Metal Halide Catalyzed Ortho Ester Formation[1a,b]

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Received September 14, 1964

Carbon tetrachloride, in excess or in stoichiometric equivalent, reacts with fluoro alcohols, such as 1,1,5-trihydroperfluoropentanol, in the presence of anhydrous ferric chloride catalyst to produce the corresponding trihydroperfluoropentyl orthocarbonate, $(R_fCH_2O)_4C$, bis carbonate, $(R_fCH_2O)_2C{=}O$, and halide, R_fCH_2Cl. In the presence of water the fluoroalkyl chlorocarbonate and bis(fluoroalkyl) carbonate are formed. This novel reaction is applicable to the preparation of orthobenzoates and orthoformates from benzotrichloride and chloroform. A complex of the metal halide catalyst with the trichloromethyl compound is proposed as a highly reactive intermediate which reacts with the fluoro alcohol yielding successively mono-, bis-, and trisfluoroalkoxychloromethanes and the orthocarbonate.

Recently the ferric chloride catalyzed hydrolysis of carbon tetrachloride to phosgene was reported.[2] In a study extending this reaction in order to obtain fluoroalkyl derivatives (R_f) *in situ*, we found that a fluoroalcohol added to the water–ferric chloride–carbon tetrachloride mixture produces not only a small amount of the expected alcohol bis carbonate, but also produces the alcohol chlorocarbonate as the primary product. Furthermore under anhydrous conditions the reaction produces the fluoroalcohol orthocarbonate. This result

$$R_fCH_2OH + CCl_4 + H_2O \xrightarrow{FeCl_3} R_fCH_2OCOCl + 3HCl$$

$$4R_fCH_2OH + CCl_4 \xrightarrow{FeCl_3} (R_fCH_2O)_4C + 4HCl$$

prompted us to study the heretofore unreported reaction of fluoro alcohols with carbon tetrachloride and other trichloromethyl compounds in the presence of ferric chloride catalyst. The reaction provides a new class of halogenated ortho esters and the first example of the direct conversion of carbon tetrachloride to an orthocarbonate. The acidic conditions for this reaction contrast sharply to the normal syntheses of ortho esters from trichloromethyl compounds in which the alcohol alkoxides are used to obtain orthoformates from chloroform,[3] orthocarbonates from chloropicrin,[4] and aliphatic ortho esters from the corresponding aliphatic terminal trichloromethyl compounds.[5] Alternative syntheses of ortho esters not involving halogen starting materials involve principally the alcoholysis of other ortho esters and imino hydrochlorides.[5]

Results

Orthocarbonates were obtained by the reaction of a fluoro alcohol with carbon tetrachloride at reflux temperature in the presence of catalytic amounts of anhydrous ferric chloride. The carbon tetrachloride was used as both reactant and solvent, or alternatively as a reactant added to the alcohol dissolved in chloroform. When carbon tetrachloride was used as solvent, the reaction system was very sensitive to conditions, temperature control being most critical. Best results were obtained at 76–78°; little or no orthocarbonate was formed below 76°. Above 78° the bis carbonates of the fluoro alcohols were formed exclusively and in all reactions which provided the orthocarbonate, the bis carbonate was the principal by-product. The narrow optimum temperature range presented the practical problem of providing a high heat input because the reaction temperature always dropped when reaction started, possibly from the cooling effect of hydrogen chloride evolution and solvent entrainment.

The reactant ratios which consistently provided orthocarbonate in 20–42% yields based on unrecovered fluoro alcohol were about 2:1 for carbon tetrachloride to alcohol, and 5:1 for alcohol to anhydrous ferric chloride catalyst. The ratios could be varied somewhat in catalyst quantity without effect, but greater dilution of the alcohol by additional carbon tetrachloride, already in excess, was detrimental. Anhydrous catalyst was essential since small amounts of water favored carbonate formation. The catalyst could be recovered unchanged after the reaction and used again for succeeding experiments.

