Fluoro Olefins. XIII.[1] The Cycloaddition Reactions of Some Fluorobutadienes

DON LOMAS AND PAUL TARRANT[2]

Department of Chemistry, University of Florida, Gainesville, Florida 32601

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At 150–200°, in the presence of a polymerization inhibitor (terpineol), 1,1-difluoro-1,3-butadiene reacts with chlorotrifluoroethylene and 1,1-dichloro-2,2-difluoroethylene to give 1:1 addition products arising from 3,4 cycloaddition. Under similar conditions 1,1,2-trifluoro-1,3-butadiene reacts with tetrafluoroethylene, chlorotrifluoroethylene, and 1,1-dichloro-2,2-difluoroethylene giving 1:1 addition products arising from 1,2 and 3,4 cycloaddition. Products arising from the dimerization of 1,1,2-trifluoro-1,3-butadiene were also isolated. These results are consistent with the hypothesis that a bifunctional, diradical intermediate is formed as the first step in the cycloaddition process. The structures of the 1:1 cycloaddition products were elucidated on the basis of their ^1H and ^{19}F nuclear magnetic resonance and infrared spectra.

One of the characteristic reactions of fluoro olefins containing a terminal difluoromethylene group is their ability to undergo a cycloaddition reaction with themselves or with different olefins,[3] but little attention has been paid to the cycloaddition reactions of fluorine-containing butadienes, presumably owing to either their unavailability or their tendency to polymerize on heating.

Sharkey and coworkers[4] have shown that 1,1,4,4-tetrafluorobutadiene and perfluorobutadiene readily form cycloaddition products with tetrafluoroethylene to yield the respective polyfluorovinylcyclobutanes. Coffman, *et al.*,[5] obtained an equimolar mixture of 1:1 cycloaddition products arising from 1,2 and 3,4 addition of tetrafluoroethylene to 2-fluoro-1,3-butadiene.

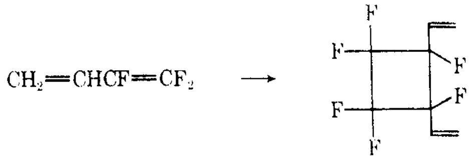
We are interested in observing the effects, if any, on the cycloaddition process when fluoro olefins were added to unsymmetrically substituted fluorobutadienes. 1,1-Difluoro-1,3-butadiene I and 1,1,2-trifluoro-1,3-butadiene II were chosen as reactants in this study as these were the most readily synthesized from available starting materials.

Results

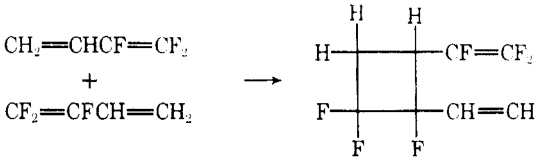
The cyclodimerization reactions between the fluoro olefins and the butadienes were carried out in a 130-ml stainless steel autoclave at 150–200° using a mole excess of the fluoro olefin in the presence of plolymerization inhibitor. In each reaction, together with the 1:1 codimerization products, there were obtained substantial amounts of perfluorochlorocyclobutanes produced by the self dimerization of the fluoro olefin. As would be expected, large amounts of polymeric material were obtained, presumably arising from the polymerization of the butadiene; in fact both I and II polymerized at temperatures above −10° to give a white rubbery material. As a direct consequence, yields of the 1:1 cycloaddition products were generally quite low, usually in the region of 10–15% based on the amount of diene used. The physical properties, together with elemental analysis results, of the new fluorine-containing vinylcyclobutanes are reported in Table I.

I with chlorotrifluoroethylene III yielded an equimolar mixture of *cis*- and *trans*-1-(1,1-difluorovinyl)-3,3,4-trifluoro-4-chlorocyclobutanes IV together with 1,2-dichlorohexafluorocyclobutane V. With 1,1-dichloro-2,2-difluoroethylene VI, I afforded 1-(1,1-difluorovinyl)-3,3-difluoro-4,4-dichlorocyclobutane VII as well as 1,1,2,2-tetrachlorotetrafluorocyclobutane VIII. No cycloaddition products arising from 1,2 addition were obtained in either of these reactions. No products arising from the dimerization of I were obtained.

