linearity. Analysis under the restraint of collinearity, however, can be fruitful—one degree of freedom (three observations minus two parameters)—as is seen in Table V. In this event, minimum R values are clearly associated with the correct structures and higher R values with mismatched structures. Chemical shifts and observed and calculated relative slopes, assuming collinearity, appear in Table VI.

Table V. Minimum R Values (%) for Binary Combinations of Methylacrylonitrile Models **5**–**7** with Sets of Relative Slopes, with Collinearity Restraint

	LIS data set		
	5	6	7
Model 1-CH_3	2.9	31.7	9.7
Model *cis*-2-CH_3	6.0	26.6	2.8
Model *trans*-2-CH_3	29.3	1.5	27.1
Second best/best	2.06	17.7	3.46
Confidence level (%) for rejection of second best model	27	4	19

Table VI. Chemical Shifts and Observed and Calculated Relative Slopes, Methylacrylonitrile: Yb(dpm)$_3$, with Collinearity Restraint

Type of hydrogen	Chem shift (δ)	Rel slopes	
		Obsd	Calcd
	1-Methylacrylonitrile[a]		
CH_3	1.96	8.17	8.34
H_1 cis	5.74	10.00	10.10
H_1 trans	5.60	6.94	6.56
	cis-2-Methylacrylonitrile[b]		
CH_3	2.04	6.59	6.74
H_1	5.26	10.00	10.08
H_2	6.46	5.83	5.49
	trans-2-Methylacrylonitrile[c]		
CH_3	1.96	4.02	3.86
H_1	5.32	10.00	9.96
H_2	6.62	8.20	8.32

[a] $R = 2.9\%$. [b] $R = 2.8\%$. [c] $R = 1.5\%$.

We are encouraged to believe that the collinearity hypothesis will receive support from additional studies now underway, and that the potentially exciting opportunities in structure determination offered by the nitrile group may be realized.

Acknowledgment. We acknowledge with gratitude the financial support of this work provided by the National Science Foundation (to W. von E. D.) and by the Robert A. Welch Foundation (Grant E-183 to M. R. W. and Grant F-233 to R. E. D.).

(7) John Simon Guggenheim Fellow, 1972–1973.

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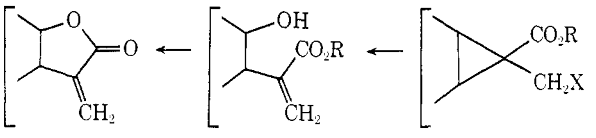
Synthesis of α-Methylene-γ-butyrolactones by Rearrangements of Functionally Substituted Cyclopropanes

Sir:

The wide variety[1] and biological activity[2] of natural products, particularly sesquiterpenes, containing the α-methylene-γ-butyrolactone ring have been of much interest recently. Although this ring system has been the objective of synthetic projects in a number of laboratories,[3] the number of basically different approaches is not large. In many syntheses,[3b,c,f,h,i,m–q] the methylene group is constructed on a preformed lactone ring. We now report a new synthesis of α-methylene-γ-butyrolactones, utilizing a novel acid or metal-ion promoted cyclopropane rearrangement.

The rationale for our synthetic approach is the fact that the desired lactone ring (A) can be considered as a derivative of a homoallylic alcohol (B), which should be derivable from a suitable cyclopropylcarbinyl derivative (C).[4]



A B C

For an initial test of this hypothesis, the synthesis of the unsubstituted α-methylene-γ-butyrolactone (**4**), a natural product isolated from tulips,[5] was attempted.

---

(1) For reviews, see (a) W. Parker, J. S. Roberts, and R. Ramage, *Quart. Rev., Chem. Soc.*, **21**, 331 (1967); (b) J. Romo and A. Romo de Vivar, *Progr. Chem. Org. Natur. Prod.*, **25**, 90 (1967); (c) T. A. Geissman and M. A. Irwin, *Pure Appl. Chem.*, **21**, 167 (1970); (d) W. Stöcklin, T. G. Waddell, and T. A. Geissman, *Tetrahedron*, **26**, 2397 (1970), and references cited therein.