In carbon tetrachloride the reaction not only was sensitive to temperature but was apparently affected by the heterogeneity of the system. After about 25–50% of the alcohol had been added, two phases were always present with catalyst suspended in both phases. In chloroform, the carbon tetrachloride was added in stoichiometric equivalent to the alcohol–chloroform solution and catalyst at reflux temperature, giving a reaction system in which the alcohol and the various intermediates were more soluble, and homogeneity except for catalyst was maintained. Although yields were not improved using chloroform as solvent, more reproducible results were achieved. A small amount of the fluoro alcohol orthoformate was formed from chloroform but its rate of formation was much slower than the orthocarbonate from carbon tetrachloride. A good yield of orthoformate from chloroform required a 93-hr. reaction period compared to 6–8 hr. for the orthocarbonate synthesis from carbon tetrachloride. Nitrobenzene, diethyl ether, and 1,2-dichloroethane were not useful as solvents.

$$3R_fCH_2OH + HCCl_3 \xrightarrow{FeCl_3} (R_fCH_2O)_3CH + 3HCl$$

The preparation of an orthobenzoate can be carried out in chloroform solvent at reflux temperature in about 24 hr. Ether was used successfully as solvent in this

$$3R_fCH_2OH + C_6H_5CCl_3 \xrightarrow{FeCl_3} (R_fCH_2O)_3CC_6H_5 + 3HCl$$

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(1) (a) This work was supported in part by the U. S. Navy Bureau of Ships, Contract NObs 88248. (b) Presented in part before the Organic Chemistry Division, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

(2) M. E. Hill, *J. Org. Chem.*, **25**, 1115 (1960).

(3) P. Sah and T. Ma, *J. Am. Chem. Soc.*, **54**, 2964 (1932).

(4) B. Rose, *Ann.*, **205**, 249 (1880).

(5) For general reviews of preparative methods for ortho esters, see R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 542; H. W. Post, "The Chemistry of the Aliphatic Orthoesters," Reinhold Publishing Corp., New York, N. Y., 1943.

reaction, providing the product in 62% yield, although some diminution of the catalytic effect of the ferric chloride was expected. The orthobenzoate formation was accompanied by a side reaction forming the fluoro alcohol benzoate ester.

Trichloromethyl compounds which were most useful were carbon tetrachloride, chloroform, and benzotrichloride. Aliphatic trichloromethyl compounds such as 1,1,1-trichloroethane dehydrohalogenated with anhydrous ferric chloride which forestalled their use in the ortho ester reaction. Halogen alcohols, such as the 1,1,3-trihydroperfluoropropanol, 1,1,5-trihydroperfluoropentanol, and 1,1,7-trihydroperfluoroheptanol, and 2,2,2-chlorodifluoroethanol, all were converted to ortho esters. The normal aliphatic primary alcohols, ethanol, pentanol, and nonanol, are not converted to orthocarbonates or bisalkyl carbonates. Ethanol, under the same conditions as used in the fluoro alcohol reactions, produced hydrogen chloride, phosgene, and ethylene.[6] Pentanol and nonanol were little affected, with low yields of oxidation products being obtained. In the fluoro alcohol reaction, aluminum chloride catalysis produced only the bis carbonate; antimony pentachloride was ineffective.

Product Identification.—Fractionation of the compounds produced by the reaction of 1,1,5-trihydroperfluoropentanol with carbon tetrachloride in the anhydrous system gave three principal products which were tentatively identified, in ascending boiling point, as the fluoroalkyl halide, the bisfluoroalkyl carbonate, and a possible orthocarbonate. Infrared analysis of the proposed orthocarbonate was similar to the spectrum of a perfluoroalkyl group, providing evidence only for the absence of hydroxyl and carbonyl groups or other functional groups. Elemental analysis for carbon and hydrogen gave values almost the same as contained in the parent alcohol, suggesting that the alcohol did not undergo appreciable change. A calculated empirical formula from the analysis did not permit a choice between possible self-condensation of the alcohol or reaction with carbon tetrachloride to form the orthocarbonate or orthoformate. However, n.m.r. spectra of the products gave proton spectra expected for the $-CF_2H$, with a τ-value of 4.05 for the proton peak relative to tetramethylsilane which was split into a triplet by the two fluorine atoms on the same carbon and split again by the β-CF_2 group. The methylene moiety was a triplet at τ 5.78 whose integrated peak area ratio to the HCF_2 proton was very close to the calculated 2 to 1. Consequently, it was concluded that the alcohol moiety had not undergone reaction at the terminal HCF_2 position, and the requisite proton arrangement for an orthocarbonate was present in the molecule. Finally the molecular weight by the osmometer method (967) of the 1,1,5-trihydroperfluoropentanol product was within 3% of the calculated value (936) for an orthocarbonate. A similar result was obtained in the molecular weight determination of the orthocarbonate of trihydroperfluoroheptanol. The molecular weight measurements, coupled with the n.m.r. spectra of all products and elemental analyses, were considered sufficient evidence to assign the orthocarbonate structure to the highest boiling of the products produced by the reaction. The bisfluoroalkyl carbonates were identified by their infrared and n.m.r. spectral analyses, elemental analyses, and molecular weight determinations. N.m.r. spectra, elemental analysis, and comparison of physical properties with known fluoroalkyl halides indicated that the lowest boiling product was a fluoroalkyl chloride.

