Spectral Studies. The solution of **2** in *n*-hexane was mixed with the appropriate alcohol under dry conditions and then quickly diluted with the same solvent mixture. Spectra were run at room temperature.

Acknowledgment. This investigation was supported in part by Grant No. 31-26-S1-0641 from the Consejo Nacional de Investigaciones Cientificas y Tecnológicas (CONICIT).

Registry No.—1, 120-72-9; **2**, 2959-02-06; **3**, 66037-05-6; **5**, 16863-96-0.

References and Notes

(1) Accepted for presentation in part at the 174th National Meeting of the American Chemical Society, Chicago, Ill., August 1977.
(2) From the Tesis Especial de Grado of J. L. Triana Alonso submitted in partial fulfilment of the degree requirements for the Licenciatura degree, Universidad Simón Bolivar, 1976.
(3) For recent reviews on the chlorination of indole and its derivatives see: (a) J. C. Powers in "Indoles", Part II, W. J. Houlihan, Ed., Wiley-Interscience, New York, N.Y., 1972, pp 137–39 and 155–59; (b) R. J. Sundberg, "The Chemistry of Indoles", Academic Press, New York, N.Y., 1970, pp 14–17.
(4) G. Mazzara and A. Borgo, *Gazz. Chim. Ital.*, **35**, 320, 563 (1905).
(5) J. C. Powers, *J. Org. Chem.*, **31**, 2627 (1966).
(6) G. M. Brooke, R. D. Chambers, W. K. R. Musgrave, R. A. Storey, and J. Yeadon, *J. Chem. Soc., Perkin Trans. 1*, 162 (1976).
(7) M. Kunori, *Nippon Kagaku Zasshi*, **81**, 1431 (1960); *Chem. Abstr.*, **56**, 3441 (1962).
(8) J. Bergman, *Acta Chem. Scand.*, **25**, 2865 (1971).
(9) G. Pappalardo and T. Vitali, *Gazz. Chem. Ital.*, **88**, 1147 (1958).
(10) R. Weissgerber, *Chem. Ber.*, **46**, 651 (1913).
(11) R. J. Bass, *Tetrahedron*, **27**, 3263 (1971).
(12) J. M. Muchowski, *Can. J. Chem.*, **48**, 422 (1970).
(13) T. A. Foglia and D. Swern, *J. Org. Chem.*, **33**, 440 (1968).
(14) P. Chabrier, *Ann. Chim. (Paris)*, **17**, 353 (1942).
(15) V. Snieckus and M. S. Lin, *J. Org. Chem.*, **35**, 3994 (1970).
(16) R. J. Owellen, *J. Org. Chem.*, **39**, 69 (1974).
(17) S. Gabriel, W. Gerhard, and R. Wolter, *Chem. Ber.*, **56B**, 1024 (1923).
(18) (a) R. J. Owellen and C. A. Hartke, *J. Org. Chem.*, **41**, 102 (1976), and references cited therein; (b) A. Walser, J. F. Blount, and R. I. Fryer, *J. Org. Chem.*, **38**, 3077 (1973).
(19) P. G. Gassman, G. A. Campbell, and G. Mehta, *Tetrahedron*, **28**, 2749 (1972).
(20) M. De Rosa, *J. Chem. Soc., Chem. Commun.*, 482 (1975).
(21) For a recent example in the area of indole alkaloids see E. Wenkert, J. S. Bindra, C. J. Chang, D. W. Cochran, and D. E. Rearick, *J. Org. Chem.*, **39**, 1662 (1974). See also ref 16 for other leading references.
(22) D. F. Paul and P. Haberfield, *J. Org. Chem.*, **41**, 3170 (1976).
(23) P. G. Gassman and G. A. Campbell, *J. Am. Chem. Soc.*, **94**, 3891 (1972).
(24) P. G. Gassman and G. A. Campbell, *J. Am. Chem. Soc.*, **93**, 2567 (1971).
(25) B. C. Challis and E. M. Millar, *J. Chem. Soc., Perkin Trans. 2*, 1111 (1972).
(26) B. C. Challis and H. S. Rzepa, *J. Chem. Soc., Perkin Trans. 2*, 1209 (1975).
(27) A similar relation between concentration and stability has been observed for certain *N*-chloroanilines.[28]
(28) D. F. Paul, Ph.D. Thesis, The City University of New York, New York, N.Y., 1968.
(29) Occasionally increases in the apparent concentration of **2** larger than illustrated in Figure 2 were observed.
(30) G. Yagil, *Tetrahedron*, **23**, 2855 (1967).
(31) T. Hino, M. Endo, M. Tonozuka, and M. Nakagawa, *Heterocycles*, **2**, 565 (1974).
(32) W. A. Remers, ref 3a, Part II, p 23.

Generation and Reactions of Halodifluoromethide Ions[1]

Gregory A. Wheaton and Donald J. Burton*

Department of Chemistry, The University of Iowa, Iowa City, Iowa 52242

Received August 5, 1977

Methyl chlorodifluoroacetate undergoes facile thermal decarbomethoxylation induced by the 1:1 lithium chloride/hexamethylphosphoric triamide complex (LiCl/HMPA). This ester decomposition generates either the chlorodifluoromethide ion or the chlorodifluoromethyllithium/hexamethylphosphoric triamide complex. The nucleophilic intermediate from this ester decomposition may be trapped upon decomposition of the ester in the presence of appropriate electrophilic reagents.

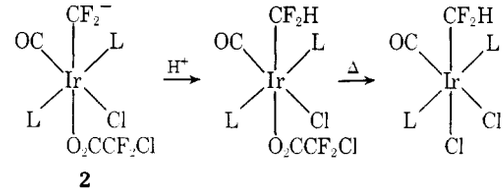
The increasing interest in organofluorine chemistry has resulted in the rapid development of methods for the introduction of fluorinated groups into organic molecules. One area which has received considerable attention in recent years is the generation and reactions of polyfluorinated carbanions.[2,3] Although a wide variety of fluorinated carbanions are known, halodifluoromethide ions have been considered to have no finite existence. The major contributors to this hypothesis are the investigations by Hine and co-workers[4–6] which indicate that the formation of difluorocarbene by either the action of a base upon halodifluoromethanes or the thermally induced decarboxylation of halodifluoroacetate ions is a concerted process not involving the intermediacy of halodifluoromethide ions. In addition, none of the numerous reports in the literature involving difluorocarbene generation via decarboxylation of alkali metal chlorodifluoroacetates present any concrete evidence to indicate the existence of halodifluoromethide ions as reaction intermediates.

In spite of the lack of evidence for the existence of halodifluoromethide ions in the literature, substituted difluoromethide ions which possess substituents that are good carbanion stabilizing groups have been demonstrated to exist as reaction intermediates. Treatment of difluoromethyl phenyl sulfone with sodium methoxide in methanol in the presence of thiophenoxide results in the formation of difluoromethyl phenyl sulfide via trapping of difluorocarbene by the thiophenoxide.[7] In this case, however, the formation of difluorocarbene is a two-step process involving an intermediate difluoromethide ion **1**. The intermediacy of **1** in the

$$PhSO_2CF_2H \xrightarrow[MeOH]{NaOMe} PhSO_2CF_2^- \rightarrow PhSO_2^- + :CF_2$$

1

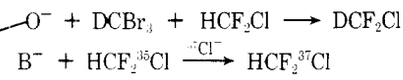
formation of carbene is indicated by the observation that the sulfone undergoes deuterium exchange much more rapidly than it consumes thiophenoxide. Evidence for a metal-stabilized difluoromethide ion has been reported in the literature recently.[8] Refluxing sodium chlorodifluoroacetate and $IrCl(CO)(PPh_3)_2$ in diglyme resulted in the isolation of either of two difluoromethyl complexes. The formation of these complexes was taken as evidence for the intermediacy of the metallocarbanion **2**.



2

Kesling and Burton[9] have recently reported that treatment of halodifluoromethylphosphonium halides with fluoride ion in the presence of appropriate electrophilic reagents results in the transfer of halodifluoromethyl groups. While the intermediacy of halodifluoromethide ions was not definitely established, the reactions which were reported may best be interpreted as involving such carbanions.

More recently Kimpenhaus and Buddrus[10] have reported that the generation of difluorocarbene by the reaction of halide ions with epoxides in the presence of chlorodifluoromethane in aprotic solvents proceeds via the chlorodifluoromethide ion. The intermediacy of the methide ion was established by H–D exchange studies. Isotopic chlorine exchange also indicated that an equilibrium exists between chlorodifluoromethide ion, carbene, and chloride ion in this system.



In a preliminary report[11] we outlined evidence for the generation and capture of the chlorodifluoromethide ion upon treatment of methyl chlorodifluoroacetate (**3**) with lithium chloride in hexamethylphosphoric triamide (HMPA) in the presence of polyfluoromethyl ketones. We now wish to report in greater detail on the generation of halodifluoromethide ions by the decomposition of methyl halodifluoroacetates induced by halide ions. This report discusses the mechanism of the halide-induced ester decomposition as well as the scope and utility of this method of halodifluoromethide ion generation.

Results and Discussion

The facilitation of decarboalkoxylation reactions by alkali metal halides has been reported.[12-14] However, the use of hexamethylphosphoric triamide (HMPA) as either a solvent or a cosolvent has been reported to effect decarboalkoxylation by alkali halides under much milder conditions than are normally required in the absence of HMPA.[12,15]

In addition to the previously reported[11] facile decomposition of **3** by lithium chloride in HMPA, treatment of **3** with a 1:1 lithium chloride/HMPA complex (LiCl/HMPA)[16] in a variety of aprotic solvents effects the facile decarbomethoxylation of the ester to yield methyl chloride and carbon dioxide. Addition of **3** to a refluxing solution of LiCl/HMPA in THF results in an essentially quantitative yield of carbon dioxide after 4 h. Decarbomethoxylation of **3** by LiCl/HMPA occurs slowly even in refluxing methylene chloride (92% of CO_2 after 12 h), but in general much faster rates of decomposition are obtained utilizing ethereal solvents such as THF or glymes.