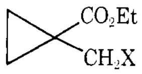
(2) For example, (a) antibiotic activity, C. J. Cavallito in "Medicinal Chemistry," Vol. I, C. M. Suter, Ed., Wiley, New York, N. Y., 1951, pp 221–235; (b) root promotion, H. Shibaoka, M. Shimokoriyama, S. Iriuchijima, and S. Tamura, *Plant Cell Physiol.*, **8**, 297 (1967); (c) dermatitis, G. A. W. Verspyck Mijnssen, *Brit. J. Dermatol.*, **81**, 737 (1969); (d) cytotoxic activity, S. M. Kupchan, *Trans. N. Y. Acad. Sci.*, **32**, 85 (1970); K.-H. Lee, E.-S. Huang, C. Piantadosi, J. S. Pagano, and T. A. Geissman, *Cancer Res.*, **31**, 1649 (1971); S. M. Kupchan, M. A. Eakin, and A. M. Thomas, *J. Med. Chem.*, **14**, 1147 (1971).

(3) (a) E. R. H. Jones, T. Y. Shen, and M. C. Whiting, *J. Chem. Soc.*, 230 (1950); (b) W. J. McGraw, U. S. Patent 2624723; *Chem. Abstr.*, **47**, 11232*h* (1953); (c) E. E. van Tamelen and S. R. Bach, *J. Amer. Chem. Soc.*, **80**, 3079 (1958); (d) V. B. Piskov, *J. Gen. Chem. USSR*, **30**, 1421 (1960); (e) J. A. Marshall and N. Cohen, *J. Org. Chem.*, **30**, 3475 (1965); (f) H. Minato and I. Horibe, *Chem. Commun.*, 531 (1965); (g) A. Löffler, R. D. Pratt, J. Pucknat, G. Gelbard, and A. S. Dreiding, *Chimia*, **23**, 413 (1969); (h) J. Martin, P. C. Watts, and F. Johnson, *Chem. Commun.*, 27 (1970); (i) E. S. Behare and R. B. Miller, *ibid.*, 402 (1970); (j) E. Öhler, K. Reininger, and U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **9**, 457 (1970); (k) J. W. Patterson and J. E. McMurry, *Chem. Commun.*, 488 (1971); (l) V. R. Tadwalkar and A. S. Rao, *Indian J. Chem.*, **9**, 1416 (1971); *Chem. Abstr.*, **77**, 34710 (1972); (m) L. K. Dalton and B. C. Elmes, *Aust. J. Chem.*, **25**, 625 (1972); (n) A. E. Greene, J.-C. Muller, and G. Ourisson, *Tetrahedron Lett.*, 2489, 3375 (1972); (o) P. A. Grieco and K. Hiroi, *J. Chem. Soc., Chem. Commun.*, 1317 (1972), 500 (1973); (p) A. D. Harmon and C. R. Hutchinson, *Tetrahedron Lett.*, 1293 (1973); (q) K. Yamada, M. Kato, M. Iyoda, and Y. Hirata, *J. Chem. Soc., Chem. Commun.*, 499 (1973).

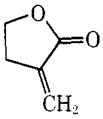
(4) The nature of the intermediates in the solvolytic interconversions of cyclopropylcarbinyl, cyclobutyl, and homoallyl systems has attracted much interest in the past two decades. For leading references, see V. Buss, R. Gleiter, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3927 (1971); G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *ibid.*, **94**, 146 (1972); C. D. Poulter and S. Winstein, *ibid.*, **94**, 2297 (1972); W. J. Hehre and P. C. Hiberty, *ibid.*, **94**, 5917 (1972); Y. E. Rhodes and V. G. DiFate, *ibid.*, **94**, 7582 (1972).

(5) U. W. Brongersma-Oosterhoff, *Recl. Trav. Chim. Pays-Bas*, **86**, 705 (1967); B. H. H. Bergman, J. C. M. Beijersbergen, J. C. Overeem, and A. Kaars Sijpesteijn, *ibid.*, **86**, 709 (1967). See also C. J. Cavallito and T. H. Haskell, *J. Amer. Chem. Soc.*, **68**, 2332 (1946), and ref 2c.

