To this was added platinum oxide catalyst (0.1 g.). The vessel was then attached to the hydrogenation apparatus and evacuated until the alcohol began to boil. Hydrogen was introduced into the system until a pressure of 60 p.s.i. was attained. The shaker was started and allowed to continue until a total pressure drop of 8 p.s.i. had occurred (*i.e.*, the theoretical drop for the reduction of 0.033 mole of nitrocompound to amine). The shaker was stopped and the system allowed to come to atmospheric pressure. The catalyst was allowed to settle and then most of the supernatant alcoholic amine solution was decanted off. The remaining amine solution was filtered, with care being taken to avoid sucking air over the dry platinum black. To the amine solution was added sufficient 85% phosphoric acid to render the solution acid to litmus. The mixture was cooled in an ice-bath, and the resulting precipitate filtered off. The precipitate was washed with cold ether, and then dissolved in excess 25% sodium hydroxide. The solution was then saturated with potassium carbonate, chilled and extracted with ether. After drying over sodium sulfate, the ether was removed and the residue distilled through a Podbielniak column. 6-Fluorohexylamine (1.43 g., 37%) was thus obtained as a colorless liquid.

Method II. **7-Fluoroheptylamine.**—To a solution of lithium aluminum hydride (4.42 g., 0.116 mole) in anhydrous ether (200 ml.), contained in the usual apparatus, was added a solution of 7-fluoroheptanonitrile[4] (15 g., 0.116 mole) in anhydrous ether (130 ml.), dropwise and with stirring. Water was then added slowly to decompose the excess hydride. The complex was hydrolyzed by addition of excess 20% sodium potassium tartrate (*ca.* 290 ml.). The ether layer was separated and the aqueous phase extracted with ether. The combined extracts, after drying over anhydrous calcium sulfate, were fractionated through a 30-cm. Vigreux column. After removal of the ether, 7-fluoroheptylamine (12.0 g., 77.5%) was obtained as a colorless liquid.

Method III. **5-Fluoroamylamine.**—To a solution of lithium aluminum hydride (6.8 g., 0.178 mole) in anhydrous ether (400 ml.), contained in the usual apparatus, was added 5-fluoro-1-nitropentane[4] (12.0 g., 0.089 mole) in anhydrous ether, dropwise and with stirring. Water was then added slowly to decompose the excess hydride. The complex was hydrolyzed by addition of excess 20% sodium potassium tartrate (*ca.* 225 ml.). Isolation and purification were carried out as under method II, using a Podbielniak column. 5-Fluoroamylamine (0.90 g., 10%) was obtained as a colorless liquid.

Method IV. N-4-Fluorobutylacetamide.—A suspension of methylmagnesium chloride was prepared by the procedure described by Kharasch and Reinmuth,[18] using magnesium turnings (3.9 g., 0.16 mole), preactivated with butyl chloride, in anhydrous ether (60 ml.), and gaseous methyl chloride. A solution of 4-fluorobutyl isocyanate[19] (10.0 g., 0.085 mole) in anhydrous ether (90 ml.) was added dropwise with stirring to the Grignard reagent. A vigorous exothermic reaction took place, accompanied by the formation of a precipitate. After standing overnight under an atmosphere of nitrogen, the reaction mixture was hydrolyzed by the addition of a minimum quantity of saturated aqueous ammonium chloride. The supernatant solution was decanted and the residue washed with several portions of ether. The combined ethereal solutions were dried over anhydrous magnesium sulfate. After removal of the ether, the residue on fractionation yielded N-4-fluorobutylacetamide (1.5 g., 13%) as a colorless liquid with a characteristic odor of mice. The material turned yellow after several weeks in a sealed glass ampoule.

Carbamate Salts.—The ω-fluoroalkylamines deposited white solids after a few minutes exposure to the atmosphere. These effervesced on treatment with dilute hydrochloric acid. The solid obtained from 8-fluoroöctylamine was analyzed without purification.