Mechanism. The selective cleavage of methyl esters of carboxylic acids in the presence of higher alkyl esters by either lithium chloride[12] or sodium cyanide[17] in HMPA suggested that the decomposition of **3** by LiCl/HMPA proceeds via initial nucleophilic attack by chloride ion upon the methoxyl carbon with subsequent displacement of the chlorodifluoroacetate group. Treatment of **3** with LiCl/HMPA, formed in situ, at 40 °C in THF for 2 h resulted in the isolation of a hygroscopic white solid upon evaporation of the solvent in vacuo. This white solid was characterized as the lithium chlorodifluoroacetate/HMPA complex (**4**) by ^{19}F and ^{1}H

$$3 + \text{LiCl/HMPA} \xrightarrow[\text{THF}]{40\ ^\circ\text{C}} CH_3Cl + ClCF_2CO_2Li/\text{HMPA}$$

4

NMR spectroscopy as well as by its infrared spectrum. Due to the hygroscopic nature of **4**, however, a satisfactory elemental analysis could not be obtained. Quantitative ^{19}F NMR analysis indicated that **4** was formed in essentially quantitative yield after 2 h in the above reaction. Subsequent refluxing of a solution of **4** in THF resulted in an 88% yield of carbon dioxide and complete disappearance of the ^{19}F NMR signal of **4** after 4 h. Based on the above observations, the mechanism of the decomposition of **3** upon treatment with LiCl/HMPA in THF is concluded to involve an initial S_N2 displacement of the chlorodifluoroacetate ion from the methyl group by chloride ion. The resultant complex **4** then decarboxylates under rather mild conditions.

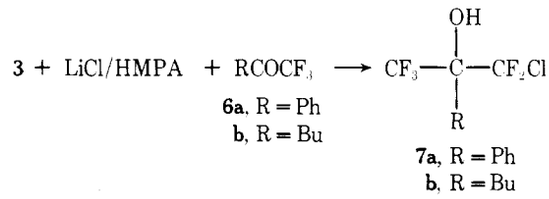
The decomposition of **3** by LiCl/HMPA in THF in the presence of 2,2,2-trifluoroethanol gave an essentially quantitative yield of chlorodifluoromethane (**5**) as determined by

$$3 + \text{LiCl/HMPA} + CF_3CH_2OH \rightarrow HCF_2Cl$$

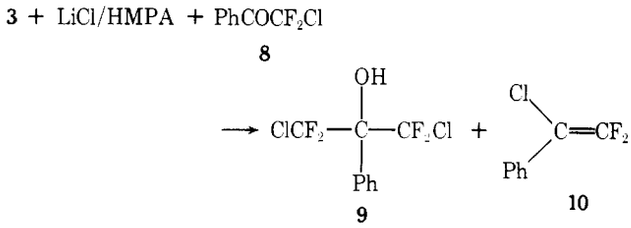
5

^{19}F NMR analysis. No difluoromethyl ether derived from insertion of difluorocarbene into the O–H bond of the alcohol was observed by ^{19}F NMR spectroscopy. The formation of **5** and the absence of any carbene insertion product suggest that decarbomethoxylation of **3** by LiCl/HMPA in THF results in the formation of either a chlorodifluoromethide ion or a chlorodifluoromethyllithium/HMPA complex.

Like the previously reported decomposition of **3** by LiCl in HMPA in the presence of polyfluoromethyl ketones,[11] treatment of **3** with LiCl/HMPA in refluxing THF in the presence of polyfluoromethyl ketones resulted in the formation of tertiary alcohols. Addition of **3** to a refluxing solution of LiCl/HMPA and trifluoromethyl ketones **6** in THF resulted



in the formation of alcohols **7a** and **7b** in yields of 63 and 39%, respectively, upon steam distillation. Authentic samples of **7a** and **7b** were prepared for comparison purposes in 28 and 46% yields, respectively, via the addition of phenyllithium and *n*-butyllithium to chloropentafluoroacetone, similar to related organolithium additions to this ketone reported by Dyatkin and co-workers.[18] The alcohols were the only fluorinated products observed. Similar decomposition of **3** in the presence of α-chloro-α,α-difluoroacetophenone (**8**) resulted in only an

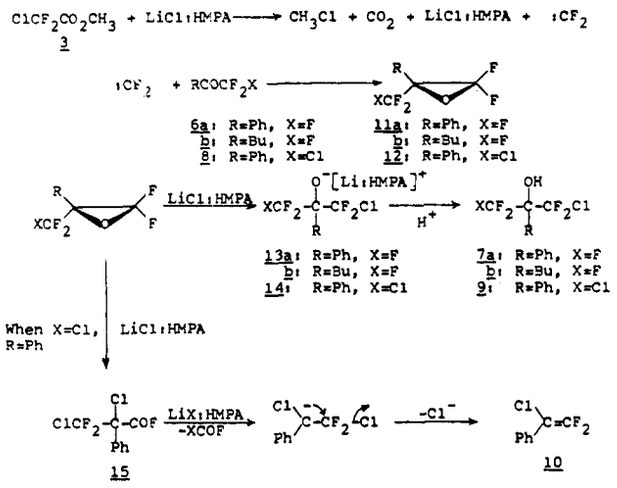


9 **10**

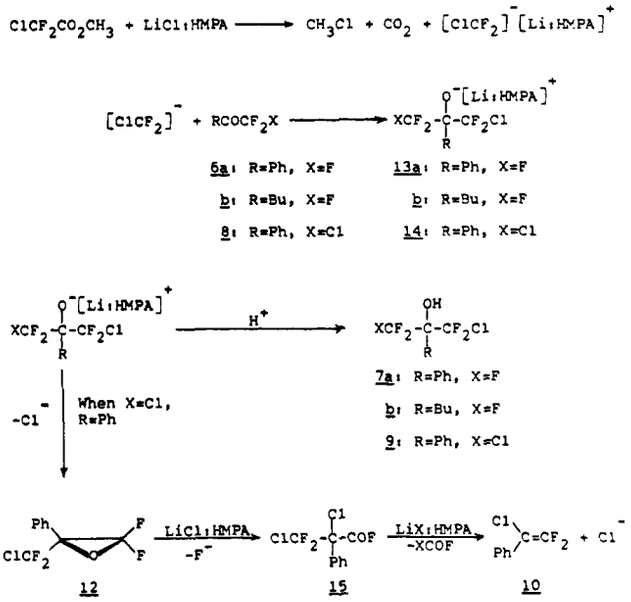
18% yield of the expected alcohol **9**. The major product of this reaction was the olefin **10** which was obtained in a 50% yield. These results are identical with those previously reported.[11]

Two mechanistic interpretations were considered most plausible to account for the observed results of the decomposition of **3** in the presence of the polyfluoromethyl ketones. One mechanism involves concerted formation of difluorocarbene upon decarbomethoxylation of **3**. The carbene thus formed would add across the carbon–oxygen double bond of the ketone[19] **6** to yield intermediate 1,2-epoxides **11** and **12**, as depicted in Scheme I. The epoxides would then be ring opened by chloride ion to yield the observed products. The

Scheme I



Scheme II



formation of the alcohols **7** as the only products of the reaction involving ketones **6** requires that epoxides **11a** and **11b** be ring opened exclusively by chloride ion attack at the 1 position to give lithium alkoxides **13a** and **13b.** On the other hand, ring opening of epoxide **12** would have to occur primarily by chloride attack at the 2 position, resulting in formation of acid fluoride **15,** which would then react further with halide to yield ultimately the observed olefin **10.** Attack by chloride at the 1 position of **12** to give alkoxide **14** would have to occur to only a minor extent to account for the observed low yield of alcohol **9.**

Exclusive attack by chloride at the 1 position of epoxides **11a** and **11b** is considered highly unlikely in view of the fact that nucleophilic ring opening of analogous fluorinated 1,2-epoxides occurs at the 2 position to form acid fluorides rather than at the 1 position in all cases but those involving extremely bulky nucleophiles.[20] Coordination of the epoxide oxygen by the lithium ion might result in chloride attack at the terminal carbon as observed in the electrophilic ring opening of fluorinated 1,2-epoxides by Lewis acid catalysts or by strong protonic acids.[20] Such participation in ring opening by the lithium ion is most likely not operative in this system, however, since the use of the complex LiCl/2HMPA in the decomposition of **3** in the presence of ketones **6** and **8** gave results identical with those observed utilizing LiCl/HMPA. The doubly complexed lithium ion has been demonstrated to be incapable of such coordination to oxiranes.[16b] Therefore, ring opening of the oxiranes **11** and **12** would most likely occur solely by nucleophilic attack by chloride at the 2 position to yield acid fluorides.

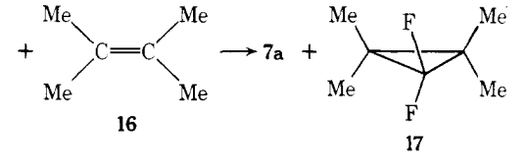
The second mechanism considered, outlined in Scheme II, involves the formation of either chlorodifluoromethide ion or chlorodifluoromethyllithium/HMPA complex upon decarbomethoxylation of **3.** The methide ion or the HMPA-complexed organolithium compound ($ClCF_2Li$/HMPA) would then add to the carbonyl carbon of the ketones to generate the lithium alkoxides **13** and **14** directly. The alkoxides would yield the observed alcohols upon hydrolysis. This mechanism, however, requires that alkoxide **14** undergo an intramolecular S_N2 displacement of chloride by the alkoxy oxygen to form the 1,2-epoxide **12** while alkoxides **13,** which contain the trifluoromethyl substituent, would have to be inert to this intramolecular displacement of chloride. Epoxide **12** would then be ring opened by chloride to ultimately yield olefin **10** as described previously.