When the known[6] tosylate (**2**) of ethyl 1-hydroxymethylcyclopropanecarboxylate (**1**) was solvolyzed in acetic acid (100°, 3 hr),[7] only the unrearranged acetate (**3**)[9] was formed. However, treatment of the alcohol (**1**) with excess zinc bromide[10] in 48% hydrobromic acid (100°, 50 min) caused the desired rearrangement to take place, forming α-methylene-γ-butyrolactone[11] (**4**) directly in 25% yield.[12a]



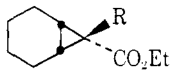
1, X = OH
2, X = OTs
3, X = OAc



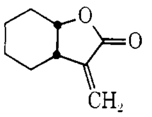
4

To examine the stereochemistry of this reaction, and its applicability to the synthesis of more complex molecules, the rearrangements of the bicyclic hydroxy esters **7** and **13** were studied, since the expected rearrangement products are analogous to the ring systems in many naturally occurring lactones.[1,3e] The hydroxy ester **7**[13] was prepared from diethyl norcarane-7,7-dicarboxylate (**5**)[14,15] by saponification to the known[14b] exo acid **6**, conversion to the acid chloride (oxalyl chloride, benzene, 25°), and reduction ($NaBH_4$, THF, reflux).[16] The hydroxy ester **13**[13a] was similarly prepared from the diester **12**.[17] When each of the alcohols, **7** and **13**, was treated with excess zinc bromide in 48% hydrobromic acid (ethanol, 100°, 6 hr), the cis lactones **11** (50%)[12] and **14** (43%)[12a] were formed, respectively.[18]

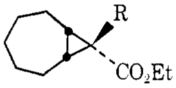
The rearrangements of **7** and its derivatives were investigated in more detail. Treatment of **7** with concentrated sulfuric acid at 0° (2 hr) formed the lactone **11** in 30% yield.[12] Several other acids caused this rearrangement to occur.[19]



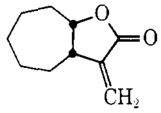
5, R = CO_2Et **8**, R = H
6, R = CO_2H **9**, R = CH_2OMe
7, R = CH_2OH **10**, R = CH_2Br



11



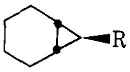
12, R = CO_2Et
13, R = CH_2OH



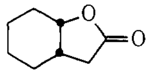
14

To develop milder reaction conditions, the possibility of silver ion promoted rearrangements was investigated.[20] When the methyl ether (**9**)[13a] derived from **7** (NaH, MeI, THF; 56%) was treated with silver perchlorate (1 equiv, benzene, 40°, 16 hr), lactone **11** was formed in 30% yield.[12,21]

The exclusive formation of the cis lactones is of interest. Acetolysis of the tosylate **15** is reported[22] to give mainly a trans homoallylic acetate, while sulfuric acid treatment of cyclopropanecarboxylic acids gives cis γ-lactones.[23]



15, R = CH_2OTs
16, R = CO_2H
17, R = CO_2Et



18

We find that the rearrangement of the hydroxy ester **7** to the α-methylenelactone **11** occurs under milder conditions than are required for the rearrangement of the cyclopropanecarboxylic acid **16** to the lactone **18**. Although **16**[14b] rearranges to **18**[24] in concentrated sulfuric acid at 50° (1 hr), it is stable to sulfuric acid at 0° (2 hr). Similarly, when either **16** or **17**[14b] is treated with zinc bromide under our reaction conditions (48% hydrobromic acid, ethanol, 100°, 6 hr), a mixture of **16** and **17** is formed which contains no lactone. In the rearrangement of **7**, it appears that the secondary homoallylic cation formed by the ring opening of the initially formed cyclopropylcarbinyl cation reacts intramolecularly with the ester group, giving rise to the cis stereochemistry.[25]

We are continuing to study the mechanism and the stereochemistry of these novel rearrangements. Although the yields are not yet optimized, we have clearly demonstrated that α-methylene-γ-butyrolactones can be synthesized from cyclopropane precursors under mild

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(6) H. Najer, R. Giudicelli, and J. Sette, *Bull. Soc. Chim. Fr.*, 2118 (1965); R. M. Coates and A. W. W. Ho, *J. Amer. Chem. Soc.*, **91**, 7544 (1969).

(7) Under these conditions we found that cyclopropylcarbinyl tosylate did undergo rearrangement to give a mixture of products similar to that reported,[8] and that its solvolysis was somewhat faster than that of **2**.

(8) D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964); **30**, 23 (1965).

(9) A comparison sample of the acetate **3** was prepared from **1** by treatment with acetic anhydride in pyridine.