II with tetrafluoroethylene IX gave both the 1:1 addition products, 1-vinylheptafluorocyclobutane X and 1-(trifluorovinyl)-3,3,4,4-tetrafluorocyclobutane XI, arising from 1,2 and 3,4 addition together with octafluorocyclobutane XII. With III, II afforded an equimolar mixture of *cis* and *trans* isomers of 1-vinyl-1,2,2,3,3,4-hexafluoro-4-chlorocyclobutane XIII and 1-(trifluorovinyl)-3,3,4-trifluoro-4-chlorocyclobutane XIV with some V. II and VI afforded 1-vinyl-1,2,2,3,3-pentafluoro-4,4-dichlorocyclobutane XV and 1-(trifluorovinyl)-3,3-difluoro-4,4-dichlorocyclobutane XVI together with some VIII. In the reaction of II with fluoro olefins some *trans*-1,4-divinylhexafluorocyclobutane XVII arising from the 1,2 cyclodimerization of II was obtained. A further higher boiling material was obtained and tentatively identified as the 1,2:3,4-cyclodimerization product, 1-(trifluorovinyl)-3,3,4-trifluoro-4-vinylcyclobutane XVIII.



XVII



XVIII

Determination of Structure

The orientations of the new fluorine-containing vinylcyclobutanes were obtained on the basis of their nuclear magnetic resonance spectra (nmr). The ^1H nmr spectrum, although in every case giving a complex split-

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[1] Part XII: P. Tarrant and H. Oliver, *J. Org. Chem.*, **31**, 1143 (1966).

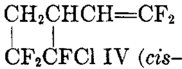
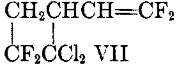
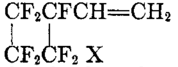
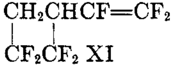
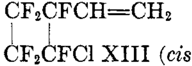
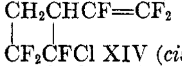
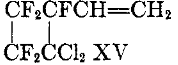
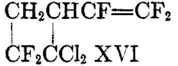
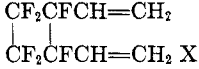
[2] To whom all correspondence should be addressed.

[3] W. H. Sharkey, *Fluorine Chem. Rev.*, in press.

[4] R. E. Putnam, J. L. Anderson, and W. H. Sharkey, *J. Amer. Chem. Soc.*, **83**, 386 (1961).

[5] D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, *ibid.*, **71**, 490 (1949).

TABLE I
THE CYCLOADDITION PRODUCTS ARISING FROM THE REACTION BETWEEN FLUORO OLEFINS AND FLUORINE-CONTAINING BUTADIENES

Olefin[a]	Diene	Product	Bp, °C	$n^{22.5}D$	Mol wt[e]	Calcd,[d] % C	Calcd,[d] % H	Found,[d] % C	Found,[d] % H
$CF_2{=}CFCl$ III	$CH_2{=}CHCHCF_2$ I	 $\begin{array}{l}CH_2CHCH{=}CF_2\\ \vert\ \ \vert\\ CF_2CFCl\end{array}$ IV (*cis-trans*)	108–109	1.3726	206	34.86	1.94	35.47	2.23
$CF_2{=}CCl_2$ VI	I	 $\begin{array}{l}CH_2CHCH{=}CF_2\\ \vert\ \ \vert\\ CF_2CCl_2\end{array}$ VII	131–133	1.4102	222	32.29	1.78	32.34	1.94
$CF_2{=}CF_2$ IX	$CF_2{=}CFCH{=}CH_2$	 $\begin{array}{l}CF_2CFCH{=}CH_2\\ \vert\ \ \vert\\ CF_2CF_2\end{array}$ X	55[b]	1.3072		34.61	1.44	34.74	1.64
		 $\begin{array}{l}CH_2CHCF{=}CF_2\\ \vert\ \ \vert\\ CF_2CF_2\end{array}$ XI	93[b]	1.3350	208	34.61	1.44	35.45	1.92
III	II	 $\begin{array}{l}CF_2CFCH{=}CH_2\\ \vert\ \ \vert\\ CF_2CFCl\end{array}$ XIII (*cis-trans*)	87.5[b]	1.3508	224	32.07	1.34	32.10	0.77
		 $\begin{array}{l}CH_2CHCF{=}CF_2\\ \vert\ \ \vert\\ CF_2CFCl\end{array}$ XIV (*cis-trans*)	115.0[b]	1.3665	224	32.07	1.34	32.22	1.45
VI	II	 $\begin{array}{l}CF_2CFCH{=}CH_2\\ \vert\ \ \vert\\ CF_2CCl_2\end{array}$ XV	119[b]	1.3895		29.88	1.24	29.95	1.43
		 $\begin{array}{l}CH_2CHCF{=}CF_2\\ \vert\ \ \vert\\ CF_2CCl_2\end{array}$ XVI	141[b]	1.4018	240	29.88	1.24	29.84	1.42
VI	II	 $\begin{array}{l}CF_2CFCH{=}CH_2\\ \vert\ \ \vert\\ CF_2CFCH{=}CH_2\end{array}$ XVII (*trans*)	(112)[c]	1.3654	216	44.44	2.77	44.40	2.83