Anal. Calcd. for $C_{17}H_{36}F_2N_2O_2$: N, 8.28. Found: N, 8.29.

Acknowledgments.—The work described herein was carried out under Contract (DRB X-24) with the Defence Research Board of Canada, to whom grateful acknowledgment is made for financial assistance, and for permission to publish this work. The authors wish also to express their indebtedness to Drs. M. K. McPhail and F. C. G. Hoskin and Mr. P. A. Adie, Suffield Experimental Station, Ralston, Alberta, and Dr. J. M. Parker, Defence Research Medical Laboratories, Toronto, for carrying out the toxicity determinations; and to Mr. W. J. Cott for valuable contributions to this investigation.

[18] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 25.

[19] ω-Fluoroalkyl isocyanates will be described in a future publication.

LONDON, ONTARIO

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, POLAROID CORPORATION]

The Properties of Some Fluorinated Vinyl Ethers[1]

BY RICHARD S. CORLEY, JOGINDER LAL AND MARSHALL W. KANE

RECEIVED AUGUST 8, 1955

The preparation and characterization of $CH_3OCF{=}CFCl$ is reported. Some properties and reactions of this ether and of $C_6H_5OCF{=}CFCl$ are described. The alkyl vinyl ether, $CH_3OCF{=}CFCl$, was readily oxidizable by air and polymerized to a low molecular weight resin; the aryl vinyl ether, $C_6H_5OCF{=}CFCl$, did not autoxidize or polymerize.

Since the difficulty of polymerization of many fluorinated olefins may be due, at least in part, to the strong inductive effect of contiguous fluorine substituents on the double bond, we have examined the preparation and properties of two representative fluorinated olefins with substituents of opposite inductive effect, *viz.*, $CH_3O{-}CF{=}CFCl$ and the previously reported $C_6H_5O{-}CF{=}CFCl$.[2] These vinyl ethers were prepared by dehydrofluorination of the saturated ethers CH_3OCF_2CHFCl and $C_6H_5OCF_2CHFCl$.[2]

We prepared CH_3OCF_2CHFCl by base-catalyzed addition of methanol to chlorotrifluoroethylene, using a simplified version of the established technique,[3] and also by an anomalous Williamson synthesis in which sodium methoxide or potassium hydroxide was allowed to react in excess methanol with $CF_2ClCFCl_2$ in an attempt to prepare CH_3-

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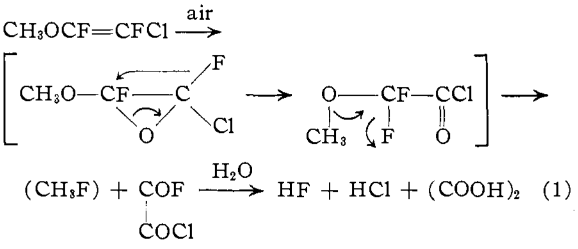
[1] This work was sponsored by the Signal Corps, Department of the Army; a summary of it was presented at the 124th National Meeting of the American Chemical Society, Chicago, Illinois, September 6-11, 1953.

[2] P. Tarrant and H. C. Brown, THIS JOURNAL, **73**, 5831 (1951).

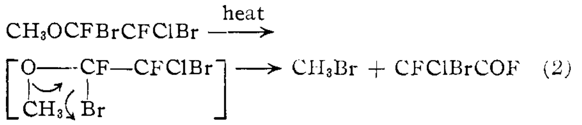
[3] (a) J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson and R. H. Lafferty, Jr., *ibid.*, **72**, 4480 (1950); (b) W. T. Miller, Jr., E. W. Fager and P. H. Griswold, *ibid.*, **70**, 431 (1948); (c) J. D. Park, D. K. Vail, K. R. Lea and J. R. Lacher, *ibid.*, **70**, 1550 (1948).