(10) Zinc bromide has been used previously for the conversion of cyclopropylcarbinyl derivatives to homoallylic bromides. See J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951); M. Julia, S. Julia, and S.-Y. Tchen, *Bull. Soc. Chim. Fr.*, 1849 (1961); S. F. Brady, M. A. Ilton, and W. S. Johnson, *J. Amer. Chem. Soc.*, **90**, 2882 (1968).

(11) The ir and nmr spectra of a purified (vpc) sample were identical with those reported for the natural product.[5] The other compounds formed in the reaction have not been identified.

(12) (a) The yield of lactone was determined by nmr using an internal standard. (b) The lactone has been purified by preparative vpc and by column chromatography.

(13) (a) Satisfactory ir, nmr, and mass spectra were obtained for this compound. (b) Elemental analysis (C, H) was within 0.2% of the calculated value.

(14) (a) T. V. Mandel'shtam, L. D. Kristol, L. A. Bogdanova, and T. N. Ratnikova, *J. Org. Chem. USSR*, **4**, 963 (1968); (b) H. Musso, *Chem. Ber.*, **101**, 3710 (1968).

(15) Prepared from cyclohexene and diethyl diazomalonate by the procedure of B. W. Peace, F. Carman, and D. S. Wulfman, *Synthesis*, 658 (1971). See also B. W. Peace and D. S. Wulfman, *ibid.*, 137 (1973).

(16) The overall isolated yield from **6** to **7** was 60%.

(17) W. Kirmse and F. Scheidt, *Chem. Ber.*, **103**, 3711 (1970).

(18) Both lactones were identified by comparison of ir and nmr spectra with those reported by Marshall and Cohen.[3e]

(19) Trifluoromethanesulfonic acid and *p*-toluenesulfonic acid were also found to cause this rearrangement. With sulfuric acid in benzene, use of a catalytic amount of acid resulted in much less rearrangement than did one equivalent. In most of these reactions, the mono ester **8**,[14b] presumably formed by a retro-aldol type reaction, was a significant by-product. The trans isomer[3e,i] of lactone **11** was not detected in any of these reactions.

(20) Silver ion promoted rearrangements of other cyclopropylcarbinyl ethers have been reported: L. A. Paquette and G. Zon, *J. Amer. Chem. Soc.*, **94**, 5096 (1972).

(21) The analogous bromide **10**[13a] also rearranged to **11** on treatment with silver perchlorate (benzene, 25°, 1 hr), or on treatment with zinc bromide in 48% hydrobromic acid (ethanol, 100°, 6 hr). So far the bromide **10** has been difficult to obtain in pure form.

(22) F. T. Bond and L. Scerbo, *Tetrahedron Lett.*, 4255 (1965); K. B. Wiberg and J. G. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 553 (1970). The solvolysis of the analogous bicyclo[5.1.0] system has also been studied: K. B. Wiberg and T. Nakahira, *J. Amer. Chem. Soc.*, **93**, 5193 (1971); see also R. W. Thies and J. E. Billigmeier, *J. Org. Chem.*, **38**, 1758 (1973).

(23) J. Meinwald, A. Lewis, and P. G. Gassman, *J. Amer. Chem. Soc.*, **84**, 977 (1962); R. R. Sauers and P. E. Sonnet, *Tetrahedron*, **20**, 1029 (1964). See also ref 14a and J. Bus, H. Steinberg, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **91**, 657 (1972), and references cited therein.

(24) J. Klein, *J. Amer. Chem. Soc.*, **81**, 3611 (1959).

(25) The trans isomer[3e,i] of lactone **11** is apparently not an intermediate in the reaction, since it is stable to acid under conditions (H_2SO_4, 0° or HBr, $ZnBr_2$, 100°) which cause rearrangement of **7** to **11**.

conditions. We hope to utilize these methods for the synthesis of both cis and trans α-methylene-γ-butyrolactones.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Portions of this work were also supported by a Biomedical Sciences Support Grant to Rutgers University from the National Institutes of Health, by Research Corporation, and by the National Science Foundation. We thank Dr. Noal Cohen for providing some useful literature references, and Professor R. B. Miller for samples and helpful correspondence.