The attempted synthesis of the suspected intermediate epoxides **11** and **12** in order to investigate their ring opening behavior was successful only in the case of **12.** Treatment of the alcohols **7a** and **7b** with aqueous potassium hydroxide as by the method of Knunyants et al.[21] resulted in no epoxide formation. Acidification of the reaction mixture, in both cases, resulted in essentially quantitative recovery of the unchanged alcohols. However, treatment of **9** with aqueous potassium hydroxide followed by heating gave a 65% yield of epoxide **12.**

Addition of **12** to a solution of excess LiCl/HMPA in THF at 0 °C resulted in a 96% yield of acid fluoride **15** by ^{19}F NMR analysis. Subsequent refluxing of this solution gave the olefin **10** in 95% yield by NMR spectroscopy. Significantly, no alcohol **9** was observed upon hydrolysis by either ^{19}F NMR or GLC analyses. Thus, ring opening of epoxide **12** occurs exclusively via chloride ion attack at the 2 position. No attack at the 1 position with subsequent alkoxide formation occurs. Therefore, alcohol **9** obtained from the decomposition of **3** in the presence of **8** must be the result of addition of $ClCF_2^-$ or $ClCF_2Li$/HMPA to the ketone as depicted in Scheme II. While the failure of alkoxides **13a** and **13b** to yield epoxides, under the same conditions which yield **12** from **14,** makes comparative predictions of the ring opening behavior of epoxides **11a, 11b,** and **12** somewhat tenuous, it is unlikely that such structurally similar epoxides would exhibit markedly different ring opening behavior. In addition, the failure of alkoxides **13a** and **13b** to ring close is consistent with the requirements of the mechanism outlined in Scheme II. The ring opening of analogous epoxides[20] supports the conclusion that alcohols **7a** and **7b** were also formed by nucleophilic addition of $ClCF_2^-$ or $ClCF_2Li$/HMPA to the ketones (as was **9**) and that they did not result from the ring opening of the epoxides **11a** or **11b.**

That the formation of the alcohols upon decarbomethoxylation of **3** in the presence of ketones **6** and **8** was the result of interception of either $ClCF_2^-$ or $ClCF_2Li$/HMPA and not the result of initial carbene formation, as depicted in Scheme I, was further substantiated by the following two experiments. Addition of **3** to a refluxing solution of LiCl/HMPA, excess **6a,** and excess 2,3-dimethyl-2-butene (**16**) in THF resulted in the formation of a 66% yield of **7a** and a 27% yield of cyclopropane **17.** If difluorocarbene were initially formed upon

3 + LiCl/HMPA + **6a**



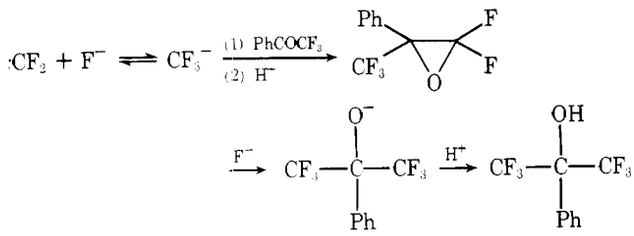
16 **17**

decomposition of **3**, the olefin **16** would compete very effectively with either chloride ion or ketone **6a** for the carbene.[22] Thus, decomposition of **3** to give difluorocarbene directly would have resulted in the formation of cyclopropane **17** as the predominant product. However, the alcohol **7a** was observed to be the predominant product. In fact, the yield of **7a** obtained in the presence of the olefin is essentially the same as that obtained when no olefin was present. These results are interpreted as indicating that either $ClCF_2^-$ or $ClCF_2Li$/HMPA was formed initially upon decarbomethoxylation of **3**. Either of these nucleophilic species then added to the carbonyl carbon of the ketone to yield **7a** upon hydrolysis. The cyclopropane which was formed was the result of difluorocarbene formed by the decomposition of either the methide ion or $ClCF_2Li$/HMPA before reaction with the ketone.

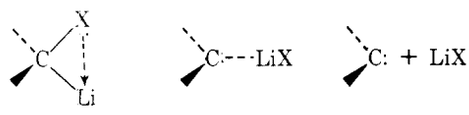
Treatment of **3** with potassium fluoride/18-crown-6 complex[23] in refluxing THF in the presence of **6a** resulted in the consumption of only 35% of the ester **3** after 4 h. However, a 21% yield of the alcohol **7a** was obtained upon hydrolysis.

$$3 + KF/18\text{-crown-}6 + \mathbf{6a} \rightarrow 7a + PhC(CF_3)_2OH$$
$$\mathbf{18}$$

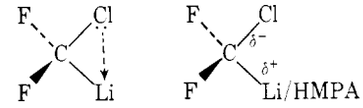
More significantly, however, no 2-phenylhexafluoro-2-propanol (**18**) was detected in the reaction mixture. The failure to obtain alcohol **18** from this reaction is significant in two respects. The lack of formation of **18** in this system indicates that methide ion formation is not the result of capture of initially formed difluorocarbene by halide ion. Also, the absence of **18** indicates once again that the alcohols which are formed by decomposition of **3** in the presence of the polyfluoromethyl ketones do not arise by halide ion ring opening of intermediate epoxides.



While the exact nature of the reactive species formed upon decarboxylation of complex **4** is open to much speculation, little doubt remains that it is indeed a nucleophilic species such as chlorodifluoromethide ion ($ClCF_2^-$) or the complexed carbenoid $ClCF_2Li$/HMPA. The stability of a free carbanion such as $ClCF_2^-$ should be enhanced by the slight degree of coordination or solvation expected in this system, as well as its reactivity increased. A methide ion would be only slightly solvated and only loosely associated with a very highly solvated lithium ion in this reaction medium. Such enhancement of carbanion stability has been observed for the trichloromethide ion formed by the reaction of tris(dimethylamino)-phosphine with carbon tetrachloride.[24] The stability of an organometallic species such as $ClCF_2Li$/HMPA would definitely be enhanced by the complexation of the lithium atom by HMPA. The most generally accepted mechanism for the decomposition of carbenoids such as $ClCF_2Li$ involves the initial loss of an α halogen.[25] Such a mode of decomposition is facilitated by the interaction of the nonbonding electrons on the halogen with the metal. This metal–halogen interaction



would be decreased by either complexation or solvation of the metal atom.[25a] Complexation of the lithium atom in $ClCF_2Li$/HMPA by the strongly electron-donating HMPA[25b] and solvation by THF would result in stabilization of this carbenoid by greatly decreasing the strength of the interaction between the lithium and chlorine atoms.[25b] In addition to



hindering the interaction between the lithium and chlorine atoms, complexation of the lithium atom of $ClCF_2Li$ by HMPA and solvation by THF would also increase the polarity of the carbon–lithium bond,[25b] enhancing the carbanionic character of the carbon atom. This would result in the subsequent acceleration of those reactions in which the nucleophilicity of the carbon atom is important; that is, with electrophilic substrates such as the polyfluoromethyl ketones.

Scope and Limitations. While treatment of **3** with LiCl/HMPA in the presence of polyfluoromethyl ketones in refluxing THF resulted in good yields of tertiary polyfluoro alcohols, presumably via the trapping of a carbanionic intermediate by the ketones, attempts to extend this reaction to less reactive nonfluorinated carbonyl compounds met with little success. Treatment of **3** with LiCl/HMPA in refluxing THF in the presence of benzaldehyde or acetophenone yielded none of the expected chlorodifluoromethyl alcohols. In both cases, steam distillation resulted only in the isolation of tarry residues. In neither case was consumption of the carbonyl compound significant. Analysis of the reaction mixtures by ^{19}F NMR spectroscopy showed that a 15% yield of **5** was formed in the reaction employing acetophenone. The failure of benzaldehyde and acetophenone to yield the expected alcohols suggests that while the carbanionic intermediate in the ester decomposition exhibits sufficient stability to react with carbonyl compounds which are very susceptible to nucleophilic attack, such as the polyfluoromethyl ketones, the rate of reaction with less reactive carbonyl compounds such as benzaldehyde and acetophenone is slower than the rate of decomposition of the intermediate.

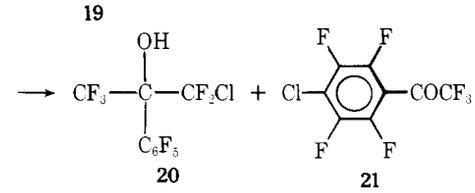
Decarbomethoxylation of **3** in the presence of benzoyl chloride, however, yielded the expected products. Ester decomposition in the presence of the acid chloride, which is very susceptible to nucleophilic displacement of the chloride by an addition/elimination mechanism,[26] resulted in a 40% yield of ketone **8** and small amounts of **10** (15%) and **9** (5%), which

$$3 + LiCl/HMPA + PhCOCl \rightarrow PhCOF + \mathbf{8\text{–}10}$$

resulted from addition of $ClCF_2^-$ or $ClCF_2Li$/HMPA to **8** as described previously. In addition, a 20% yield of benzoyl fluoride was produced. That **8** was not the result of insertion of difluorocarbene into the carbon–chlorine bond is indicated by the observation that no trifluoroacetophenone (**6a**) was formed in the reaction via carbene insertion into the carbon–fluorine bond of the benzoyl fluoride which was produced in the reaction. The benzoyl fluoride was apparently the result of chloride displacement on benzoyl chloride by fluoride ion generated during ester decomposition.

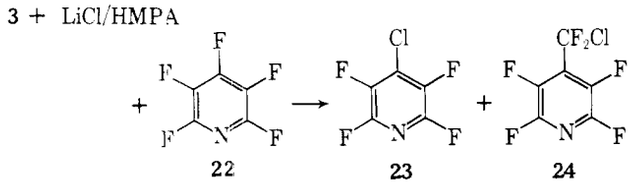
Decarbomethoxylation of **3** in THF in the presence of octafluoroacetophenone (**19**) resulted in the isolation of two products. Alcohol **20** was obtained in 38% yield and the 4-

$$3 + LiCl/HMPA + C_6F_5COCF_3$$
$$\mathbf{19}$$



chloro ketone **21** in 52% yield from this reaction. The ketone **21** was also formed in an essentially quantitative yield when **19** was treated with LiCl/HMPA alone in refluxing THF. These results indicate that either substitution of the para fluorine by chloride decreases the reactivity of the carbonyl group of **21** toward nucleophilic attack relative to the carbonyl in **19**, or the ortho fluorines of **19** and **21** deactivate the carbonyl carbon toward nucleophilic attack relative to **6a** or both. Similar inhibition by ortho fluorines in nucleophilic attack at the α position has been reported previously.[18] Other fluorinated products were detected in trace amounts in this reaction mixture by ^{19}F NMR spectroscopy. None of these products were identified, but they are believed to have resulted from formation of small amounts of the perfluoro analogue of epoxide **12** and subsequent ring opening of this oxirane by halide ion or from displacement of ring fluorines of **19** by methide ion or $ClCF_2Li$/HMPA. The relatively low yield of **20** and the large amount of **21** formed in this reaction indicate that attack at the carbonyl carbon by either $ClCF_2^-$ or $ClCF_2Li$/HMPA does not compete very favorably with attack by chloride ion at the para position of the aromatic ring.

Similar results were observed when **3** was treated with LiCl/HMPA in refluxing THF in the presence of pentafluoropyridine (**22**). Pentafluoropyridine is known to be very



susceptible to nucleophilic attack,[27] and indeed **22** was totally consumed in this reaction. Again, the predominant product of the reaction was the result of displacement of the para fluorine by chloride ion. Thus, 4-chlorotetrafluoropyridine (**23**) was obtained in 66% yield. The only other product which was formed was 4-chlorodifluoromethyltetrafluoropyridine (**24**) obtained in 34% yield. No other fluorinated products were observed by ^{19}F NMR spectroscopy in contrast to the transfer of a bromodifluoromethyl group to **22** upon decomposition of bromodifluoromethyltriphenylphosphonium bromide by fluoride ion in the presence of **22**.[28] In this latter case, polysubstitution products as well as those resulting from the transfer of a trifluoromethyl group were observed in addition to bromodifluoromethyl group transfer. A similar attempt at displacement of fluorine from hexafluorobenzene by either the chlorodifluoromethyl group or the chloride ion failed.