Confirmatory evidence for ortho ester formation from trichloromethyl compounds was provided by the synthesis of the corollary 1,1,7-trihydroperfluoroheptyl orthoformate and orthobenzoate. The n.m.r. proton spectra of these compounds had the requisite peaks and integrated peak area ratio for the ortho structures.

Bisalkyl Carbonate and Chlorocarbonate Formation.—The reaction producing the orthocarbonate was always accompanied by the formation of the bis carbonate, $(R_fCH_2O)_2C{=}O$, as a by-product. Originally the carbonate was thought to arise from the hydrolysis of the possible intermediate, $(R_fCH_2O)_2CCl_2$, during work-up which involved an aqueous wash to remove ferric chloride. However, the carbonate was isolated directly from the reaction mixture in an experiment which employed strictly anhydrous conditions and inert atmosphere. In addition to the carbonate, a new compound was isolated which analyzed as the trihydroperfluoroalkyl halide. The formation of the carbonate under anhydrous conditions indicated that the alcohol, which was the only source of oxygen, provided oxygen of the carbonate by-product and produced the fluoroalkyl chloride.

In an attempt to obtain formation of the carbonate *in situ*, water was added to the carbon tetrachloride–fluoro alcohol–ferric chloride system during the reflux period in order to hydrolyze a possible dialkoxydichloromethane intermediate. In addition to the bisfluoroalkyl carbonate a new compound was isolated which was relatively low boiling and had an infrared spectrum showing the presence of a carbonyl. The new product reacted with water giving a solution which produced a positive test for chlorine. The compound was assigned a fluoroalkyl chlorocarbonate structure, which was verified experimentally by identification of carbonate derivatives. The chlorocarbonate from 1,1,5-trihydroperfluoropentanol reacted vigorously with methanol to produce methyl trihydroperfluoropentyl carbonate. This carbonate was independently synthesized from methyl chlorocarbonate and the fluoro alcohol using metal halide catalysis.[7] The two products were identical in all respects, confirming the assignment of the chlorocarbonate structure to the new product.

$$CH_3OCOCl + R_fCH_2OH \xrightarrow{TiCl_4} R_fCH_2OCOOCH_3$$

The addition of water to a ferric chloride–fluoro alcohol–carbon tetrachloride mixture at a reflux temperature provides a convenient new synthesis for fluoroalkyl chlorocarbonates. The water may be added in solution in the alcohol or simultaneously with the alcohol, care being taken not to hydrate the ferric chloride too extensively and stop the reaction. The amount of bis carbonate product can be minimized by continued addition of water. The system is self-drying by the competing reaction of water with the carbon tetrachloride which produces phosgene and by the hydrolysis of the chlorocarbonate to the original alcohol.

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(6) M. E. Hill and D. T. Carty, unpublished information.

(7) M. E. Hill, *J. Am. Chem. Soc.*, **76**, 2329 (1954).

A reaction of phosgene and 1,1,5-trihydroperfluoropentanol in the presence of ferric chloride gave a low yield of chlorocarbonate and bis carbonate.

The fluoro alcohol ortho ester compounds are thermally stable. In some cases distillation conditions for the trihydroperfluoroheptanol products required pot temperatures at 250°, with no detectable decomposition. The compounds are resistant to acid cleavage as shown by the synthetic conditions. This resistance is in direct contrast to the usual sensitivity of normal alkyl ortho esters to acidic conditions. No reaction of the orthoformates could be obtained with Grignard reagents, nor could hydrolysis of the ortho esters be obtained at temperatures up to 100° over a period of 72 hr.