$OCFClCF_2Cl$. Tarrant and co-workers[4] have demonstrated that apparent Williamson displacement reactions of fluorinated ethanes actually proceed by elimination of hydrogen halide followed by addition of ROH to the resulting olefin. In the above case, as well as in the reported reaction $C_6H_5ONa + CF_2ClCFCl_2 \rightarrow C_6H_5OCF_2CHCl_2$,[5] no hydrogen is available for dehydrohalogenation. The products in these cases apparently must again result from addition of ROH to the olefins, but here the olefins must be produced by a dechlorination reaction.[6] Defluorination[7] of CH_3OCF_2CHFCl over silica at 290° gave the known methyl chlorofluoroacetate, which constitutes an independent proof of structure.

The methoxytrifluorochloroethane proved difficult to dehydrofluorinate, but on refluxing over solid potassium hydroxide gave 25–35% of the desired $CH_3O{-}CF{=}CFCl$. The vinyl ether and, to a lesser extent, its dibromide were readily autoxidized, and the dibromide was unstable to heat. The vinyl ether gave on exposure to air an oxalyl halide, probably COF–COCl,[8] converted by moisture to oxalic acid dihydrate, and by ammonia to oxamide. The dibromide was also converted on exposure to moist air to oxalic acid and HF, and on heating by itself at 160–170°, or with zinc at 100°, was decomposed in high yield to methyl bromide and the known CFClBrCOF.[9] The above transformations are similar to those described by Tarrant and Brown[10] and have a number of analogies[11] in the complex chemistry of halogenated ethers. All can be formulated in similar fashion as



$$CH_3OCF{=}CFCl \xrightarrow{air} \cdots \qquad (CH_3F) + \underset{\displaystyle COCl}{COF} \xrightarrow{H_2O} HF + HCl + (COOH)_2 \quad (1)$$

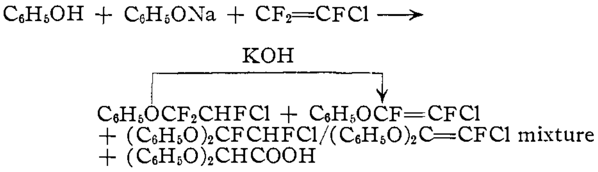


$$CH_3OCFBrCFClBr \xrightarrow{heat} \cdots \longrightarrow CH_3Br + CFClBrCOF \quad (2)$$

The autoxidation and hydrolysis of CH_3OCFBr-$CFClBr$ to oxalic acid would presumably have to proceed by prior elimination of Br_2 to give CH_3-$OCF{=}CFCl$, followed by reaction (1).

Polymerization of $CH_3OCF{=}CFCl$ with acid catalysts gave 30–40% yields of a light brown, viscous polymer which was unstable, losing HF and HCl slowly on standing.

The less reactive phenyl vinyl ether, $C_6H_5OCF{=}CFCl$, was prepared from $C_6H_5OCF_2CHFCl$ by the reported method.[2] The dehydrofluorination with solid potassium hydroxide gave up to 53% yields of the vinyl ether. It was found, in agreement with Tarrant and Brown,[2] that the preparation and dehydrofluorination reactions constituted a connected system. Some 5 to 20% of the unsaturated ether always accompanied the saturated ether in the addition reaction, only *ca.* 60% conversion to the vinyl ether could be attained under a range of conditions and some phenol was formed in the dehydrofluorination reaction, and the same diphenoxyether by-products were formed in both reactions.



$$C_6H_5OH + C_6H_5ONa + CF_2{=}CFCl \longrightarrow$$
$$C_6H_5OCF_2CHFCl \xrightarrow{KOH} C_6H_5OCF{=}CFCl + (C_6H_5O)_2CFCHFCl/(C_6H_5O)_2C{=}CFCl \text{ mixture} + (C_6H_5O)_2CHCOOH$$

Pure $C_6H_5O{-}CF_2CHFCl$ and $C_6H_5O{-}CF{=}CFCl$ were separated by fractional distillation. The compositions of given mixtures of the ethers were thereafter determined by use of a refractive index–composition diagram. The pure saturated ether was inert to permanganate in acetone whereas the vinyl ether was rapidly oxidized, but both were inert to bromine. The unsaturated compound displayed infrared absorption at 5.75 μ due to the C=C str. vibration, which was absent in the saturated ether. The spectra were otherwise nearly identical and about that expected for the given structures.

