br)CH₂(CH₂)₃CH₃ and CH₃C(CFClCF₂Br)=

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		PROTON MA	GNETIC RESONANCE DATA ^a		
	Chemical shifts, § (ppm)				
Adduct	Alkyl H	Isolated -CH2-	Methine H	Other	intensities
I	0.8-2.2 (m)	2.4-3.1 (m)	4.4 (m)		9:2:1
II	1.2-2.6 (m)	2.6-3.4 (m)		$CBrCH_3, 1.0 (3),$ $J_{HH} = 6.5$	7:2:3
II^{b}	0.7 - 3.2 (m)			CH=C, 5.0-5.8 (m)	10:1
III	0.7-2.2 (m)		4.5 (m) 2.4–3.5 (m)		13:1:1
IV	1.2-3.3 (m)		4.1-5.1 (m)		9:1
VII IX	1.2 (3), $J_{\rm HH} = 7.0$		4.4 (m)	All CH ₂ , $2.2-4.0$ (m) All H, $3.0-4.7$ (m)	3:1:6
XI	0.8-2.5 (m)		$6.5 (2), J_{\rm HH} = 1.0$ 3.2 (m)		7:1:1
XII	2.8(1) 1.9(2) $J_{\rm HW} = 6.5$		$3.6(4), J_{\rm HH} = 6.5$		3:3:1
XIV	0.7-3.4 (m)			CH==C, 6.4 (2 of 2), $J_{\rm HH} = 4.5, J_{\rm HF} = 13.5$ CH==C, 5.6 (4).	9:1:1

TABLE II Proton Magnetic Resonance Data

^a In parentheses is given the multiplicity of the peak; the coupling constants are in cps. ^b Olefinic product.

CH(CH₂)₄CH₃. Anal. Calcd for C₁₀H₁₅BrClF₃: C, 39.1; H, 4.89. Found: C, 39.2; H, 5.23. Both the ir and the pmr spectra (with a very broad signal, δ 5.5-6.3, for the two vinyl protons) were consistent with the above structure.

Dehydrohalogenation of $CCl_3CH_2CHBrCH_2C1$ (X).—The attempted dehydohalogenation of X gave a mixture of products, none of which were identified. This complex product mixture was similar to that obtained from the attempted dehydrohalogenation of CHClBrCH₂CHBr(CH₂)₆CH₃ described previously.⁵

Dehydrohalogenation of $CHBr_2CH(CCl_3)CH_2CH_2CH_3$ (XII).— The attempted dehydrohalogenation of XII, similar to the reaction of X, gave a mixture of products, none of which was identified.

Dehalogenation of $CF_2BrCFClCH_2CHBr(CH_2)_3CH_3$ (II).—Compound II (113 g) in isopropyl alcohol (50 ml) was added slowly to a slurry of granulated zinc (22.7 g) in isopropyl alcohol (100 ml) at 100°. After refluxing for 4 hrs the reaction mixture was poured into water and the organic layer was separated, washed,

and dried. Distillation gave 47.3 g of product, bp 68-69° (10 mm), identified as CF_2 =CFCH₂CHBr(CH₂)₈CH₃. Anal. Calcd for C₈H₁₂BrF₈: C, 39.2; H, 4.9. Found: C, 38.8; H, 4.91. The pmr and ir spectra were consistent with the above structure.

 $J_{\rm HH} = 5.5$

Dehalogenation of $CCl_3CH_2CHBrCH_2Cl$ (X).—Surprisingly, the attempted dehalogenation of X gave no identifiable product. However, only 40% of the starting material was recovered after the reaction.

Dehalogenation of $CHBr_2CH(CCl_3)CH_2CH_2CH_3$ (XI).—The attempted dehalogenation of XI gave no reaction and the starting material was recovered unchanged.

Registry No.—Copper chloride, 7758-89-6; ethanolamine, 141-43-5; CH₃CH=C(CFClCF₂Br)CH₂(CH₂)₃-CH₃, 30428-57-0; CH₃C(CFClCF₃Br)=CH(CH₂)₄CH₃, 30428-58-1; CF₂=CFCH₂CHBr(CH₂)₃CH₃, 30428-59-2; CF₂BrCFClCH=CH(CH₂)₃CH₃ 30428-56-9.

Mannich Reactions of 2-Fluoro-2,2-dinitroethanol¹

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2-Fluoro-2,2-dinitroethanol undergoes the Mannich reaction with primary and secondary amines to give the corresponding 2-fluoro-2,2-dinitroethylamines. In one example (allylamine), forcing conditions were used to obtain the corresponding bis(2-fluoro-2,2-dinitroethyl) amine. Hydrazine gave N,N'-bis(2-fluoro-2,2-dinitroethyl) hydrazine. Ammonia gave 2-fluoro-2,2-dinitroethylamine which reacted with chloroformates to give N-fluorodinitroethylcarbamates.

 β , β -Dinitro alcohols undergo the Mannich reaction with a variety of amines to give β , β -dinitroalkylamines.² Published examples of the Mannich reaction of 2fluoro-2,2-dinitroethanol are limited to ammonia^{3,4} and

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(4) R. G. Gafurov, S. I. Sviridov, F. Ya. Natsibullin, and L. T. Eremenko, Izv. Akad. Nauk SSSR, Ser. Khim., 383 (1970). to $\rm NH_2C(\rm CH_2OAc)_{3.5}$ Ammonia yielded 2-fluoro-2,2dinitroethylamine³ or bis(2-fluoro-2,2-dinitroethyl)amine,^{3,4} depending on the reaction conditions, whereas $\rm NH_2C(\rm CH_2OAc)_3$ gave the 1:1 condensation product. The present study explores the scope of the Mannich reaction of 2-fluoro-2,2-dinitroethanol.

The reactions of a variety of primary and secondary amines with 2-fluoro-2,2-dinitroethanol are summarized in Table I. In aqueous solution at low temperatures, high yields of 1:1 condensation products were formed, and other functional groups, such as carboxy, acetal, and hydroxy groups, did not interfere. The condensa-

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