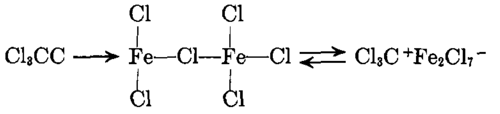
Discussion

The simplicity of the reaction system for the preparation of ortho esters indicates that a principal factor influencing the reaction must be an unexpected activation of the trichloromethyl compounds by complex formation with the ferric chloride. The formation of the orthocarbonate from carbon tetrachloride and the orthoformate from chloroform by Lewis acid catalysis is unusual since the halomethanes are in excess. A reaction mechanism which accounts for the observed experimental results involves the probable stepwise substitution of the chlorine atoms which proceeds very quickly in the latter stages of the reaction. The reaction must proceed by a nucleophilic attack by the alcohol on a reactive trichloromethyl–ferric chloride complex, followed by successive nucleophilic substitutions until the ortho ester is obtained, as exemplified by the carbon tetrachloride–fluoro alcohol reaction. Without succeeding fast reaction steps after the initial formation of the trichloromethyl ether, (I), the reaction would not be expected to proceed to completion in excess carbon tetrachloride.

$$CCl_4 + R_fCH_2OH \xrightarrow[\substack{slow\\ -HCl}]{FeCl_3} \underset{I}{(R_fCH_2OCCl_3)} \xrightarrow[\substack{fast\\ -HCl}]{R_fCH_2OH} \underset{II}{(R_fCH_2O)_2CCl_2}$$

$$\underset{II}{(R_fCH_2O)_2CCl_2} \xrightarrow[\substack{fast\\ -HCl}]{R_fCH_2OH} \underset{III}{(R_fCH_2O)_3CCl} \xrightarrow[\substack{fast\\ -HCl}]{R_fCH_2OH} (R_fCH_2O)_4C$$

Numerous examples of alkyl halide activation by Lewis acids in Friedel–Crafts reactions have recently been reviewed,[8] but no systems have been reported analogous to a carbon tetrachloride–ferric chloride donor acceptor complex. Jensen and Brown[9] have found that ferric chloride existed in significant amounts as a dimer complexed with benzoyl chloride. The weak basicity of carbon tetrachloride, which is a nonionizing solvent, probably precludes the complete dissociation of the ferric chloride dimer to the monomer form. That carbon tetrachloride interacts with metal halides was shown by Wallace and Willard,[10] who found that the chlorine in aluminum chloride exchanged readily with carbon tetrachloride and chloroform under very mild conditions. Thus only one halogen bridge is opened to give a complex involving one iron atom with a chlorine of the halomethane, of the form IV in equilibrium with the very reactive carbonium ion metal halide pair V.



$$Cl_3CC \longrightarrow \underset{Cl}{\overset{Cl}{Fe}}—Cl—\underset{Cl}{\overset{Cl}{Fe}}—Cl \rightleftharpoons Cl_3C^+Fe_2Cl_7^-$$

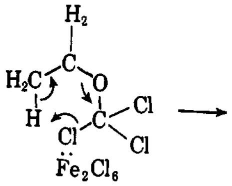
IV V

In analogy to the carbonium character of the halo-substituted carbon in "normal" alkyl halide complexes, the carbon of the carbon tetrachloride is relatively positive and susceptible to nucleophilic substitution by the fluoro alcohol.

Such a reaction provides as the first product the trichloromethyl ether of the fluoro alcohol I complexed with ferric chloride. The complex I is highly reactive and has sufficient stability to react further with other alcohol molecules. The stability of I appears to be a key factor in allowing the reaction to proceed to the ortho esters in excess halomethanes. Park and coworkers[11] have found that the trichloromethyl ether of 2,2-dichloroperfluoroethanol, $Cl_3COCF_2CFCl_2$, and similar halo ethers were relatively unreactive compounds which were only difficultly cleaved by aluminum chloride. From this and from the experimental products of the ortho ester reaction it would appear that in the presence of ferric chloride, alcoholysis of I is preferred over a cleavage reaction. That the electronegative fluorine atoms contribute to the stability of I is further supported by the contrasting reaction of ethanol with carbon tetrachloride in the presence of ferric chloride. In this system, phosgene, ethylene, and hydrogen chloride are produced, whose source may be explained by a β-elimination mechanism involving an analogous trichloromethyl ether intermediate.[6] In the fluoro alcohol trichloromethyl ether complex I, the inductive effect of the fluorine β to the ether oxygen would minimize the electron shift to form a carbonyl group and stabilize this intermediate at the ether oxygen bond. Similar considerations would apply to the other intermediate steps proceeding to the orthocarbonate and to orthoformate and orthobenzoate formation.