The attempted preparation of chlorodifluoroiodomethane (**25**) by decarbomethoxylation of **3** in the presence of positive

$$3 + \text{LiCl/HMPA} + I_2 \rightarrow \underset{\mathbf{25}}{ClCF_2I} + \underset{\mathbf{26}}{CF_2I_2}$$

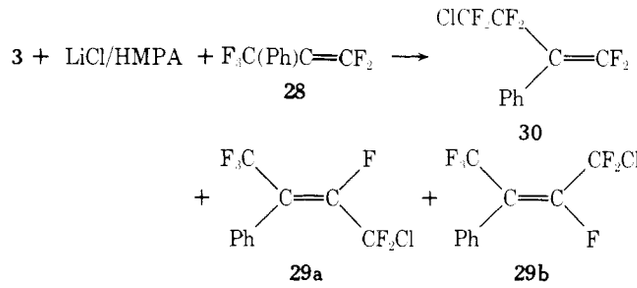
iodine sources met with little success. Treatment of **3** with LiCl/HMPA in refluxing THF in the presence of iodine resulted in no ester decomposition. However, decomposition of **3** did occur in the presence of iodine when triethylene glycol dimethyl ether (triglyme) was used as the solvent. The temperature required for decomposition was somewhat higher than normal, however. Thus, treatment of **3** with LiCl/HMPA in triglyme at 90–95 °C in the presence of iodine resulted in a 15% yield of **25** as well as a 5% yield of difluorodiiodomethane (**26**). The formation of **25** was most likely the result of abstraction of positive iodine from I_2 by either $ClCF_2^-$ or $ClCF_2Li$/HMPA, but it may also have been the result of insertion of difluorocarbene into iodine monochloride (ICl), which may have been formed in the reaction mixture. The formation of **26** most likely occurred by insertion of carbene into I_2, as reported by Mitsch.[29]

The use of iodine monobromide (IBr) as the positive iodine source resulted in a slightly improved yield of **25**. When **3** was

$$3 + \text{LiCl/HMPA} + IBr \rightarrow \mathbf{25} + \underset{\mathbf{27}}{BrCF_2I}$$

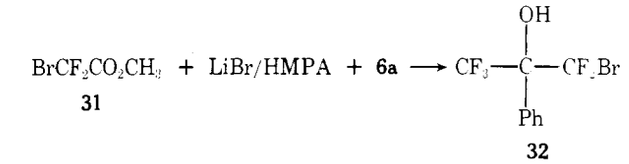
treated with LiCl/HMPA in triglyme at 90–95 °C in the presence of IBr, a 30% yield of **25** resulted as well as a 10% yield of the carbene insertion product **27**. The reason for the higher yield of **25** obtained utilizing IBr as the positive iodine source is not understood at present, although similar results have been observed by others in this laboratory.

Highly fluorinated electrophilic carbon–carbon double bonds are very susceptible to attack by nucleophiles while being rather inert to attack by electrophilic reagents.[30] Especially susceptible to nucleophilic attack are terminal difluoromethylene olefins which have substituents on the β carbon which stabilize an adjacent negative charge. When **3** was treated with LiCl/HMPA in refluxing THF in the presence of 2-phenylpentafluoropropene (**28**), three isomeric



butenes were isolated in a total yield of 53% after 48 h. The predominant product of the reaction was (*Z*)-1-chloro-3-phenylhexafluoro-2-butene (**29a**), which comprised 64% of the product mixture. The minor products were the *E* isomers of the 2-butene **29b** and the 1-butene **30**, which comprised 17 and 19% of the product mixture, respectively. All three products were the result of addition of the $ClCF_2$ group to the 1 carbon followed by elimination of fluoride ion. The isomeric 2-butenes were characterized on the basis of the magnitude of the vicinal $F–CF_3$ ^{19}F NMR coupling constants, which were 24.1 and 10.9 Hz for the *Z* and *E* isomers, respectively.[31] Essentially identical results were obtained from decomposition of **3** by LiCl/HMPA in the presence of 2-(3-bromophenyl)-pentafluoropropene. The two isomers of the corresponding 2-butene and the 1-butene were formed in an overall yield of 25% with the isomer ratios being the same as those for the reaction involving **28**.

The extension of the decarbomethoxylation reaction to the generation of bromodifluoromethide ion or its alkyllithium analogue has met with limited success. Treatment of methyl bromodifluoroacetate (**31**) with either LiCl/HMPA or LiBr/



HMPA in refluxing THF resulted in essentially quantitative decarbomethoxylation over a period of 12 h. Treatment of **31** with LiBr/HMPA in THF in the presence of ketone **6a** resulted in a 40% yield of a single product upon steam distillation which has tentatively been assigned the structure 1-bromo-2-phenylpentafluoro-2-propanol (**32**) solely on the basis of its ^{19}F NMR spectrum. All attempts at isolating **32** resulted in its decomposition; thus, a vigorous characterization of **32** was not possible. However, the similarity of the ^{19}F NMR chemical shifts and coupling constants of **32** to **7a** and to

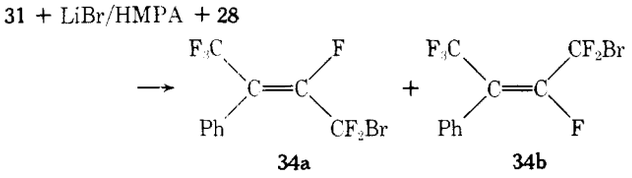
compounds with very similar structures containing the bromodifluoromethyl group gives us confidence in this structural assignment.

Similar treatment of **31** with LiCl/HMPA in the presence of **6a** resulted in the formation of a 12% yield of **7a** as well as a 33% yield of **32.** The ratio of alcohols **32** and **7a** remained constant over a 48-h period in the presence of excess LiCl/HMPA, indicating that **7a** was not the result of displacement of bromide from **32** by chloride ion.

The formation of **7a** suggested the possibility of the formation of either $ClCF_2^-$ or $ClCF_2Li$/HMPA during the course of the decomposition of **31,** possibly via capture of difluorocarbene by chloride ion. However, when **31** was treated with LiCl/HMPA in the presence of both ketone **6a** and olefin **16,** the yields of **32** (35%) and **7a** (13%) were essentially identical with the yields obtained in the absence of the olefin. A 40% yield of cyclopropane **17** was also obtained, indicating that difluorocarbene was indeed formed in the reaction. While carbene was intercepted by **16,** the formation of **7a** in the same yield as observed in the absence of the olefin indicates that formation of this alcohol was not the result of capture of difluorocarbene by chloride ion to generate $ClCF_2^-$, which then added to the ketone. Chloride ion would not be expected to compete with **16** as a scavenger of difluorocarbene; thus, if carbene was an intermediate in the formation of **7a,** the presence of the olefin would have caused a drastic reduction in the amount of alcohol formed due to selective scavenging of the carbene by the olefin.

Treatment of ester **31** with LiCl/HMPA in THF at 40 °C resulted in the formation of **4** (38%) as detected by ^{19}F NMR spectroscopy. A similar experiment at room temperature resulted in the formation of $BrCF_2CO_2Li$/HMPA (**33**) and **4** as detected by ^{19}F NMR spectroscopy. At no time during the course of the reaction was ester **3** observed by NMR spectroscopy. These results indicate that **4** was not formed by displacement of bromide from ester **31** by chloride with subsequent cleavage of ester **3** so formed by chloride ion. Thus, the alcohol **7a** formed during decarbomethoxylation of **31** in the presence of ketone **6a** employing LiCl/HMPA was the result of decarboxylation of **4,** as described previously, which was formed by chloride–bromide exchange occurring, most likely, in the HMPA-complexed lithium bromodifluoroacetate (**33**).

That decarbomethoxylation of **31** results in the generation of either $BrCF_2^-$ or $BrCF_2Li$/HMPA was also demonstrated by treatment of **31** with LiBr/HMPA in the presence of fluoro olefin **28.** This reaction yielded 25% of the isomeric 1-bromo-3-phenylhexafluoro-2-butenes (**34a** and **34b**) with a



34a **34b**

Z/E isomer ratio of 4:1. Thus, $BrCF_2^-$ or its complexed alkyllithium analogue may also be generated and utilized as a reactive intermediate in both nucleophilic addition and nucleophilic substitution reactions.

Conclusions

The ability to generate halodifluoromethide ions (XCF_2^-; X = Cl or Br) or their HMPA-complexed alkyllithium analogues (XCF_2Li/HMPA) has been demonstrated. These nucleophilic intermediates may be utilized in a variety of nucleophilic addition or substitution reactions. The products observed in these reactions may best be accounted for in terms of carbanion intermediates $ClCF_2^-$ and $BrCF_2^-$. Competition reactions indicate that the formation of these carbanionic intermediates is not the result of concerted difluorocarbene formation with subsequent halide ion–carbene recombination but that the carbanions are the direct result of decarboxylation of HMPA-complexed lithium halodifluoroacetates **4** and **33** formed by displacement of the halodifluoroacetate ions from the corresponding methyl esters **3** and **31** by halide ions.

In contrast to the generation and transfer of halodifluoromethyl groups by the decomposition of halodifluoromethylphosphonium salts with fluoride ion,[9] the generation of these carbanions by the ester decarbomethoxylation method[21] results in relatively clean reactions without the accompanying formation of myriad side products.[28] In addition, transfer of halodifluoromethide groups to ketones with subsequent alcohol formation may not be accomplished by the phosphonium salt decomposition route.[28] Thus, the halide ion induced decomposition of methyl halodifluoroacetates serves as a very promising, convenient, and useful method for the generation of halodifluoromethide ions.