[a] A 1 mol excess used. [b] By capillary. [c] Polymerized at this temperature. [d] Analysis carried out by Peninsular ChemResearch, Inc., Gainesville, Fla. 32601, and by Galbraith Laboratories, Knoxville, Tenn. [e] From mass pattern.

ting pattern due to the H–H and F–H coupling, was utilized to indicate whether the cycloaddition which had taken place involved either the 1–2 or 3–4 carbon–carbon double bonds. It is now well established that nonconjugated olefinic proton frequencies fall between τ 4.3 and 5.4[6] and the cyclic proton frequency in cyclobutane is at τ 8.04 relative to tetramethylsilane (TMS).[7] Using these standards for comparison the orientations of the vinylcyclobutanes could be identified. In several cases the splitting pattern due to the individual protons could be assigned and these together with the other vinylcyclobutanes are listed in Table II.

TABLE II
^1H NMR FREQUENCIES[a] (τ VALUES)

Vinylcyclobutane	Vinylic hydrogen	Ring hydrogen
IV	5.62–6.18 (1 H)	6.54–7.26 (1 H) 7.40–8.33 (2 H)
VII	5.35–5.89 (1 H)	6.32–6.82 (1 H) 6.93–7.87 (2 H)
X	4.25–4.82	
XI		6.28–7.3 (1 H) 7.36–8.04 (2 H)
XIII	4.2–4.82	
XIV		6.11–7.77
XV	4.07–4.68	
XVI		6.14–7.49
XVII	4.27–5.0	

[a] Nmr spectra were recorded as neat liquids with tetramethylsilane as the external reference.

The ^{19}F nmr spectra[8] were consistent with those expected from the proposed structures. The exocyclic trifluorovinyl group in XI, XIV, and XVI gave a characteristic AMX spectrum with further small coupling due to the fluorines and the hydrogens on the ring. The fluorine α to the ring always appeared upfield with respect to the two fluorines β to the ring, at +175–180 ppm from $CFCl_3$. The fluorine *trans* to the α fluorine occurred in the region +118–123 ppm from $CFCl_3$ while the β fluorine *cis* to the α fluorine was +98–105 ppm from $CFCl_3$.

The exocyclic difluoromethylene group in IV and VII comprised the AB part of an ABX pattern. The chemical shifts of the compound IV were +84.0 and +80.6 ppm from $CFCl_3$ while the chemical shifts due to VII were +82.1 and +84.8 ppm upfield from $CFCl_3$.

The difluoromethylene group in the ring system exhibited an AB quartet. Each half of the quartet coupled differently to the other hydrogens and fluorines in the ring. The chemical shifts due to this difluoromethylene group ranged from +97 to +135 ppm from $CFCl_3$.

The ring chlorofluoromethylene group in IV, XIII, and XIV ranged from +110 to +142 ppm from $CFCl_3$. The coupling pattern in this case of course depended on the other fluorine and hydrogens in the ring, not only in bond distance but also in geometric relationship, that is whether the other species are *cis* or *trans* to the observed fluorine.

The fluorine α to the trifluorovinyl group in X, XIII, and XV appeared upfield from +171 to +192 ppm from $CFCl_3$. This was coupling not only with the other fluorines and hydrogens in the ring, but also with the exocyclic trifluorovinyl group.

Although the cyclodimerization reaction between fluoro olefins and fluorobutadienes led to the formation of fluorine-containing vinylcyclobutane, an alternative synthesis was carried out in one case to illustrate the generality of the method that could be used to identify the orientations of the products from the cyclodimeriza-