A high boiling, unstable by-product obtained in highly variable yield from both the additional reaction and the dehydrofluorination was a mixture whose properties and analysis indicated the composition 31% $(C_6H_5O)_2C{=}CFCl$, 69% $(C_6H_5O)_2$-$CFCHFCl$.[12] This mixture lost HF readily and could not be separated by fractional distillation. In contrast with the monophenoxy compounds, bromine was absorbed readily, but the resulting material very readily decomposed. The instability of these materials is not unexpected since $(C_6H_5O)_2$-$C{=}CFCl$ is a halo-ketene acetal. Such compounds

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[4] P. Tarrant and J. Young, THIS JOURNAL, **75**, 932 (1953); and ref. 2.

[5] E. T. McBee and R. O. Bolt, *Ind. Eng. Chem.*, **39**, 412 (1947).

[6] *Cf.* P. Tarrant in "Fluorine Chemistry," Vol. II, J. H. Simons, Ed., Academic Press, New York, N. Y., 1954, p. 234, who has stated the same conclusion.

[7] *Cf.* W. E. Hanford and G. W. Rigby (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,049,274 (October 15, 1946).

[8] Our product had b.p. *ca.* 49.5°. The mixed halide, COF–COCl, is unknown, but by interpolation between the b.p.'s of oxalyl chloride (64°) and oxalyl fluoride (26°; N. Fukuhara and L. A. Bigelow, THIS JOURNAL, **63**, 788 (1941) its b.p. would be *ca.* 45°.

[9] F. Swarts, *Bull. soc. chim. France*, [3] **15**, 1135 (1896).

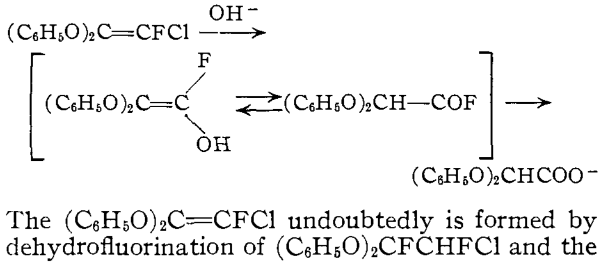
[10] P. Tarrant and H. G. Brown, THIS JOURNAL, **73**, 1781 (1951).

[11] *E.g.*, (a) $CCl_2{=}CClOMe \xrightarrow{air} HCl + (COOH)_2$ (L. Henry, *Ber.*, **12**, 1839 (1879)); (b) $CCl_2{=}CClOEt \xrightarrow{air} EtOCCl_2COCl$ (L. Henry, *Chem. Zentr.*, **I**, 587 (1899)); (c) $CCl_2{=}CHOEt \xrightarrow{air} EtOCHClCOCl + COCl_2 + HCOOEt$ (J. Foster, THIS JOURNAL, **31**, 598 (1909)); (d) $CH_2CHClOEt \xrightarrow{80°} EtCl + CH_3CHO$ (A. Geuther and A. Bachman, *Ann. Chem.*, **218**, 54 (1883)); (e) $CH_2ClCHClOEt \xrightarrow{heat} HCl + EtCl + CH_2ClCHO$ (J. Wislicenus, *ibid.*, **226**, 263 (1884)).