Experimental Section

Melting points were obtained in capillary tubes using a Thomas-Hoover unimelt apparatus and are corrected. The boiling points were obtained during fractional distillation by means of a partial immersion thermometer and are uncorrected. The infrared spectra were recorded on a Beckman IR-20A spectrophotometer. ^1H NMR spectra were recorded using ca. 10% (w/v) solutions in either $DCCl_3$ or CCl_4 on a Varian A-60 spectrometer with tetramethylsilane (Me_4Si) as an internal standard. ^{19}F NMR spectra were recorded using either aliquots of reaction mixtures or ca. 10% (w/v) solutions operating at 94.075 MHz. All chemical shifts are reported in ϕ^* values upfield from the external (ext) (capillary) $CFCl_3$ standard. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-66 mass spectrometer operating at 70 eV. Mass spectral samples were isolated from reaction or product mixtures by the analytical GLC capillary technique of Burson and Kenner.[32] Analytical and preparative GLC were performed on a Hewlett-Packard F & M Model 720 dual column gas chromatograph. Product yields were determined by comparison of the relative areas under peaks vs. an appropriate internal standard, corrected for differences in detector responses. Column A was a 10 ft × 0.25 in copper column packed with 15% (w/w) SE-30 on 80–100 mesh Chromosorb P. Column B was a 10 ft × 0.25 in copper column packed with 20% (w/w) SE-30 on 80–100 mesh Chromosorb P. Column C was a 10 ft × 0.25 in copper column packed with 15% (w/w) 20M Carbowax on 80–100 mesh Chromosorb P. Column D was a 10 ft × 0.5 in copper column packed with 20% (w/w) 20M Carbowax on 80–100 mesh Chromosorb P. Quantitative determination of carbon dioxide was performed by sweeping the CO_2 through a saturated solution of barium hydroxide.

Tetrahydrofuran and triglyme were distilled from sodium benzophenone ketyl and stored over 4A molecular sieves under nitrogen. Benzene was distilled from sodium and stored over sodium wire. Hexamethylphosphoric triamide (HMPA) was distilled from sodium at reduced pressure and stored over 4A molecular sieves under nitrogen. The alkali metal halides were dried at 120 °C in a vacuum oven (ca. 1 mmHg) for 24 h and then stored in a desiccator over phosphorus pentoxide. Lithium chlorodifluoroacetate was prepared by neutralization of chlorodifluoroacetic acid with lithium carbonate and was dried at 40 °C in vacuo (ca. 0.2 mmHg) for 24 h. The salt was stored in a desiccator over phosphorus pentoxide. All solids were handled in a glovebag under dry nitrogen and transferred in solid addition tubes sealed by rubber serum stoppers. The polyfluoromethyl ketones were prepared by the method of Dishart and Levine[33] as modified by Herkes and Burton.[34] The 2-arylpentafluoropropenes were prepared by the method of Naae and Burton.[35] The macrocyclic polyether 18-crown-6 was prepared by the literature method.[36]

Methyl Chlorodifluoroacetate (3). Methyl chlorodifluoroacetate was prepared by refluxing a solution of chlorodifluoroacetic acid (Halocarbon Chemical) (130.5 g, 1.00 mol) and excess anhydrous methanol (48.0 g, 1.50 mol) in the presence of concentrated sulfuric acid (40 mL) for 18 h. The reaction mixture was poured into ice water (600 mL), and the lower organic phase was separated, washed with 5% $NaHCO_3$ (2 × 250 mL) and water (2 × 200 mL), dried over 4A molecular sieves, and distilled under nitrogen through a 15 cm Vigreux

column to give a 69% (99.8 g, 0.69 mol) yield of **3**, bp 77.5–78.5 °C (lit.[37] bp 79–81 °C).

Methyl Bromodifluoroacetate (31). Methyl bromodifluoroacetate was prepared in 58% yield by the method of Paleta, Liska, and Posta.[38]

Preparation of LiX/HMPA In Situ. The lithium halide/HMPA complexes (LiX/HMPA) were prepared in situ for each reaction by adding anhydrous lithium halide via a solid addition tube to an equimolar amount of HMPA in the appropriate solvent with vigorous stirring. Formation of the complex was accompanied by a slight exotherm in each case. Complex formation was deemed complete when all of the lithium halide had gone into solution and the exotherm had subsided.

Reaction of 3 with LiCl/HMPA: Isolation of 4. To a solution of LiCl/HMPA (20 mmol) in THF (20 mL) was added **3** (4.35 g, 3.18 mmol) under nitrogen. The solution was heated to 40 °C and analyzed by ^{19}F NMR spectroscopy after 2 h. Using $C_6H_5CF_3$ as an internal standard indicated that an essentially quantitative yield of lithium chlorodifluoroacetate/HMPA complex (**4**) had been formed. The solvent was evaporated under vacuum to yield a viscous orange oil which was crystallized from benzene (10 mL) by freezing the solution and then allowing the benzene to slowly melt. The white solid which precipitated was collected by filtration under dry nitrogen through a Schlenk funnel.[39] The solid was dried in vacuo to give a 42% (2.65 g, 8.4 mmol) isolated yield of **4**: mp 178–180 °C with decomposition; IR (KBr) 2918 (m), 1690 (bs), 1413 (m), 1308 (m), 1190 (s), 1142 (bs), 1070 (w), 990 (s), 870 (w), 845 (w), 814 (m), 738 (s) cm^{-1}; ^1H NMR (10% $DCCl_3$, Me_4Si) δ 2.62 (d), J(PNCH) = 9.2 Hz; ^{19}F NMR (10% $DCCl_3$, $CFCl_3$ ext) ϕ^* +60.9 ppm (s). Anal. Calcd for $C_8H_{18}N_3O_3ClF_2PLi$: C, 30.44; H, 5.75; N, 13.31. Found: C, 28.65; H, 6.36; N, 10.59.

Reaction of 3 with LiCl/HMPA and 2,2,2-Trifluoroethanol. To a solution of LiCl/HMPA (40 mmol) in THF (20 mL) was added 2,2,2-trifluoroethanol (4.05 g, 40.5 mmol) and **3** (2.90 g, 2.12 mL, 20 mmol). The reaction system was connected in series to a cold trap (dry ice–2-propyl alcohol), a large bubbler containing 100 mL of a saturated solution of barium hydroxide, and a mineral oil bubbler, and then the solution was refluxed for 12 h. Analysis of the contents of the cold trap by both ^{19}F and ^1H NMR spectroscopy using $C_6H_5CF_3$ as an internal standard for both indicated that an essentially quantitative yield of chlorodifluoromethane (**5**) was obtained as well as a 92% yield of methyl chloride. The precipitate in the barium hydroxide bubbler was collected by suction filtration in a tared sintered glass crucible to give 3.47 g (17.6 mmol, 88%) of barium carbonate.

Reaction of 3 with LiCl/HMPA and 6a: Preparation of 7a. Ester **3** (4.35 g, 3.18 mL, 30 mmol) was added to a solution of LiCl/HMPA (60 mmol) and **6a** (5.22 g, 3.78 mL, 30 mmol) in THF (30 mL). The reaction mixture was refluxed for 24 h and then steam distilled. The organic layer was separated, and the aqueous layer was extracted with ether (2 × 20 mL). The ether extracts and the organic layer were combined, washed with water (2 × 100 mL), and dried over anhydrous magnesium sulfate, and the ether was evaporated. The residue was then fractionally distilled through a 15 cm Vigreux column to give a 63% (4.91 g, 18.9 mmol) isolated yield of pure **7a**: bp 68–70 °C (8 mmHg); mass spectrum, *m/e* (relative intensity) 260 (9), 175 (88), 127 (19), 105 (100), 77 (44), 69 (15), 51 (20) (calcd for **7a**, 260.6 g/mol); IR (neat) 3588 (s), 3070 (w), 1502 (w), 1453 (w), 1356 (m), 1258 (m), 1218 (bs), 1128 (w), 1103 (w), 1076 (m), 1038 (m), 1021 (m), 948 (w), 918 (s), 845 (s), 756 (m), 728 (w), 716 (s), 692 (m), 669 (w) cm^{-1}; ^1H NMR (10% CCl_4, Me_4Si) δ 8.24–7.28 (m, 5 H, C_6H_5), 3.89 (broad s, 1 H, OH); ^{19}F NMR (10% CCl_4, $CFCl_3$ ext) ϕ^* +61.9 ppm (q, 2 F, CF_2Cl), +73.5 ppm (t, 3 F, CF_3), J(CF_3, CF_2Cl) = 9.5 Hz.

Preparation of 7b. Refluxing a solution of **3** (7.23 g, 5.3 mL, 50 mmol), LiCl/HMPA (100 mmol), and **6b** (15.4 g, 11.5 mL, 100 mmol) in THF (50 mL) for 24 h followed by steam distillation resulted in the isolation of a yellow oil. Fractional distillation through a 15 cm Vigreux column gave a 39% (4.69 g, 19.5 mmol) isolated yield of 98% pure **7b**: bp 52–53 °C (18 mmHg); IR (neat) 3490 (bm), 2970 (m), 2882 (w), 1465 (w), 1283 (w), 1265 (w), 1200 (s), 1132 (w), 1109 (w), 1019 (w), 997 (w), 928 (m), 833 (m) cm^{-1}; ^1H NMR (10% $DCCl_3$, Me_4Si) δ 2.98 (broad s, 1 H, OH), 2.25–0.69 (unresolved m, 9 H, C_4H_9); ^{19}F NMR (10% $DCCl_3$, $CFCl_3$ ext) ϕ^* +62.0 ppm (q, 2 F, CF_2Cl), +74.4 ppm (t, 3 F, CF_3), J(CF_3, CF_2Cl) = 11.4 Hz.

Preparation of 9 and 10. A solution of **3** (2.90 g, 2.12 mL, 20 mmol), LiCl/HMPA (40 mmol), and **8** (3.81 g, 20 mmol) in THF (40 mL) was refluxed for 48 h and then steam distilled to yield a mixture of **8**, **9**, and **10**. Preparative GLC on column B resulted in the isolation of a 50% yield of **10** (1.73 g, 10 mmol); mass spectrum, *m/e* (relative intensity) 176 (32), 174 (100), 139 (59), 119 (40), 89 (18) (calcd for **10**, 174.5 g/mol); IR (neat) 3195 (w), 1734 (s), 1500 (w), 1458 (w), 1305 (m), 1289 (w), 1263 (m), 1200 (w), 1013 (s), 948 (m), 922 (w), 764 (m), 698 (w) cm^{-1}; ^{19}F NMR (10% $DCCl_3$, $CFCl_3$ ext) ϕ^* +83.5 ppm (d, 1 F, vinyl F cis to Cl), +89.1 ppm (d of t, 1 F, vinyl F trans to Cl), J(F, ortho H's) = 1.2 Hz, J(FCF) = 33.2 Hz.