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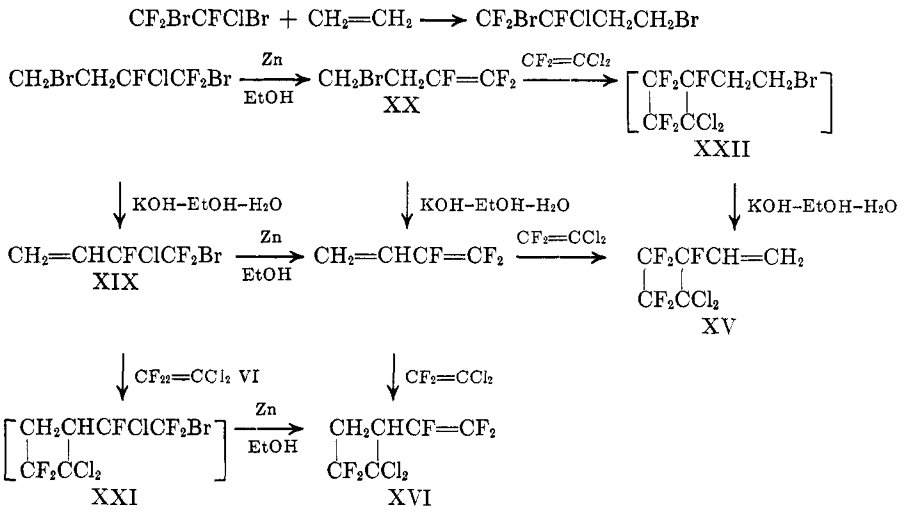
[6] R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Inc., Boston, Mass., 1966, p 426.

[7] I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967)

[8] Owing to the complexity of the spectrum a more detailed account will be published at a later date.

SCHEME I
SYNTHESES OF CYCLOBUTANES

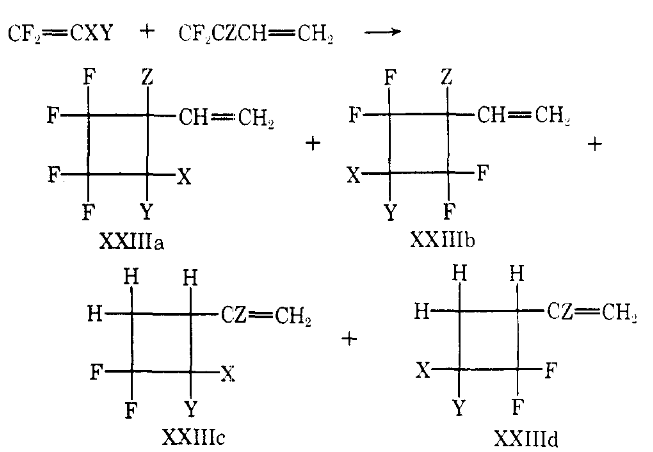


tion. This route, together with the original cyclodimerization reaction, is shown in Scheme I.

3-Chloro-3,4,4-trifluoro-4-bromobut-1-ene XIX on heating with a mole excess of VI gave XXI which was dehalogenated to give XVI. Similarly 1,1,2-trifluoro-4-bromobut-1-ene XX on heating with VI gave XXII which was dehydrobrominated to XVI.

Discussion

In an excellent study on the cyclodimerization of 1,1-dichloro-2,2-difluoroethylene with several butadienes, Bartlett[9] proposed that the structure of the product could be predicted by the rule that the most stable biradical intermediate determines the course of the reaction. In the codimerization reaction between unsymmetrically substituted fluoro olefins and fluorodienes it is theoretically possible that four 1:1 addition products could be formed (XXIIIa, b, c, or d) neglecting *cis–trans* isomers. The initial step in the cyclodimerization process is the formation of a single carbon–carbon bond between the diene and the fluoro olefin. As chlorine is able to stabilize a radical to a greater extent than fluorine,[10] it would be predictable that this initial step would take place between the difluoromethylene group on the fluoro olefin with a methylene group attached to the diene leaving the methylene group containing a chlorine atom free to stabilize the intermediate radical. This was shown to be the case. Only derivatives XXIIIa and XXIIIc arising from the intermediates XXIVa and XXIVb were obtained.

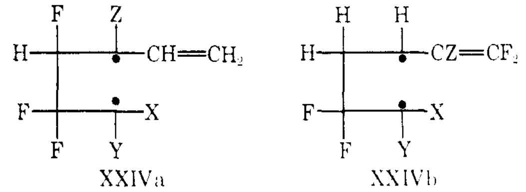


X = F or Cl
Y = Cl
Z = H or F

TABLE III
TYPE OF ADDITION REACTION

Olefin	Diene	Percentage addition[a] 1,2	3,4
$CF_2=CFCl$ III	$CF_2=CHCH=CH_2$ I		100
$CF_2=CCl_2$ VI	$CF_2=CHCH=CH_2$ I		100
$CF_2=CF_2$ IX	$CF_2=CFCH=CH_2$ II	26.2	73.8
$CF_2=CFCl$ III	$CF_2=CFCH=CH_2$ II	27.5	72.5
$CF_2=CCl_2$ VI	$CF_2=CFCH=CH_2$ II	40.9	59.1

[a] Estimated from vapor phase chromatography.



