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(13) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee 1972–1977 and Fellow of the Alfred P. Sloan Foundation 1973–1975.

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[CF_2Cl^-], Chlorodifluoromethide Ion. The Capture of an Elusive Species

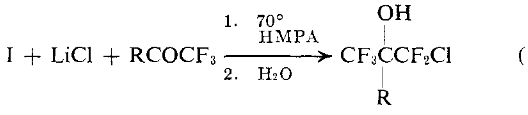
Sir:

The concerted nature of difluorocarbene formation *via* the decomposition of chlorodifluoroacetic acid and its derivatives is presently accepted as there is no concrete evidence for the existence of the chlorodifluoromethide ion in the literature to date. Herein is reported evidence supporting the existence of the chlorodifluoromethide ion as a reactive intermediate in the decarboxylation of methyl chlorodifluoroacetate. Independent experiments show that the observed products do not result from the initial formation and subsequent reactions of difluorocarbene.

The usefulness of trichloroacetic acid and its derivatives as dichlorocarbene precursors has been known for years.[1-4] More recently, this interest has been extended to the potential use of chlorodifluoroacetic acid and its derivatives as synthetically useful sources of difluorocarbene. Alkali metal chlorodifluoroacetates have been used in the synthesis of steroid derivatives[5] and *gem*-difluorocyclopropanes,[6] in homologation reactions,[7] and in the preparation of 1,1-difluoroolefins.[8] Sodium ethoxide induced decomposition of ethyl chlorodifluoroacetate resulted in difluoromethylation of 2,3-dimethylindole.[9] Decomposition of lithium chlorodifluoroacetate in the presence of 9,10-phenanthrene quinone gave a hydroxy ketone which might possibly be a chlorodifluoromethide ion trapping product.[10] However, since initial studies by Hine and coworkers, it has been accepted that halodifluoromethide ions have no finite existence. In studies of both the hydrolysis of chlorodifluoromethane[11] and the decarboxylation of chlorodifluoroacetic acid,[12] it was concluded that difluorocarbene formation is a concerted process and that there is no intermediate formation of halodifluoromethide ion. Attempts to trap these carbanions even by protonation have met with little success.[12]

We have observed in this laboratory that lithium chloride initiates the facile decarboxylation of methyl chlorodifluoroacetate (I) in hexamethylphosphoramide (HMPA). A study of this decarboxylation in the presence of polyfluorinated ketones has been done, and the results are reported below.

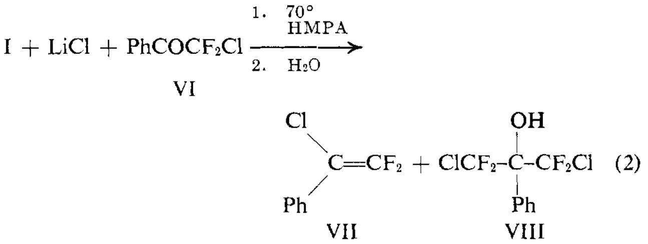
Decarboxylation of I by lithium chloride in the presence of trifluoroacetophenone (II) in HMPA proceeded smoothly at 65 to 70°.[13] After 20 hr, steam distillation resulted in isolation of 1-chloro-2-phenylpentafluoro-2-propanol (III) as the only product in 62% yield. Similarly, decarboxylation of I in the presence of 1,1,1-trifluoro-2-hexanone (IV) afforded 1-chloro-1,1-difluoro-2-trifluoromethyl-2-hexanol (V) as the only product in 39% yield. Decarboxylation of I in the presence of chlorodifluoroacetophenone (VI), however, yielded an olefin, 1-chloro-1-phenyldifluoroethylene (VII), as the major product (50%) as well as 1,3-dichloro-2-phenyltetrafluoro-2-propanol (VIII) (18%) after steam distillation.



$$\mathrm{I + LiCl + RCOCF_3 \xrightarrow[2.\ H_2O]{1.\ 70^\circ,\ HMPA} CF_3\overset{OH}{\underset{R}{C}}CF_2Cl} \qquad (1)$$

II, R = Ph
IV, R = n-C_4H_9

III, R = Ph
V, R = n-C_4H_9



$$\mathrm{I + LiCl + PhCOCF_2Cl \xrightarrow[2.\ H_2O]{1.\ 70^\circ,\ HMPA}} \qquad (2)$$

VI

VII

VIII

Two mechanistic interpretations have been considered to explain the observed results. The first interpretation is that the products in each case result from initial formation of the chlorodifluoromethide ion upon decarboxylation of I with subsequent attack of the carbanion at the carbonyl carbon atoms of ketones II, IV, and VI to form alcoholates IX, X, and XI, respectively (Scheme I). For reasons as yet unexplained, alcoholate XI can undergo an intramolecular SN2 displacement of chloride ion by oxygen to form oxirane