$$R_fCH_2CH_2OCCl_3 \cdot Fe_2Cl_6$$

I



$$HCl + CH_2{=}CH_2 + COCl_2 + Fe_2Cl_6$$

The proposed mechanism is consistent with the formation of the bis carbonate and the alkyl halide during the reaction. The lack of oxygen in the system and the formation of the alkyl halide indicate that the alcohol eventually provides the carbonyl oxygen. It is difficult to rationalize the removal of two chlorine atoms and formation of a carbonyl group from the intermediate II in an anhydrous system. A much easier path for the carbonate formation is available by the thermal

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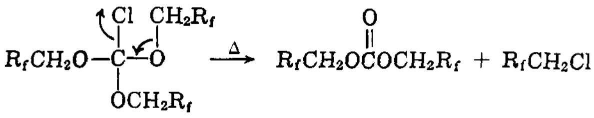
[8] G. W. Olah, "Friedel Crafts and Related Reactions," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, p. 630f.

[9] F. R. Jensen and H. C. Brown, *J. Am. Chem. Soc.*, **80**, 3039 (1958).

[10] C. H. Wallace and J. E. Willard, *ibid.*, **72**, 5275 (1950).

[11] J. D. Park, D. M. Griffin, and J. R. Lacher, *ibid.*, **74**, 2292 (1952).



III

decomposition of the trialkoxy monochloromethane III. An examination of the molecular models of III and the orthocarbonate shows that for orthocarbonate formation considerable steric hindrance must be overcome, which attests to the reactivity of this monochloro intermediate. The intermediate is probably decomposing to form the carbonate and alkyl halide at a rate competing with the orthocarbonate formation rate. This mechanistic viewpoint is supported experimentally by the unusual sensitivity of the reaction to heat when carbon tetrachloride is used as solvent and reactant; *i.e.*, high reaction temperatures give the carbonate product exclusively.

The formation of the fluoroalkyl chlorocarbonate in the nonanhydrous reactions is related to hydrolysis of trichloromethyl compounds by ferric chloride catalysis previously reported in which carbon tetrachloride and other trichloromethyl compounds were hydrolyzed to phosgene and acid chlorides by ferric chloride hydrate.[2] In an analogous manner, the fluoroalkyl chlorocarbonate may arise principally from hydrolysis of the trichloromethyl ether, I. Phosgene is formed also in the

$$\underset{\text{I}}{(\mathrm{R_fCH_2OCCl_3})} + \mathrm{H_2O} \longrightarrow \mathrm{R_fCH_2OCOCl} + 2\mathrm{HCl}$$

anhydrous reaction systems, and may be a source of the chlorocarbonate. However, the contribution from the reaction of phosgene is probably minor, inasmuch as the chlorocarbonate could not be prepared in reasonable yield by saturating an alcohol–catalyst mixture with phosgene at reflux temperature.

Experimental

The trihydroperfluoro alcohols were obtained from the E. I. du Pont de Nemours and Company. Chlorodifluoroethanol, b.p. 95°, was prepared by the reduction of chlorodifluoroacetyl chloride with lithium aluminum hydride. The ferric chloride was commercial, sublimed, anhydrous grade, redried before each experiment by refluxing in carbon tetrachloride for at least 16 hr.[3] N.m.r. spectra are summarized in Table I.