Compound **10** was identical in all respects with an authentic sample previously prepared in these laboratories via the reaction of $C_6H_5CHClCF_2Cl$ and $LiCO_3$.[40] An 18% (1.00 g, 3.6 mmol) isolated yield of **9** was also obtained which was identical in all respects with an authentic sample prepared via the addition of phenylmagnesium bromide to difluorotetrachloroacetone.[18]

Attempted Preparation of 11a. A solution of potassium hydroxide (2.0 g, 35 mmol) in water (15 mL) was added dropwise to **7a** (5.21 g, 20 mmol) with vigorous stirring. The solution was heated to 85–90 °C for 10 min. The reaction mixture was then cooled to 0 °C, but no organic layer separated. The solution was acidified with 6 N HCl, and the organic layer which separated was analyzed by ^{19}F NMR spectroscopy, which showed it to be the unchanged alcohol **7a** which was recovered in 96% yield (5.00 g, 19.2 mmol).

Attempted Preparation of 11b. Treatment of **7b** (12.0 g, 50 mmol) with potassium hydroxide (5.60 g, 100 mmol) in water (70 mL) resulted only in the recovery of 98% (11.8 g, 49.0 mmol) of unchanged **7b** as described above.

Preparation of 12. To **9** (27.7 g, 100 mmol) was added with vigorous stirring potassium hydroxide (11.2 g, 200 mmol) in water (35 mL). The resulting solution was then heated to 70–80 °C for 20 min, and the lower organic layer which formed upon heating was separated, washed with water, taken up in ether, and dried over anhydrous magnesium sulfate. Fractional distillation through a 15 cm Vigreux column gave 65% (15.6 g, 65 mmol) of pure **12**: bp 74–75 °C (27 mmHg) [lit.[20] bp 93 °C (68 mmHg)]; ^{19}F NMR (10% CCl_4, $CFCl_3$ ext) ϕ^* +59.4 ppm (d of d, 2 F, CF_2Cl), +101.8 ppm (d of t, 1 F, F trans to CF_2Cl), +109.5 ppm (d of t, 1 F, F cis to CF_2Cl), J($ClCF_2$, trans F) = 2.1 Hz, J($ClCF_2$, cis F) = 19.4 Hz, J(trans F, cis F) = 41.2 Hz.

Reactions of 12 with LiCl/HMPA. To a solution of LiCl/HMPA (50 mmol) in THF (20 mL) cooled to 0 °C in an ice–water bath was added **12** (9.63 g, 40 mmol) at such a rate that the temperature of the reaction did not exceed 5 °C. After stirring at 0 °C for 1 h, ^{19}F NMR analysis using $C_6H_5CF_3$ as an internal standard indicated the formation of acid fluoride **15** in a 96% yield. The reaction mixture was flash distilled and then fractionally distilled through a 15 cm Vigreux column to give a 30% (3.20 g, 12 mmol) isolated yield of 97% pure **15**: bp 78–80 °C (5 mmHg); IR (neat) 1860 (s), 1203 (bs), 1159 (bs), 1050 (m), 1036 (m), 962 (m), 846 (m), 829 (w), 756 (m), 720 (m), 648 (w) cm^{-1}; ^{19}F NMR (10% $CFCl_3$) ϕ^* −32.9 ppm (t, 1 F, COF), +59.8 ppm (d of d, 1 F, CF^1Cl), +60.0 ppm (d of d, 1 F, CF^2Cl), J($ClCF_2$, COF) = 9.1 Hz, J(F^1, F^2) = 169.7 Hz. Additional confirmation of **15** was obtained by conversion to the known methyl ester via treatment of **15** with methanol.[41] In addition, a 69% (4.80 g, 27.6 mmol) yield of **10** [bp 50–52 °C (7 mmHg)] was isolated, which was identical with an authentic sample.

When **12** (7.22 g, 30 mmol) was added to a refluxing solution of LiCl/HMPA (70 mmol) in THF (20 mL) and stirred for 16 h, ^{19}F NMR analysis using $C_6H_5CF_3$ as an internal standard indicated the formation of **10** in a 95% yield. The reaction mixture was flash distilled, the distillate was washed with water (2 × 100 mL), the organic layer was separated, and the aqueous layer was extracted with ether (2 × 10 mL). The ether extracts and the organic layer were combined, dried over anhydrous calcium sulfate, and fractionally distilled through a 15 cm glass helices column to give a 46% (2.40 g, 13.8 mmol) isolated yield of pure **10** which was identical with an authentic sample.

Decomposition of 3 in the Presence of 6a and 16. To a solution of LiCl/HMPA (20 mmol), **6a** (9.25 g, 53 mmol), and **16** (4.32 g, 51 mmol) in refluxing THF (40 mL) was added **3** (2.90 g, 20 mmol). After refluxing for 48 h, GLC analysis using toluene as an internal standard indicated a 67% consumption of **6a** and the formation of a 27% yield of **17**. Compound **17** was identified via comparison of its GC retention time and ^{19}F NMR absorption with an authentic sample.[22]

The reaction mixture was cooled to room temperature, acidified with 6 N HCl (3 mL), and poured into water (100 mL). The organic layer was separated and dried over anhydrous magnesium sulfate. GLC analysis of the organic layer indicated that a 27% yield of **17** and a 66% yield of **7a** were obtained.

Reaction of 3 with KF/18-Crown-6 and 6a. To a solution of 18-crown-6 (6.60 g, 25 mmol), potassium fluoride (5.81 g, 100 mmol), and **6a** (8.71 g, 50 mmol) in THF (50 mL) was added **3** (7.24 g, 5.3 mL, 50 mmol) under nitrogen. The system was connected to a bubbler containing a saturated solution of barium hydroxide. The reaction mixture was refluxed for 4 h to give, upon hydrolysis with 6 N HCl, a 21% yield of **7a** as determined by ^{19}F NMR analysis using $C_6H_5CF_3$

as an internal standard. The precipitated barium carbonate indicated that only 35% decarboxylation had occurred. The absence of **18** was confirmed by comparison (^{19}F, singlet 75.5 ppm) with an authentic sample prepared via addition of phenyllithium to hexafluoroacetone.[18]

Reaction of 3 with LiCl/HMPA and Benzaldehyde. To a solution of LiCl/HMPA (80 mmol) and benzaldehyde (4.24 g, 4.1 mL, 40 mmol) in THF (60 mL) was added **3** (5.78 g, 4.2 mL, 40 mmol). The reaction mixture was refluxed for 48 h. GLC analysis using toluene as an internal standard showed consumption of 2.2 mmol of benzaldehyde. Upon hydrolysis with 6 N HCl no discernible products were detected by ^{19}F NMR analysis.

Reaction of 3 with LiCl/HMPA and Acetophenone. To a solution of LiCl/HMPA (40 mmol) and acetophenone (2.40 g, 20 mmol) in THF (25 mL) was added **3** (2.90 g, 2.12 mL, 20 mmol). The reaction mixture was refluxed for 20 h. GLC analysis using toluene as an internal standard showed consumption of 2.0 mmol of acetophenone. ^{19}F NMR analysis using $C_6H_5CF_3$ as an internal standard showed, after hydrolysis of the reaction mixture with 6 N HCl, the formation of a 15% yield of **5**: ϕ^* +72.6 ppm (d), J(HCF) = 62.6 Hz.

Reaction of 3 with LiCl/HMPA and Benzoyl Chloride. Ester **3** (2.90 g, 2.12 mL, 20 mmol) was added to a solution of LiCl/HMPA (40 mmol) and benzoyl chloride (2.81 g, 20 mmol) in THF (25 mL), and the solution was refluxed for 48 h. The reaction mixture was then poured into 3 N HCl. GLC analysis of the organic layer using toluene as an internal standard showed the formation of a 20% yield of benzoyl fluoride, 40% of **8**, 15% of **10**, and 5% of **9**, as identified by a comparison of their GLC retention times with those of authentic samples.

Reaction of 3 with LiCl/HMPA and Octafluoroacetophenone (19). Ester **3** (7.23 g, 5.3 mL, 50 mmol) was added to a solution of LiCl/HMPA (100 mmol) and **19** (12.8 g, 49 mmol) in THF (100 mL), and the reaction mixture was refluxed for 20 h. GLC analysis indicated that total consumption of **19** had occurred. The reaction mixture was poured into water (500 mL) containing 6 N HCl (10 mL). The lower organic layer was separated, washed with water (3 × 100 mL), and dried over anhydrous magnesium sulfate. The product mixture was then distilled through a 15 cm Vigreux column to give a 52% (7.46 g, 26 mmol) isolated yield of **21**: bp 78–80 °C (43 mmHg); mass spectrum, *m/e* (relative intensity) 280 (7), 213 (29), 211 (100), 185 (15), 183 (47), 148 (16), 133 (28), 98 (10), 79 (15), 69 (16) (calcd for **21**, 280.5 g/mol); IR (neat) 2899 (w), 1758 (s), 1650 (s), 1499 (s), 1473 (w), 1420 (m), 1326 (m), 1272 (m), 1225 (s), 1181 (s), 1076 (s), 991 (s), 918 (m), 818 (m), 798 (w), 752 (m), 718 (m), 701 (w) cm^{-1}; ^{19}F NMR (10% THF, $CFCl_3$ ext) ϕ^* +78.1 ppm (t, 3 F, CF_3), +139.1 ppm (m, 2 F, ortho F's), +140.5 ppm (m, 2 F, meta F's), J(CF_3, ortho F's) = 11.1 Hz, all other coupling remains unresolved.

A second fraction was collected to give a 38% (6.53 g, 18.6 mmol) isolated yield of **20** (bp 85–87 °C (21 mmHg), which was identical with an authentic sample prepared by the method of Dyatkin.[18]

Reaction of LiCl/HMPA with 19. Ketone **19** (5.28 g, 20 mmol) was added to a solution of LiCl/HMPA (40 mmol) in refluxing THF (20 mL). After refluxing for 3 h, the reaction mixture was poured into a brine solution (200 mL), and the lower organic layer was separated, washed with water (3 × 50 mL), and dried over anhydrous magnesium sulfate. Preparative GLC on column B gave a 95% (5.33 g, 19.0 mmol) yield of 99% pure (GLC) **21**.