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(1) F. H. Verhoek, *J. Amer. Chem. Soc.*, **56**, 571 (1934).
(2) W. E. Parham and F. C. Loew, *J. Org. Chem.*, **23**, 1705 (1958).
(3) W. M. Wagner, *Proc. Chem. Soc., London*, 229 (1959).
(4) W. M. Wagner, *et al.*, *Recl. Trav. Chim. Pays-Bas*, **80**, 740 (1961).
(5) See, for example, L. H. Knox, E. V. Velarde, S. M. Berger, and D. H. Caudriello, *Chem. Ind. (London)*, 860 (1962); L. H. Knox, E. V. Velarde, S. M. Berger, D. H. Caudriello, P. W. Landis, and A. D. Cross, *J. Amer. Chem. Soc.*, **85**, 1851 (1963); C. Beard, N. H. Dyson, and J. H. Fried, *Tetrahedron*, **28**, 3281 (1966); C. Beard, I. T. Harrison, L. Kirkham, and J. H. Fried, *ibid.*, **28**, 3287 (1966); T. L. Popper, F. E. Carlon, H. M. Marigliano, and M. D. Yudis, *Chem. Commun.*, 277 (1968); P. Hodge, J. A. Edwards, and J. H. Fried, *Tetrahedron Lett.*, 5175 (1966); P. Crabbé, H. Carpio, E. V. Velarde, and J. H. Fried, *J. Org. Chem.*, **38**, 1478 (1973).
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(8) See, for example, S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 2543 (1965); D. J. Burton and F. E. Herkes, *Tetrahedron Lett.*, 1883 (1965); F. E. Herkes, Ph.D. Thesis, University of Iowa, 1966; D. J. Burton and F. E. Herkes, *J. Org. Chem.*, **32**, 1311 (1967); **33**, 1854 (1968).
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(10) M. Derenberg and P. Hodge, *J. Chem. Soc., Perkin Trans.*, 1056 (1972).
(11) J. Hine and P. B. Langford, *J. Amer. Chem. Soc.*, **79**, 5497 (1957).
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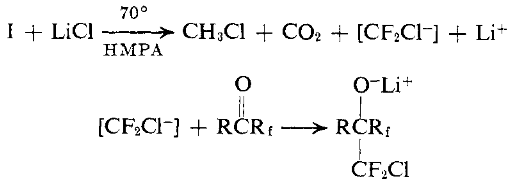
(13) In one experiment methyl chloride was detected and identified by ^1H nmr and infrared spectroscopy. Quantitative analysis by ^1H nmr showed a 92% yield of methyl chloride. A yield of 88% CO_2 was determined by precipitation as barium carbonate.

Scheme I

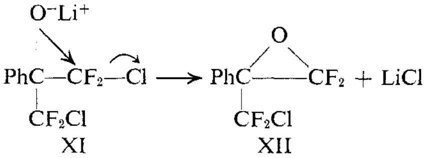


$$\mathrm{I} + \mathrm{LiCl} \xrightarrow[\mathrm{HMPA}]{70°} \mathrm{CH_3Cl} + \mathrm{CO_2} + [\mathrm{CF_2Cl^-}] + \mathrm{Li^+}$$

$$[\mathrm{CF_2Cl^-}] + \mathrm{R\overset{O}{\overset{\|}{C}}R_f} \longrightarrow \mathrm{R\overset{O^-Li^+}{\overset{|}{C}}R_f}\ (\underset{|}{}\mathrm{CF_2Cl})$$

II, R = Ph; $R_f = CF_3$ IX, R = Ph; $R_f = CF_3$
IV, R = n-C_4H_9; $R_f = CF_3$ X, R = n-C_4H_9; $R_f = CF_3$
VI, R = Ph; $R_f = CF_2Cl$ XI, R = Ph; $R_f = CF_2Cl$

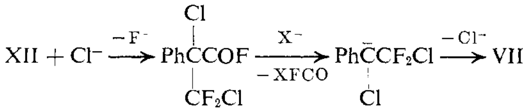
XII, while IX and X are stable toward this intramolecular displacement and do not give oxiranes. In each case, protonation of the alcoholates IX, X, and XI upon steam distillation yields the corresponding alcohols. XII, in the presence of chloride ion, undergoes ring opening to form acid fluoride XIII which decomposes in



(3)

XI XII

the presence of either chloride or fluoride ion[14] to yield the final product VII *via* displacement of chloride ion.