1,1,7-Trihydroperfluoroheptyl Orthocarbonate. Method A.—To a vigorously stirred mixture of 16 g. (0.01 mole) of anhydrous ferric chloride in 75 ml. of carbon tetrachloride at reflux temperature, 83 g. (0.25 mole) of 1,1,7-trihydroperfluoroheptanol was added dropwise over a period of 2.5 hr. The heat input from the heating mantle was adjusted to maintain the temperature of the reaction at 76–78°. After the addition of the alcohol, heating was continued until hydrogen chloride evolution was very slow (6 hr.). The ferric chloride was filtered from the dark reaction mixture, and the reaction solution was dissolved in ether, washed several times with water, and dried. The solvents were removed at 20–35-mm. pressure, leaving dark viscous oil. The oily product was fractionated, yielding 40 g. (48%) of bis-(1,1,7-trihydroperfluoroheptyl) carbonate, b.p. 76° (0.02 mm.),[12] and 28 g. (35%) of 1,1,7-trihydroperfluoroheptyl orthocarbonate, b.p. 170° (0.008 mm.). Refractionation of foreruns produced 9.8 g. of the alcohol halide, b.p. 145° (760 mm.),[13] identified by n.m.r., infrared, and elemental analysis.

Table I

N.m.r. Data on Trihydroperfluoroheptyl Ortho Esters[a]

Assignment	τ-value	Splitting	J-value, c.p.s.
$[\mathrm{H(CF_2)_6CH_2O]_4C}$			
$-\mathrm{CH_2}-$	5.78	Triplet	12.0
$-\mathrm{HCF_2}$	4.05	Triplet, α-$\mathrm{CF_2}$	5.1
		Triplet, β-$\mathrm{CF_2}$	48.2
$[\mathrm{H(CF_2)_6CH_2O]_3CC_6H_5}$			
$-\mathrm{CH_2}-$	5.97	Triplet	12.0
$\mathrm{HCF_2}-$	4.05	Triplet, α-$\mathrm{CF_2}$	4.5
		Triplet, β-$\mathrm{CF_2}$	48.5
Phenyl	2.50	Singlet	...
$[\mathrm{H(CF_2)_6CH_2O]_3CH}$			
$-\mathrm{CH_2}-$	5.76	Triplet	12.2
$\mathrm{HCF_2}-$	4.07	Triplet, α-$\mathrm{CF_2}$	4.9
		Triplet, β-$\mathrm{CF_2}$	47.8
HC–	4.18	Singlet	...
$[\mathrm{H(CF_2)_6CH_2O]_2C{=}O}$			
$-\mathrm{CH_2}-$	5.32	Triplet	13.2
$\mathrm{HCF_2}-$	3.99	Triplet, α-$\mathrm{CF_2}$	6.0
		Triplet, β-$\mathrm{CF_2}$	51.2

[a] N.m.r. spectra on other trihydroperfluoro alcohol derivatives were very similar to the trihydroperfluoroheptanol derivatives. Chemical shifts are in p.p.m. on the τ-scale, determined on a Varian HR 60 spectrometer with tetramethylsilane as internal reference.

Anal.[14] Calcd. for $\mathrm{C_{29}H_{12}F_{48}O_4}$: C, 26.90; H, 1.22. Found: C, 26.00; H, 1.18.

1,1,5-Trihydroperfluoropentyl orthocarbonate was prepared by method A in 42% yield, b.p. 135° (0.05 mm.), bis(1,1,5-trihydroperfluoropentyl) carbonate, 36%, b.p. 67° (0.2 mm.) (lit. 127° at 17 mm.[12]), and 1,1,5-trihydroperfluoropentyl chloride, 10%, b.p. 100° (760 mm.).

Anal. Calcd. for $\mathrm{C_{21}H_{12}F_{32}O_4}$: C, 24.80; H, 1.28. Found: C, 25.20; H, 1.22. Calcd. for $\mathrm{C_5H_3F_8Cl}$: C, 24.00; H, 1.21; Cl, 14.18. Found: C, 24.40; H, 1.33; Cl, 13.86.

Also by method A were prepared **1,1,3-trihydroperfluoropropyl orthocarbonate**, 30%, b.p. 65° (0.1 mm.), and **2,2,2-chlorodifluoroethyl orthocarbonate**, 30%, b.p. 80° (2.8 mm.).

Method B.—Carbon tetrachloride (10.4 g., 0.067 mole) was added over a period of 30 min. to a refluxing mixture of 11 g. (0.06 mole) of ferric chloride and a solution of 66 g. (0.20 mole) of 1,1,7-trihydroperfluoroheptanol in 100 ml. of chloroform. The reaction mixture was held at reflux temperature an additional 5 hr., cooled, filtered, and dissolved in ether. The ether solution was washed several times with water, separated, dried, and evaporated to an oily residue. Fractionation of the crude product yielded 23 g. (35%) of the orthocarbonate, 28 g. (42%) of the bis carbonate, and 6.0 g. (9%) of the alkyl halide.