Reaction of 3 with LiCl/HMPA and *F*-Pyridine (22). Ester **3** (4.35 g, 3.2 mL, 30 mmol) was added to a solution of LiCl/HMPA (60 mmol) and **22** (5.16 g, 30 mmol) in THF (30 mL). The mixture was refluxed for 48 h, and then ^{19}F NMR analysis using $C_6H_5CF_3$ as an internal standard showed the formation of a 34% yield of **24** and a 66% yield of **23**. The reaction mixture was flash distilled (60 °C, 4 mmHg), and the flash distillate was concentrated by distillation of the THF through a 30 cm gold-plated monel spinning band column. The residue was separated by preparative GLC on column D to give a 30% (2.12 g, 9 mmol) isolated yield of **24**: mass spectrum, *m/e* (relative intensity) 237 (12), 235 (35), 216 (12), 200 (100), 150 (13), 105 (10), 100 (31), 93 (11), 69 (38) (calcd for **24**, 235.5 g/mol); IR (neat) 1649 (w), 1480 (s), 1423 (m), 1304 (s), 1255 (w), 1218 (w), 1143 (s), 1028 (w), 991 (s), 969 (s), 828 (s), 762 (m), 747 (m), 697 (w), 649 (w) cm^{-1}; ^{19}F NMR (10% CCl_4, $CFCl_3$ ext) ϕ^* +48.7 ppm (t of m, 1 F, CF_2Cl), +86.4 ppm (m, 1 F, 2-F's), +140.2 ppm (m, 1 F, 3-F's), J($ClCF_2$, 3-F's) = 26.8 Hz, J(2-F's, 3-F's) = 12.4 Hz, all other coupling remains unresolved.

23 was isolated in a 60% yield (3.33 g, 18 mmol): mass spectrum, *m/e* (relative intensity) 187 (34), 185 (100), 166 (4), 150 (11), 140 (15), 116 (12), 100 (20) (calcd for **23**, 185.5 g/mol); IR (neat) 1638 (s), 1578 (w), 1480 (s), 1415 (m), 1313 (w), 1271 (w), 1242 (s), 1018 (w), 955 (s), 915 (s), 732 (w), 698 (w) cm^{-1}; ^{19}F NMR (10% CCl_4, $CFCl_3$ ext) ϕ^* +87.5 ppm (m, 1 F, 2-F's), +141.5 ppm (m, 1 F, 3-F's), no coupling could be resolved.

Reaction of 3 with LiCl/HMPA and Hexafluorobenzene. Ester **3** (2.90 g, 2.12 mL, 20 mmol) was added to a solution of LiCl/HMPA (40 mmol) and hexafluorobenzene (3.72 g, 2.3 mL, 20 mmol) in THF (20 mL). The reaction mixture was refluxed for 24 h. ^{19}F NMR analysis using $C_6H_5CF_3$ as an internal standard indicated that no consumption of hexafluorobenzene occurred.

Reaction of 3 with LiCl/HMPA and Iodine. Ester 3 (1.45 g, 1.06 mL, 10 mmol) was added to a solution of LiCl/HMPA (20 mmol) and I_2 (2.54 g, 10 mmol) in triglyme (25 mL). The reaction mixture was heated at 90–95 °C for 48 h, and then ^{19}F NMR analysis using $C_6H_5CF_3$ as an internal standard indicated the formation of **25** in a 15% yield and **26** in a 5% yield. The products **25** and **26** were identified by enhancement of their ^{19}F NMR signals with authentic samples.[42]

Reaction of 3 with LiCl/HMPA and Iodine Monobromide. Ester **3** (1.45 g, 1.06 mL, 10 mmol) was added to a solution of LiCl/HMPA (20 mmol) and IBr (2.07 g, 10 mmol) in triglyme (25 mL). The reaction mixture was heated at 90–95 °C for 48 h, and then ^{19}F NMR analysis using $C_6H_5CF_3$ as an internal standard indicated that a 30% yield of **25** and a 10% yield of **27** had been formed. The products **25** and **27** were identified by enhancement of their ^{19}F NMR signals with authentic samples.[42]

Reaction of 3 with LiCl/HMPA and 2-Phenyl-*F*-propene (28). Ester **3** (21.7 g, 15.9 mL, 150 mmol) was added to a solution of LiCl/HMPA (300 mmol) and **28** (110.4 g, 8.0 mL, 50 mmol) in THF (150 mL). The reaction mixture was refluxed for 72 h. The reaction mixture was then steam distilled, the organic layer was separated, and the aqueous layer was extracted with pentane (3 × 20 mL). The pentane extracts and the organic layer were combined and dried over anhydrous magnesium sulfate. The pentane was then evaporated. Preparative GLC of the residue on column B gave a 46% (4.78 g, 23 mmol) recovery of **28**, a 34% (4.63 g, 17 mmol) yield of **29a**, and a mixture of **29b** (1.24 g, 4.5 mmol, 9%) and **30** (1.37 g, 5 mmol, 10%), as determined by ^{19}F NMR analysis of the mixture. **29a** was characterized as follows: mass spectrum, *m/e* (relative intensity) 276 (27), 274 (81), 239 (100), 219 (93), 189 (26), 169 (55), 151 (14) (calcd for **29a**, 274.5 g/mol); IR (neat) 3070 (w), 1695 (m), 1495 (w), 1449 (w), 1356 (s), 1234 (s), 1190 (s), 1146 (s), 1110 (w), 1076 (w), 976 (s), 948 (m), 914 (w), 812 (s), 762 (m), 723 (w), 698 (s), 658 (w), 634 (w) cm^{-1}; ^{19}F NMR (10% $DCCl_3$, $CFCl_3$ ext) ϕ^* +55.1 ppm (d of q, 2 F, CF_2Cl), +60.7 ppm (d of t, 3 F, CF_3), +111.4 ppm (q of t, 1 F, vinyl F), J($ClCF_2$, CF_3) = 1.2 Hz, J($ClCF_2$, F) = 11.2 Hz, J(CF_3, F) = 24.1 Hz.

29b was characterized by its ^{19}F NMR spectrum (10% $DCCl_3$, $CFCl_3$ ext): ϕ^* +55.7 ppm (t of d, 3 F, CF_3), +56.9 ppm (q of d, 2 F, CF_2Cl), +107.8 ppm (t of q, 1 F, vinyl F), J($ClCF_2$, CF_3) = 15.3 Hz, J($ClCF_2$, F) = 11.1 Hz, J(CF_3, F) = 10.9 Hz.

30 was characterized by its ^{19}F NMR spectrum (10% $DCCl_3$, $CFCl_3$ ext): ϕ^* +69.4 ppm (d of t, 2 F, CF_2Cl), +72.4 ppm (t of d, 1 F, vinyl F cis to C_6H_5), +73.8 ppm (t of t of d, 1 F, vinyl F trans to C_6H_5), +106.7 ppm (d of d of t, 2 F, CF_2), J($ClCF_2$, vinyl F trans to C_6H_5) = 9.4 Hz, J($ClCF_2$, CF_2) = 4.6 Hz, J(vinyl F, vinyl F) = 8.3 Hz, J(CF_2, vinyl F cis to C_6H_5) = 8.6 Hz, J(CF_2, vinyl F trans to C_6H_5) = 27.4 Hz.

Reaction of 3 with LiCl/HMPA and 2-(3-Bromophenyl)-*F*-propene. Ester **3** (2.90 g, 2.12 mL, 20 mmol) was added to a solution of LiCl/HMPA (40 mmol) and 2-(3-bromophenyl)-*F*-propene (5.74 g, 20 mmol) in THF (20 mL). The reaction mixture was refluxed for 48 h. The reaction mixture was then poured into water (150 mL). The organic layer was separated, and the aqueous layer was extracted with Skellysolve B (2 × 15 mL). The organic layer and the Skellysolve extracts were combined and dried over anhydrous magnesium sulfate. The Skellysolve was evaporated, and the residue was separated by preparative GLC on column B to give a 15% (1.06 g, 3.0 mmol) yield of (*Z*)-1-chloro-3-(3-bromophenyl)hexafluoro-2-butene, which was characterized as follows: mass spectrum, *m/e* (relative intensity) 356 (18), 354 (61), 352 (47), 273 (11), 254 (11), 238 (99), 219 (12), 188 (22), 169 (100), 98 (12), 73 (11), 69 (15), 51 (11) (calcd for $C_{10}H_4BrClF_6$, 353.6 g/mol); ^{19}F NMR (10% $DCCl_3$, $CFCl_3$ ext) ϕ^* +55.3 ppm (d of q, 2 F, CF_2Cl), +60.6 ppm (d of t, 3 F, CF_3), +109.8 ppm (q of t, 1 F, vinyl F), J($ClCF_2$, CF_3) = 1.3 Hz, J($ClCF_2$, vinyl F) = 11.4 Hz, J(CF_3, vinyl F) = 24.1 Hz.

Also isolated was a mixture of (*E*)-1-chloro-3-(3-bromophenyl)-hexafluoro-2-butene and 4-chloro-2-(3-bromophenyl)hexafluoro-1-butene (0.35 g, 1.0 mmol, 5%, and 0.35 g, 1.0 mmol, 5%, respectively) as determined by ^{19}F NMR analysis of the mixture. The *E* 2-butene was characterized by its ^{19}F NMR spectrum (10% $DCCl_3$, $CFCl_3$ ext): ϕ^* +55.6 ppm (d of t, 3 F, CF_3), +57.0 ppm (d of q, 2 F, CF_2Cl), +106.0 ppm (t of q, 1 F, vinyl F), J($ClCF_2$, CF_3) = 15.3 Hz, J($ClCF_2$, vinyl F) = 11.3 Hz, J(CF_3, vinyl F) = 11.3 Hz.

The 1-butene was also characterized by its ^{19}F NMR spectrum (10%

$DCCl_3$, $CFCl_3$ ext): ϕ^* +69.4 ppm (d of t, 2 F, CF_2Cl), +71.0 ppm (t of d, 1 F, vinyl F cis to Ar), +72.4 ppm (t of t of d, 1 F, vinyl F trans to Ar), +106.7 ppm (d of d of t, 2 F, CF_2), J($ClCF_2$, vinyl F trans to Ar) = 10.0 Hz, J($ClCF_2$, CF_2) = 4.7 Hz, J(vinyl F, vinyl F) = 5.1 Hz, J(CF_2, vinyl F cis to Ar) = 9.3 Hz, J(CF_2, vinyl F trans to Ar) = 28.0 Hz.

Reaction of 31 with LiBr/HMPA and 6a. Methyl bromodifluoroacetate (**31**; 3.74 g, 20 mmol) was added to a solution of LiBr/HMPA (40 mmol) and **6a** (3.48 g, 2.76 mL, 20 mmol) in THF (20 mL). The reaction mixture was refluxed for 48 h and then steam distilled to give a 40% yield of **32** as determined by ^{19}F NMR spectroscopy using $C_6H_5CF_3$ as an internal standard. Attempted isolation by preparative GLC on column B resulted in decomposition on the column. The structure of **32** was assigned solely on the basis of its ^{19}F NMR spectrum (Et_2O, $CFCl_3$ ext): ϕ^* +56.6 ppm (q, 2 F, CF_2Br), +73.0 ppm (t, 3 F, CF_3), J($BrCF_2$, CF_3) = 11.2 Hz, which is consistent with the assigned structure.