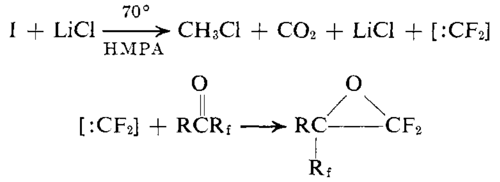


$$\mathrm{XII} + \mathrm{Cl^-} \xrightarrow{-\mathrm{F^-}} \mathrm{PhC(Cl)(CF_2Cl)COF} \xrightarrow[-\mathrm{XFCO}]{\mathrm{X^-}} \mathrm{Ph\bar{C}(Cl)CF_2Cl} \xrightarrow{-\mathrm{Cl^-}} \mathrm{VII} \quad (4)$$

XIII

An alternate mechanism is the concerted decomposition of I to yield not the chlorodifluoromethide ion but difluorocarbene and chloride ion. Difluorocarbene then inserts into the carbon–oxygen double bond of the ketone to yield an oxirane directly (Scheme II). In order to account for the observed products in eq 1 and 2, chloride ion must attack only at the difluoromethylene carbon of oxiranes XIV and XV to give alcoholates IX and X, but, in the case of oxirane XII, attack of chloride must occur at both the difluoromethylene carbon to give alcoholate XI and the benzylic carbon to give acid fluoride XIII.[15]

Scheme II



II, R = Ph; $R_f = CF_3$ XIV, R = Ph; $R_f = CF_3$
IV, R = n-C_4H_9; $R_f = CF_3$ XV, R = n-C_4H_9; $R_f = CF_3$
VI, R = Ph; $R_f = CF_2Cl$ XII, R = Ph; $R_f = CF_2Cl$

Preparation of alcohols III, V, and VIII was independently undertaken.[16] Subsequent treatment of these alcohols with aqueous potassium hydroxide resulted in oxirane formation only in the case of alcohol VIII, however.[17]

Ring-opening of XII by chloride ion under the same conditions as in eq 2 resulted in 95% glpc yield (46% isolated yield) of olefin VII. Alcohol VIII was not observed. Treatment of XII with lithium chloride at 0–10° resulted in formation of acid fluoride XIII in 68% glpc yield and VII in 30% glpc yield. XIII was then treated with lithium chloride in HMPA at 70° to give VII in quantitative yield.

$$\mathrm{XII} + \mathrm{LiCl} \xrightarrow[2.\ \mathrm{H_2O}]{2.\ 70°,\ \mathrm{HMPA}} \mathrm{VII} \qquad (5)$$

The above observations are consistent with the mechanism depicted in Scheme I, involving chlorodifluoromethide ion formation and its subsequent attack at the carbonyl carbon atom. While the stabilities of alcoholates IX and X toward the intramolecular S$_N$2 displacement reaction are not fully understood, the facts that (1) alcohol VIII is not formed by chloride ion ring-opening of XII and (2) no products derived from similar chloride ion ring opening of oxiranes XIV and XV were observed (eq 1) indicate that the reaction does not proceed *via* initial oxirane formation by insertion of difluorocarbene into the carbon–oxygen double bond of the ketones (Scheme II). This is believed to be the first report of successful trapping of a halodifluoromethide ion other than by protonation. Additional studies are now underway to further substantiate the existence of halodifluoromethide ions as reactive intermediates in organic reactions.

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[14] Treatment of either XII or XIII with lithium chloride in HMPA gave a gas, which upon passage through methanol gave dimethylcarbonate (identified by glpc retention time). These observations were taken as evidence for the decomposition of XIII to the carbanion shown in eq 4 and either carbonyl fluoride ($F_2C{=}O$) or carbonyl chlorofluoride ($ClFC{=}O$).

[15] Although a referee has suggested that the failure of alcohols III and V to form oxiranes under conditions in which VIII gives XII makes comparative predictions of the ring opening of XIV, XV, and XII somewhat tenuous, we believe it unlikely that such structurally similar oxiranes would exhibit such different ring opening behavior. However, additional experiments are required to settle this point unambiguously.

[16] The alcohols were prepared by addition of phenyl- or n-butyllithium to 4 *F* K or 5 *F* K at −70° in diethyl ether, followed by acidification with 6 *N* hydrochloric acid. The alcohols were then isolated by extraction followed by distillation at reduced pressure.

[17] This method has been used to prepare some polyfluorinated oxiranes including XII. See, for example, R. A. Bekker, G. V. Asratyan, B. L. Dyatkin, and I. L. Knunyants, *Dokl. Chem.*, **204**, 439 (1972).

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Mixed-Valence Diferrocenylacetylene Cation

Sir:

We wish to report a new mixed-valence compound derived by one-electron oxidation of diferrocenylacetylene (eq 1) (where Fc = ferrocenyl). The resulting

$$\underset{\mathrm{I}}{\mathrm{FcC{\equiv}CFc}} \xrightleftharpoons{-e^-} \underset{\mathrm{II}}{(\mathrm{FcC{\equiv}CFc})^+} \xrightleftharpoons{-e^-} \underset{\mathrm{III}}{(\mathrm{FcC{\equiv}CFc})^{2+}} \qquad (1)$$

mixed-valence compound (II) is unique in being the first example of a bridged biferrocene cation to exhibit an intervalence transfer transition in the near-infrared.[1]

The cyclic voltammogram of diferrocenylacetylene[2]

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[2] Diferrocenylacetylene was prepared by the literature procedure: M. Rosenblum, N. Braun, J. Papenmeier, and M. Applebaum, *J. Organometal. Chem.*, **6**, 173 (1966). Ferrocenylacetylene was purchased from Wind River Chemicals.