1,1,7-Trihydroperfluoroheptyl Orthoformate.—A mixture of 83 g. (0.25 mole) of 1,1,7-trihydroperfluoroheptanol, 120 g. of chloroform (1 mole), and 22 g. of anhydrous ferric chloride was held at reflux temperature for 93 hr. After cooling and filtering, the dark reaction solution was distilled at reduced pressure. The orthoformate (58 g.) was obtained at 137–139° (0.1 mm.) in 80% yield.

Anal. Calcd. for $\mathrm{C_{22}H_{70}F_{36}O_3}$: C, 25.27; H, 1.00. Found: C, 24.57; H, 0.97.

1,1,5-Trihydroperfluoropentyl orthoformate was prepared in 66% yield, b.p. 95° (0.08 mm.), by the above method.

Anal. Calcd. for $\mathrm{C_{16}H_{70}F_{24}O_3}$: C, 27.20; H, 1.42. Found: C, 26.92; H, 1.40.

1,1,7-Trihydroperfluoroheptyl Orthobenzoate.—To a solution of 350 ml. of dry diethyl ether and 695 g. (2.1 moles) of 1,1,7-trihydroperfluoroheptanol mixed with 44 g. of ferric chloride, 136 g. (0.7 mole) of benzotrichloride was added dropwise at 50° over a period of 1.25 hr. The reaction mixture was heated until the hydrogen chloride evolution was virtually nil (16 hr.) and then mixed with 500 ml. of water. The ether layer was separated, washed with water, dried over magnesium sulfate, and evaporated to an oily residue under reduced pressure. Fractionation of

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[12] N. O. Brace and W. B. McCormack [*J. Org. Chem.*, **26**, 5091 (1961)] reported b.p. 110° (11.0 mm.).

[13] P. D. Faurote and J. G. O'Rear [*J. Am. Chem. Soc.*, **78**, 4999 (1956)] reported b.p. 143° (760 mm.).

[14] Elemental analyses were by the Microanalytical Laboratory, Stanford University.

the crude product produced recovered alcohol, 198 g. of 1,1,7-trihydroperfluoroheptyl benzoate, b.p. 155° (0.5 mm.), and 295 g. of 1,1,7-trihydroperfluoroheptyl orthobenzoate, b.p. 187° (0.1 mm.), 62% yield based on unrecovered alcohol.

Anal. Calcd. for $C_{28}H_{14}F_{36}O_3$: C, 31.05; H, 1.29. Found: C, 31.21; H, 1.36.

1,1,5-Trihydroperfluoropentyl Chlorocarbonate.—A solution of 69.6 g. (0.3 mole) of 1,1,5-trihydroperfluoropentanol and 5.4 g. (0.3 mole) of water was added intermittently over a period of 1.25 hr. to a mixture of 26.4 g. of ferric chloride in 60 ml. of carbon tetrachloride at 76°. Large amounts of phosgene and hydrogen chloride were evolved over a period of 5 hr. After the addition of 2.5 ml. more of water, the reaction was allowed to continue an additional 8 hr. After cooling, the entire reaction mixture was dissolved in ether, washed very quickly with cold water, dried, and distilled. The fractionation gave recovered alcohol, 40 g. (60%) of the chlorocarbonate, b.p. 53° (13 mm.), and 15 g. (21%) of the bis carbonate.

A part of the 1,1,5-trihydroperfluoropentyl chlorocarbonate (6.0 g., 0.02 mole) was added to excess methanol in ether at 50°. Distillation after work-up yielded 4.3 g. (70% of methyl 1,1,5-trihydroperfluoropentyl carbonate, b.p. 50° (0.15 mm.).

Methyl chlorocarbonate (10.4 g., 0.11 mole) was stirred with 23.2 g. (0.1 mole) of 1,1,5-trihydroperfluoropentanol in chloroform containing 0.02 mole of titanium tetrachloride for 5 hr. at 50°. After work-up similar to above experiments, fractionation of the product yielded 24.2 g. (80%) of the methyl fluoro alcohol carbonate, b.p. 46° (0.1 mm.).