Coffman, *et al.*,[5] have shown that the addition of tetrafluoroethylene to 2-fluorobutadiene gives an equimolar mixture of vinylcyclobutanes arising from 1,2 and 3,4 cycloaddition. This indicates that the fluorine atom present at one of the radical sites has no effect on the mode of addition. We have, however, shown in our series of codimerization reactions that the presence of fluorine attached to the carbon atom in the 2 position has a pronounced effect, increasing the ratio of 1,2 to 3,4 addition products obtained. The results are tabulated in Table III.

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(9) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Amer. Chem. Soc.*, **84**, 616 (1964).

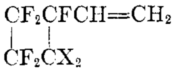
(10) A. L. Henne and D. W. Kraus, *ibid.*, **76**, 1175 (1954). These authors showed that CCl_3Br added to $CF_2=CFCl$ to give exclusively $CCl_3CF_2CFClBr$. Since CCl_3Br additions involve attack of trichloromethyl radical on olefin, $CCl_3CF_2CFCl\cdot$ must be more stable than $CCl_3CFClCF_2\cdot$.

As indicated above, I gave with III and VI only products arising from 3,4 cycloaddition indicating that the difluoroallyl radical is stabilized much more effectively than the allyl radical. This behavior is

$$-CH_2\dot{C}HCH{=}CF_2 \longleftrightarrow -CH_2CH{=}CHCF_2\cdot > -CF_2\dot{C}HCH{=}CH_2 \longleftrightarrow -CF_2CH{=}CHCH_2\cdot$$

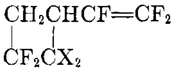
not totally unexpected since fluorine atoms are known to stabilize radicals more readily than hydrogen as shown by the fact that molecules such as CCl_3Br, CF_2Br_2, and $CF_2BrCFClBr$ add to vinylidene fluorides to give exclusively products of the type $R_hCH_2CF_2Br$ where R_h is a perhaloalkyl group.[11] Since the mechanism of addition is accepted to involve the attack of a perhaloalkyl radical on the olefin it follows that $R_hCH_2CF_2\cdot$ is much more stable than $R_hCF_2CH_2\cdot$.

Haszeldine[12] has found that CF_3I adds to $CF_2{=}CHCH_3$ to give $CF_2ICH(CF_3)CH_3$ which indicates that $CH_3(CF_3)CHCF_2\cdot$ is a more stable radical than $CH_3\dot{C}HCF_2CF_3$, a result that shows two fluorine atoms to be more effective than a methyl group in stabilizing a radical. However, with replacement of the hydrogen situated on the carbon atom in the 2 position by fluorine in the diene, *i.e.*, with II, both 1,2 and 3,4 cycloaddition products were obtained. These results can be rationalized if it is postulated that the initial carbon–carbon single bond is formed by attack of the terminal CF_2 group of the olefin on the terminal CH_2 group of the diene as indicated by the high percentage of 3,4 addition products obtained over 1,2 addition products. However, in the case where the diradical can be stabilized by the presence of a fluorine atom as happens with II, then both



$$\begin{array}{l}CF_2CFCH{=}CH_2\\ |\quad\ \ |\\ CF_2CX_2\end{array}$$

and



$$\begin{array}{l}CH_2CHCF{=}CF_2\\ |\quad\ \ |\\ CF_2CX_2\end{array}$$

are formed. Since the latter is formed preferentially $\sim CH_2\underset{\cdot}{C}HCF{=}\dot{C}F_2$ must be a more stabile radical than $\sim CF_2\underset{\cdot}{C}FCH{=}CH_2$. These results parallel those of Bartlett who in the codimerization reaction of VI with chloroprene obtained more 1,2 cycloaddition than 3,4 addition.

Owing to the free rotation about the single bond in the diradical transition states XXIVa and XXIVb (where X = F; Y = Cl), odds are even for closure for the *cis* or *trans* structures. This was shown to be true for the addition of III to I and II. Although the individual isomers were not isolated, ^{19}F nmr spectra indicated that the ratio of *cis/trans* isomers was approximately equal.