[12] The infrared absorption spectrum of the mixture provided support for this composition. It was similar to those of both of the monophenoxy ethers, showing monosubstituted benzene ring absorption at 6.3, 6.7, 14.3 and probably at 9.3 μ; C(unsatd.)-O, CF_2 and C–F absorption in the 7.4–10 μ region; $R_2C{=}CR_2$ at 11.9 μ; and C–Cl at 13.1 μ. The 5.80 μ band is at the position expected for C=C str. in the structure $(C_6H_5O)_2C{=}CFCl$, and of the correct intensity for about 30% concentration.

and their dibromides undergo facile and complex decomposition reactions.[13]

Another by-product, obtained only from potassium hydroxide dehydrofluorination, was shown to be diphenoxyacetic acid.[14] Formation of the diphenoxy acid probably proceeds through the diphenoxy unsaturated ether (a conclusion rendered plausible by the fact that the two were always found together) and can be formulated as



The $(C_6H_5O)_2C{=}CFCl$ undoubtedly is formed by dehydrofluorination of $(C_6H_5O)_2CFCHFCl$ and the latter formed by base-catalyzed addition of phenol to $C_6H_5O{-}CF{=}CFCl$.[15]

Polymerization of $C_6H_5O{-}CF{=}CFCl$ was attempted with acetyl and benzoyl peroxide in bulk and with BF_3 in solution at −80°, but no polymer was obtained.

Experimental

All m.p.'s are corrected. Combustion analyses are by Clark Microanalytical Laboratories, Urbana, Illinois.

Preparation of CH_3OCF_2CHFCl by the Addition Reaction.—The experimental procedure[3] for the addition of alcohol to trifluorochloroethylene was modified to give a more convenient method by allowing liquefied $CF_2{=}CFCl$ to evaporate from a flask exposed to ambient temperature into the potassium hydroxide–methanol mixture contained in a second flask chilled in a Dry Ice bath and fitted with a Dry Ice reflux condenser. The reaction was complete without further attention in 2–3 hours, as shown by cessation of refluxing. The product was washed with cold water, dried and distilled through a 15-plate column to give a 93–96% yield of ether, b.p. 70.6° (760 mm.), whose physical properties were substantially identical with those reported.[3]

Pyrolysis of CH_3OCF_2CHFCl over Silica.—The vapor from 50 g. of the methyl ether was passed slowly through a vertical column packed with Celite and heated to 290°. The gases after condensation of the organic material were shown to be HCl and SiF_4. The organic material was fractionated through a 30-plate Bowers–Cooke column to give starting material, which showed only a trace of unsaturation to permanganate, and 2 g. of colorless CHClFCOOMe, b.p. 116.2° (750 mm.), n^{20}_{D} 1.3916, n^{25}_{D} 1.3895 (reported[16] b.p. 116°, n^{25}_{D} 1.3902).

Anal. Calcd. for $C_3H_4O_2FCl$: C, 28.48; H, 3.18. Found: C, 28.31; H, 3.02.

Preparation of CH_3OCF_2CHFCl by the Williamson Reaction.—A mixture of 47 g. (0.25 mole) of $CF_2ClCFCl_2$, 0.35 mole of potassium hydroxide and 90 ml. of absolute methanol was heated and shaken for 20 hours at 125°. The product was taken up in diethyl ether, washed with water, dried and fractionated through a 30-plate column to give a 30% yield (range 20–36%) of CH_3OCF_2CHFCl whose properties, including infrared spectra, were identical with those of the addition product. A sample of the Williamson reaction product was also analyzed.

Anal. Calcd. for $C_3H_4OF_3Cl$: C, 24.25; H, 2.71; F, 38.4; Cl, 23.9. Found: C, 25.03; H, 2.70; F, 36.34; Cl, 22.03.

Analysis of the aqueous wash showed the presence of a small amount of brown, basic ferric salts, a moderate amount of oxalate ion, and 0.165 to 0.283 mole of chloride ion.