Reaction of 31 with LiCl/HMPA and 6a. Ester **31** (5.80 g, 31 mmol) was added to a solution of LiCl/HMPA (60 mmol) and **6a** (5.22 g, 4.14 mL, 30 mmol) in THF (50 mL). The reaction mixture was refluxed for 48 h, and then GLC analysis using toluene as an internal standard indicated that 16.3 mmol (54%) of **6a** had been consumed. The reaction mixture was steam distilled, and the organic layer was analyzed by ^{19}F NMR using $C_6H_5CF_3$ as an internal standard. This analysis showed that a 33% yield of **32** and a 12% yield of **7a** had been obtained. Attempted isolation by fractional distillation resulted in the formation of a black tarry residue. Alcohol **7a** was identified by enhancement of its ^{19}F NMR signals with an authentic sample.

Reaction of 31 with LiCl/HMPA, 6a, and 16. Ester **31** (3.74 g, 20 mmol) was added to a solution of LiCl/HMPA (40 mmol), **6a** (6.96 g, 5.52 mL, 40 mmol), and **16** (3.36 g, 4.8 mL, 40 mmol) in THF (40 mL). The reaction mixture was refluxed for 48 h and then steam distilled. ^{19}F NMR analysis of the organic layer using $C_6H_5CF_3$ as an internal standard showed a 35% yield of **32**, a 13% yield of **7a**, and a 40% yield of **17**.

Reaction of 31 with LiCl/HMPA. Ester **31** (1.87 g, 10 mmol) was added to a solution of LiCl/HMPA (20 mmol) in THF (20 mL). The reaction mixture was stirred at room temperature for 1 h, and then ^{19}F NMR analysis using $C_6H_5CF_3$ as an internal standard indicated the presence of **31** (4.0 mmol, 40%), **33** (3.5 mmol, 35%), and **4** (2.5 mmol, 25%) in the reaction mixture. No ester **3** was observed. The reaction mixture was then heated to 45 °C and maintained at this temperature for 3 h. ^{19}F NMR analysis indicated the total consumption of **31** and the presence of dibromodifluoromethane (1.5 mmol, 15%) and **4** (3.8 mmol, 38%) in the reaction mixture. Both dibromodifluoromethane and **4** were identified by enhancement of their ^{19}F NMR signals with authentic samples.

Reaction of 31 with LiBr/HMPA and 28. Ester **31** (1.87 g, 10 mmol) was added to a solution of LiBr/HMPA (20 mmol) and **28** (2.08 g, 1.60 mL, 10 mmol) in THF (20 mL), and the reaction mixture was refluxed under nitrogen for 48 h. ^{19}F NMR analysis using $C_6H_5CF_3$ as an internal standard indicated the formation of **34a** (2.0 mmol, 20%) and **34b** (0.5 mmol, 5%) as identified by enhancement of their ^{19}F NMR signals with authentic samples.[43] Unreacted **28** was present also (7.4 mmol, 74%). In addition to these signals, traces of other products were observed but these products were not identified.

Registry No.—**3**, 1514-87-0; **4**, 66070-45-9; **5**, 75-45-6; **6a**, 434-45-7; **6b**, 360-34-9; **7a**, 13006-19-4; **7b**, 53959-78-7; **8**, 384-67-8; **9**, 1892-88-2; **10**, 394-98-9; **12**, 36853-08-4; **15**, 53959-79-8; **16**, 27416-06-4; **17**, 823-25-6; **19**, 652-22-2; **20**, 13006-20-7; **21**, 66070-46-0; **22**, 700-16-3; **23**, 52026-98-9; **24**, 66070-47-1; **25**, 420-49-5; **26**, 1184-76-5; **27**, 753-66-2; **28**, 1979-51-7; **29a**, 66070-48-2; **29b**, 66070-49-3; **31**, 683-98-7; **32**, 66070-50-6; **34a**, 58201-69-7; **34b**, 58201-68-6; chlorodifluoroacetic acid, 76-04-0; LiCl/HMPA, 54215-87-1; LiBr/HMPA, 36239-89-1; 2,2,2-trifluoroethanol, 75-89-8; benzaldehyde, 100-52-7; acetophenone, 98-86-2; benzoyl chloride, 98-88-4; hexafluorobenzene, 392-56-3; iodine, 7553-56-2; iodine monobromide, 7789-33-5; 2-(3-bromophenyl)-*F*-propene, 61587-34-6; (*Z*)-1-chloro-3-(3-bromophenyl)-hexafluoro-2-butene, 66070-51-7; (*E*)-1-chloro-3-(3-bromophenyl)hexafluoro-2-butene, 66070-52-8; 4-chloro-2-(3-bromophenyl)-hexafluoro-1-butene, 66070-53-9.

References and Notes

(1) Presented in part at the 170th National Meeting of the American Chemical Society, Chicago, Ill., August 26, 1975.
(2) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969, pp 337–371.
(3) R. D. Chambers, "Fluorine in Organic Chemistry", Wiley, New York, N.Y., 1973, pp 120–129.
(4) J. Hine, "Divalent Carbon", Ronald Press, New York, N.Y., 1964, Chapter 3.
(5) W. Kirmse, "Carbene Chemistry", Academic Press, New York, N.Y., 1964, Chapter 3.
(6) M. Jones, Jr., and R. A. Moss, Ed., *Carbenes 1973*, **1**, Chapter 2 (1973).
(7) J. Hine and J. J. Porter, *J. Am. Chem. Soc.*, **82**, 6178 (1960).
(8) A. J. Schultz, G. Khance, J. McArdle, and R. Eisenberg, *J. Am. Chem. Soc.*, **95**, 3434 (1973).
(9) H. S. Kesling and D. J. Burton, *Tetrahedron Lett.*, 3355 (1975).
(10) W. Kimpenhaus and J. Buddrus, *Chem. Ber.*, **109**, 2370 (1976).
(11) D. J. Burton and G. A. Wheaton, *J. Am. Chem. Soc.*, **96**, 6787 (1974).
(12) P. Muller and B. Siegfried, *Tetrahedron Lett.*, 3565 (1973).
(13) A. P. Krapcho, E. G. E. Jahngen, A. J. Lovey, and F. W. Short, *Tetrahedron Lett.*, 1091 (1974).
(14) C. L. Liotta and F. L. Cook, *Tetrahedron Lett.*, 1095 (1974).
(15) B. M. Trost and T. R. Verhoeven, *J. Am. Chem. Soc.*, **98**, 630 (1976).
(16) See, for example: (a) T. Asahara, K. Ikeda, and N. Yoda, *J. Polym. Sci., Polym. Chem. Ed.*, **6**, 2489 (1968); (b) B. Rickborn and R. M. Gerkin, *J. Am. Chem. Soc.*, **93**, 1693 (1971); (c) B. C. Hartman and B. Rickborn, *J. Org. Chem.*, **37**, 943 (1972); (d) G. Magnusson and S. Thoren, *J. Org. Chem.*, **38**, 1380 (1973); and (e) D. C. Luehrs and J. P. Kohut, *J. Inorg. Nucl. Chem.*, **36**, 1459 (1974).
(17) P. Müller and B. Siegfried, *Hevl. Chim. Acta*, **57**, 987 (1974).
(18) R. A. Bekker, G. A. Asratyan, and B. L. Dyatkin, *J. Org. Chem. USSR* (*Engl. Transl.*), **9**, 1658 (1973).
(19) P. Tarrant, C. G. Allison, K. P. Barthold, and E. C. Stump, Jr., *Fluorine Chem. Rev.*, **5**, 77 (1971); see ref 3, p 128.
(20) See ref 3, p 230.
(21) R. A. Bekker, G. V. Asratyan, B. L. Dyatkin, and I. L. Knunyants, *Dokl. Chem.* (*Engl. Transl.*), **204**, 439 (1972).
(22) Decomposition of **3** by LiCl/HMPA in THF in the presence of **16** has been demonstrated to give excellent yields of cyclopropane **17** by addition of difluorocarbene to the double bond: G. A. Wheaton and D. J. Burton, *J. Fluorine Chem.*, **8**, 97 (1976).
(23) C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, **96**, 2250 (1974).
(24) (a) B. Castro, R. Burgada, G. Lavielle, and J. Villeras, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **268**, 1067 (1969); (b) *Bull. Soc. Chim. Fr.*, 2770 (1969).
(25) (a) G. Köbrich, H. Merkle, and H. Trapp, *Tetrahedron Lett.*, 969 (1965); (b) H. Normant, *Angew. Chem.; Int. Ed. Engl.*, **6**, 1046 (1967).
(26) P. Sykes, "A Guidebook to Mechanism in Organic Chemistry", 4th ed, Wiley, New York, N.Y., 1975, pp 232–235.
(27) (a) R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc. C*, 625 (1968); (b) A. G. Hudson, M. L. Jenkins, A. E. Pedler, and J. C. Tatlow, *Tetrahedron*, **26**, 5781 (1970).
(28) H. S. Kesling, Ph.D. Thesis, University of Iowa, 1975.
(29) R. A. Mitsch, *J. Heterocycl. Chem.*, **1**, 233 (1964).
(30) See ref 3, pp 148–172.
(31) (a) D. J. Burton and H. C. Krutzsch, *J. Org. Chem.*, **35**, 2125 (1970); (b) *ibid.*, **36**, 3251 (1971).
(32) K. R. Burson and C. T. Kenner, *J. Chromatogr. Sci.*, **7**, 63 (1969).
(33) K. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78**, 2268 (1956).
(34) D. J. Burton and F. E. Herkes, *J. Org. Chem.*, **32**, 1311 (1967).
(35) D. G. Naae and D. J. Burton, *J. Fluorine Chem.*, **1**, 123 (1971).
(36) G. W. Gokel, D. J. Cram, C. L. Liotta, H. P. Harris, and E. L. Cook, *J. Org. Chem.*, **39**, 2445 (1974).
(37) N. Yarovenko, *Zh. Obshch. Khim.*, **27**, 2796 (1957); *Chem. Abstr.*, **52**, 8042b (1958).
(38) O. Paleta, F. Liska, and A. Posta, *Collect. Czech. Chem. Commun.*, **35**, 1302 (1970).
(39) D. Shriver, "Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(40) A. L. Anderson, Ph.D. Thesis, University of Iowa, 1971.
(41) R. A. Bekker, G. V. Asratyan, B. L. Dyatkin, and I. L. Knunyants, *J. Org. Chem. USSR* (*Engl. Transl.*), **11**, 950 (1975).
(42) Authentic samples of **25–27** were generously supplied by H. S. Kesling.
(43) Authentic samples of **34a** and **34b** were obtained from H. S. Kesling.