One interesting result was the product arising from the dimerization of II. Only *trans*-1,4-divinylhexafluorocyclobutane was isolated besides a presumed 1,2:3,4 dimer. It is highly improbable that only the *trans* 1,2 dimer was formed; thus the *cis* derivative was formed but underwent further reaction typical of this type of compound.

Experimental Section

All boiling points are uncorrected. Infrared spectra were recorded on a Beckman IR-8 spectrometer. Analytical and preparative vapor phase chromatography was performed on F & M Models 700 and 775, respectively. ^1H nuclear magnetic resonance (nmr) spectra were obtained using a Varian A-60A spectrometer with tetramethylsilane as external reference. The ^{19}F nmr spectra were obtained using a Varian DP-60 spectrometer operating at 56.4 Mc. The chemical shifts were determined by placing an audiofrequency side band of the internal reference $CFCl_3$ at the peak position being measued. The coupling constants were measured graphically using the side-band technique. Molecular weights were obtained from the mass pattern recorded on Hitachi Perkin-Elmer RMU-6E mass spectrometer operating at an ionizing voltage of 70 eV. Refractive indices were measured using a Bausch and Lomb recorder.

The fluoro olefins were obtained from Peninsular ChemResearch, Inc., Gainesville, Fla., and were used without further purification. 1,1,2-Trifluorobutadiene was prepared by dehalogenation of 4-bromo-3-chloro-3,4,4-trifluoro-1-butene with zinc dust in ethanol.[13] 1,1-Difluorobutadiene was prepared[14] by dehydrobromination of $CF_2BrCH_2CH{=}CH_2$ using potassium hydroxide.

Reaction between Fluoro Olefin and Fluorobutadiene.—In a typical experiment a 130-ml stainless steel autoclave was charged with the diene (0.1 mol), the fluoro olefin (0.2 mol), and terpineol (1 g). The autoclave was then heated for 15 hr at 150–200° and then vented into a cold trap while hot. The mixture of products was then distilled and the individual products were further purified by preparative scale vpc. The cyclobutane, obtained from dimerization of the olefin, was identified by its infrared spectrum by comparison with that of an authentic sample.

Synthesis of XVI.—A stainless steel autoclave (130 ml) was charged with $CH_2{=}CHCFClCF_2Br$ (0.2 mol) and VI (0.2 mol) and heated for 36 hr at 200°. The autoclave was cooled and vented and the reaction products were then distilled. A fraction boiling between 65 and 75 (0.1 mm) (7 g) was obtained which was shown by analytical vpc to consist mainly of one component. Dehalogenation of this product using zinc dust in ethanol afforded after distillation a clear liquid, bp 140–142° (2.1 g). This compound was identified as XVI from a comparison of infrared spectra.

Synthesis of XV.—A stainless steel autoclave (130 ml) was charged with $CF_2{=}CFCH_2CH_2Br$ (0.2 mol) and VI (0.2 mol) and heated at 200–210° for 36 hr. After cooling, the autoclave was vented and the reaction product then distilled under reduced pressure. A fraction, bp 63–65° (2 mm) (8.0 g), was obtained which was shown by analytical vpc to consist mainly of one product. Treatment of this fraction with potassium hydroxide (5 g) in methanol (25 ml) and water (25 ml) for 2 hr at reflux temperature afforded, after washing well with water and distillation, a clear liquid, bp 119–120° (3.1 g). This was identified as XV from a comparison of infrared spectra.

Registry No.—*cis* IV, 18521-20-5; *trans* IV, 18521-21-6; VII, 18543-03-8; X, 18543-04-9; XI, 18543-05-0; *cis* XIII, 18521-22-7; *trans* XIII, 18521-23-8; *cis* XIV, 18521-24-9; *trans* XIV, 18521-25-0; XV, 18543-06-1; XVI, 18543-07-2; *trans* XVII, 18521-26-1.

Acknowledgments—We would like to express our thanks to C. Watkins for interpretation of ^{19}F nmr and to C. Watkins and W. S. Brey, Jr., for running the ^{19}F nmr spectra. Our thanks also are extended to Peninsular ChemResearch, Inc., for a sample of 1,1,2,2-tetrachlorotetrafluorocyclobutane.

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[11] G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The MacMillan Co., New York, N. Y., 1964, Chapter 2.

[12] R. Haszeldine, *J. Chem. Soc.*, 3565 (1953).

[13] P. Tarrant and M. R. Lilyquist, *J. Amer. Chem. Soc.*, **77**, 3640 (1955).

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