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Syntheses from Perfluoro-2-butyne. I. Fluoride Ion Promoted Telomerization of Perfluoro-2-butyne with 2-Bromoperfluoro-2-butene. *trans*-3-Bromoperfluoro-1,2,3,4-tetramethylcyclobutene[1]

Sir:

Although a virtually unlimited carbon–fluorine chemistry can now be visualized its realization is dependent upon the development of applicable synthetic methods particularly those for carbon–carbon bonds. We wish to report new results in this area centering around the synthesis of *trans,trans*-2-bromoperfluoro-3,4-dimethyl-2,4-hexadiene as a precursor for *trans*-3-bromoperfluoro-1,2,3,4-tetramethylcyclobutene and perfluorotetramethylcyclobutadiene.[1,2] The desired hexadiene isomer was prepared in a single operation in ~80% yield from perfluoro-2-butyne, 2-bromoperfluoro-2-butene, and cesium fluoride with the intermediate formation of *trans*-perfluoro-1-methylpropenylcesium[3] as shown in eq 1–5. The reaction process consists of an anionic telomerization and by increasing the ratio of butyne to butene was also utilized to prepare perfluoromethylated polyenes, $\mathrm{F(CCF_3{=}CCF_3)_nBr}$ with $n > 2$. It provides a prototype for other syntheses with carbon–fluorine–halogen compounds in which fluoroorganometal intermediates generated by fluoride ion additions react as nucleophiles on unsaturated carbon and on halogen.[7]

$$\underset{\mathrm{I}}{\mathrm{CF_3C{\equiv}CCF_3}} + \mathrm{Br_2} \xrightarrow{h\nu} \underset{\mathrm{II}}{\mathrm{CF_3CBr{=}CBrCF_3}} \qquad (1)$$

$$\mathrm{CF_3CBr{=}CBrCF_3} + \mathrm{CsF} \xrightarrow[\mathrm{CH_3CN}]{} \underset{\substack{\text{III,}\\ \text{54\% cis, 46\% trans}}}{\mathrm{CF_3CF{=}CBrCF_3}} + \mathrm{CsBr} \qquad (2)$$

(a) at reflux, slow[4]

(b) at 30° with I as a catalyst, fast

$$\mathrm{CF_3C{\equiv}CCF_3} + \mathrm{CsF} \rightleftarrows \mathrm{CF_3CF{=}CCsCF_3} \qquad (2a)$$

$$\mathrm{CF_3CF{=}CCsCF_3} + \mathrm{CF_3CBr{=}CBrCF_3} \longrightarrow \mathrm{CF_3CF{=}CBrCF_3} + \mathrm{CF_3CBr{=}CCsCF_3} \qquad (2b)$$

$$\mathrm{CF_3CBr{=}CCsCF_3} \longrightarrow \mathrm{CF_3C{\equiv}CCF_3} + \mathrm{CsBr} \qquad (2c)$$

$$\begin{tikzcd}
\textit{cis}\text{-}\mathrm{CF_3CF{=}CBrCF_3} + \mathrm{CsF} \arrow[dr, shift left] & \\
& \mathrm{CF_3CF_2CBrCsCF_3} \arrow[ul, shift left] \arrow[dl, shift left] \qquad (2d) \\
\textit{trans}\text{-}\mathrm{CF_3CF{=}CBrCF_3} + \mathrm{CsF} \arrow[ur, shift left] &
\end{tikzcd}$$

$$\mathrm{CF_3CF{=}CBrCF_3} + (n-1)\mathrm{CF_3C{\equiv}CCF_3} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{CsF}} \underset{\mathrm{IV},\ n\,=\,2}{\mathrm{F(CCF_3{=}CCF_3)_nBr}} \qquad (3)$$

$$\mathrm{CF_3C{\equiv}CCF_3} + \mathrm{CsF} \rightleftarrows \mathrm{CF_3CF{=}CCsCF_3} \qquad (3a)$$

$$\mathrm{CF_3CF{=}CCsCF_3} + \mathrm{CF_3CF{=}CBrCF_3} \rightleftarrows \mathrm{CF_3CF{=}CBrCF_3} + \mathrm{CF_3CF{=}CCsCF_3} \qquad (3b)$$

$$\mathrm{CF_3CF{=}CCsCF_3} + (n-1)\mathrm{CF_3C{\equiv}CCF_3} \longrightarrow \mathrm{CF_3CF{=}CCF_3(CCF_3{=}CCF_3)_{n-1}Cs} \qquad (3c)$$

$$\mathrm{F(CCF_3{=}CCF_3)_nCs} + \mathrm{CF_3CF{=}CBrCF_3} \rightleftarrows \mathrm{F(CCF_3{=}CCF_3)_nBr} + \mathrm{CF_3CF{=}CCsCF_3} \qquad (3d)$$