The two methyl fluoro alcohol carbonates from these experiments were found to be identical by infrared and n.m.r. analyses and determination of the same retention times by g.l.p.c.

1,1,7-Trihydroperfluoroheptyl chlorocarbonate was prepared in a similar manner except the alcohol and water were added portionwise simultaneously. The chlorocarbonate was obtained in 40% yield, b.p. 73° (14 mm.).

Anal. Calcd. for $C_8H_3ClF_{12}O_2$: C, 27.70; H, 1.54. Found: C, 27.81; H, 1.44.

Phosgene was bubbled through a mixture of 22.7 g. (0.1 mole) of 1,1,5-trihydroperfluoropentanol and 8.1 g. (0.05 mole) of ferric chloride for 6 hr. at 50°. Less than 10% of chlorocarbonate was obtained.

Acknowledgment.—This paper is related to an observation by one of us (M. E. H.) at the U. S. Naval Ordnance Laboratory, Silver Spring, Maryland. The many stimulating discussions with Dr. D. V. Sickman and Dr. O. H. Johnson are gratefully acknowledged.

Modifications of the Hunsdiecker Reaction[1a]

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Received August 18, 1964

Bromodecarboxylation of organic acids by the Cristol–Firth modification of the Hundsiecker reaction using the free acid and red mercuric oxide was found to be much more effective than the modification using the acid chloride and silver oxide. A study has been made of the possible use of oxides other than mercuric oxide and of the effectiveness of various solvents.

Replacement of the carboxyl group in organic acids by a halogen atom, especially bromine, by treatment of the anhydrous silver salt of the acid with bromine, chlorine, or iodine in an inert solvent is commonly known as the Hunsdiecker reaction.[2–4] Yields are generally quite good (usually better than 60%), but the reaction is extremely sensitive to trace amounts of water, the presence of which leads to the recovery of unchanged acid. Unfortunately, the preparation of dry silver salts of carboxylic acids is frequently very difficult and, because such salts are usually quite sensitive to heat also, they are often quite hard to dry thoroughly.

Several years ago there appeared a report[5] that the acid chloride of penta-*O*-acetyl-D-gluconic acid undergoes smooth decarboxylation when heated with bromine and silver oxide in carbon tetrachloride, furnishing aldehydo-1-bromo-D-arabinose penta-*O*-acetate in an excellent yield. A second report[6] described the reactions of benzoyl chloride and three other aromatic acid chlorides with bromine and silver oxide in carbon tetrachloride.

An investigation of this modification of the Hunsdiecker reaction was started using the following acid chlorides: benzoyl chloride, *n*-butyryl chloride, phthaloyl chloride, *p*-nitrobenzoyl chloride, and *p*-chlorobenzoyl chloride.

The silver oxide was carefully dried as was all the glassware and the carbon tetrachloride, bromine, and acid chlorides were redistilled before use. Although numerous variations of the reaction conditions were tried, only trace amounts of the desired bromides were obtained by fractional distillation of the reaction mixtures. However, fair yields of bromobenzene were obtained from silver benzoate by the original Hunsdiecker reaction.

Fund, Cristol, and Firth have reported[7] that treatment of a slurry of excess red mercuric oxide in a refluxing solution of stearic acid in carbon tetrachloride with approximately an equivalent amount of bromine in the dark gave a 93% yield of crude heptadecyl bromide. The reaction also was reported to give poor yields with benzoic acid and glutaric acids, and fair to excellent yields with cyclopropanecarboxylic acid, 9,10-dihydro-9,10-ethane-9-anthronic acid, and lauric acid. As soon as we learned of the Cristol–Firth modification, its apparent convenience and simplicity in comparison to those procedures involving preparation of silver salts or acid chlorides immediately suggested a broad study of this modified procedure using different classes of carboxylic acids and the use of solvents other than carbon tetrachloride. Since mercuric oxide is relatively expensive and mercury compounds are toxic, a study also was made of the possibility of using other oxides for this reaction.

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[1] (a) This work was made possible by Grant #897-B from the Petroleum Research Fund, administered by the American Chemical Society; (b) American Chemical Society Petroleum Research Fund Scholar.

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