$$\mathrm{F(CCF_3{=}CCF_3)_nBr} + \mathrm{CsF} \longrightarrow \underset{\mathrm{V},\ n\,=\,2}{\mathrm{F(CCF_3{=}CCF_3)_nF}} + \mathrm{CsBr} \qquad (4)$$

$$\underset{\mathrm{IV},\ 54\%}{\textit{trans,trans}\text{-}\mathrm{CF_3CF{=}CCF_3CCF_3{=}CBrCF_3}} \overset{100\text{–}150^\circ}{\rightleftarrows} \underset{\mathrm{VI},\ 46\%}{\textit{trans}\text{-}\overline{\mathrm{CF_3CFCBrCF_3CCF_3}}{=}\mathrm{CCF_3}} \qquad (5)$$

All of the compounds prepared were derived from $\mathrm{CF_3C{\equiv}CCF_3}$.[9] Reaction 1 yielded the pure dibromide, $\mathrm{CF_3CBr{=}CBrCF_3}$,[10] which was converted into an equilibrium mixture of *cis*- and *trans*-$\mathrm{CF_3CF{=}CBrCF_3}$ with CsF (eq 2).[4] Each isomer was rapidly equilibrated by CsF at 30° without bromine substitution, <1% after 30 hr.[11] Reaction with fluoride ion thus provides a general mechanism for the interconversion of cis–trans isomers of perfluoroolefins in addition to promoting their rearrangement.[5] A small amount of $\mathrm{CF_3C{\equiv}CCF_3}$ served as an effective catalyst for reaction 2 due to the ease with which the halogen–metal exchange reaction 2b took place. In the absence of an

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(1) Presented in part at the 6th International Symposium on Fluorine Chemistry, Durham, England, July 1971, and at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract FLUO-011.

(2) Treatment of *trans*-3-bromoperfluoro-1,2,3,4-tetramethylcyclobutene with MeLi at −125° yielded the cyclobutadiene.

(3) Both CsF and AgF have been shown to add readily to $\mathrm{CF_3C{\equiv}CCF_3}$ to form trans addition products.[4] The facile addition of metal fluorides to unsaturated carbon–fluorine compounds to form perfluoroorganometallic compounds was first demonstrated with KF, *i.e.*, the formation of perfluoroalkylpotassiums.[5] Cesium fluoride and $\mathrm{CF_3C{\equiv}CCF_3}$ have been utilized to prepare alkenyl and dialkenyl derivatives of perfluoro aromatics.[6]

(4) W. T. Miller, R. H. Snider, and R. J. Hummel, *J. Amer. Chem. Soc.*, **91**, 6532 (1969).

(5) J. H. Fried and W. T. Miller, Jr., *J. Amer. Chem. Soc.*, **81**, 2078 (1959); W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *ibid.*, **82**, 3091 (1960).

(6) W. T. Flowers, R. N. Haszeldine, and P. G. Marshall, *Chem. Commun.*, 371 (1970); R. D. Chambers, W. K. R. Musgrave, and S. Partington, *ibid.*, 1050 (1970).

(7) For the characteristic reactions of anionic nucleophiles on unsaturated carbon in carbon–fluorine–halogen compounds see ref 5. Bimolecular nucleophilic reactions on halogen also represent a reaction pathway of major importance to CFX chemistry which is facilitated by the formation of stabilized carbanions and steric inhibition of the $\mathrm{S_N2}$ mechanism.[8]

(8) W. T. Miller, Jr., and R. Becker, Abstracts of the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 14M.

(9) A. L. Henne and W. G. Finnegan, *J. Amer. Chem. Soc.*, **71**, 298 (1949).

(10) R. N. Haszeldine, *J. Chem. Soc.*, 2504 (1952). In our work rapid bromination of $\mathrm{CF_3C{\equiv}CCF_3}$ was observed with irradiation at reflux temperature without the formation of $\mathrm{CF_3CBr_2CBr_2CF_3}$.

(11) The exclusive formation of $\mathrm{CF_3CF_2CBrCsCF_3}$ by addition of CsF to III was consistent with the expected greater effectiveness of α-Br as compared with α-F for stabilizing carbanions and with the greater stability of $-\mathrm{CF_2}-$ relative to $-$CFX.