Preparation of $CH_3OCF{=}CFCl$. a. **From CH_3OCF_2CHFCl.**—One hundred grams of CH_3OCF_2CHFCl was refluxed with 50 g. of potassium hydroxide pellets for 22 hours. (This and all other operations described below, involving $CH_3OCF{=}CFCl$ and its dibromide, were carried out under an atmosphere of nitrogen unless otherwise stated.) Distillation to dryness through a 10-plate glass helices column gave 73 g. of distillate. After drying over fresh potassium hydroxide, this on fractionation through a 30-plate Bowers–Cooke column gave 38 g. of crude product, b.p. 58–69°. The remainder, b.p. 69–71°, was starting material. The 38-g. fraction was washed free of traces of acyl halides with concd. ammonia, dried and again fractionated through the 30-plate column to give 12.6 g. (22% yield) of nearly pure $CH_3OCF{=}CFCl$, b.p. 59° (756 mm.), n^{25}_{D} 1.3563.

Anal. Calcd. for $C_3H_3OF_2Cl$: C, 28.04; H, 2.35; F, 29.57. Found: C, 27.82; H, 2.30; F, 29.84.

The potassium hydroxide residue contained appreciable amounts of chloride and oxalate ions, as well as fluoride ion. In two experiments, use of solid sodium hydroxide gave no appreciable yield of the vinyl ether.

b. **From $CH_3OCFBrCFClBr$.**—A mixture of 40 g. of the dibromide, 10 g. of zinc dust and 30 cc. of purified, anhydrous dioxane was cautiously heated under the 10-plate column. At 70° a vigorous reaction started. Heating was stopped, the heat of reaction being enough to keep the mixture boiling for about 15 minutes, with one application of cold water necessary for control. When boiling spontaneously subsided, the bath was heated to 90° and the product fractionated, giving 7.35 g. (82.7% yield) of $CH_3OCF{=}CFCl$, b.p. 57.5–58° (760 mm.). The product was washed with ice-cold water to remove traces of dioxane and acyl halides, dried over Drierite and again fractionated to yield the pure vinyl ether, b.p. 57.6° (760 mm.), n^{25}_{D} 1.3570, d^{25}_{4} 1.2809, MR_D 20.97, AR_F 1.04.

Most of the vinyl ether was prepared by this method since difficult fractionation was avoided. The ether reduced aq. permanganate and decolorized bromine in carbon tetrachloride. When thoroughly free of acyl halides, it possessed a mild, pleasant ethereal odor.

Autoxidation of $CH_3OCF{=}CFCl$.—One preparation of the vinyl ether, employing 100 g. of CH_3OCF_2CHFCl and 90 g. of potassium hydroxide, in which the mixture was partially exposed to air during 15 hours refluxing, gave on fractionation 1.5 g. of forerun, b.p. 49.5–50° (761 mm.), n^{20}_{D} 1.3550, probably FCO–COCl. The fraction had a pungent, suffocating, acrid odor. On treatment with cold concd. aq. ammonia there was obtained a precipitate of oxamide, m.p. 420° dec. The aq. filtrate contained chloride and fluoride ions. The oxamide was confirmed by warming with aq. alkali to give ammonia, and hydrolysis to oxalic acid dihydrate.

When 2.5 g. of the vinyl ether was exposed to moist air overnight at room temperature in a flask provided with a capillary opening, the material was largely converted to a white crystalline solid. Filtration and washing gave 0.28 g. of oxalic acid dihydrate, m.p. and mixed m.p. with an authentic sample 100–101°. Sublimation gave the anhydrous acid (neutral equivalent; found 47, calcd. 45), which sublimed without melting at 178°.

Preparation of $CH_3OCFBrCFClBr$.—One hundred grams of CH_3OCF_2CHFCl was refluxed under nitrogen for 15 hours (bath temperature 90°) over 100 g. of potassium hydroxide pellets and 10 g. of anhyd. sodium fluoride. Distillation to dryness through a 10-plate glass helices column gave 79 g. of distillate which was dried over fresh potassium hydroxide and reacted cautiously with 11 g. of bromine at 0°. Fractionation through the 30-plate column gave recovered CH_3OCF_2CHFCl and 47 g. (24.5% over-all yield) of the dibromide, b.p. 68° (32 mm.), 61° (22 mm.), f.p. −43° (to a colorless flaky mass), n^{25}_{D} 1.4696; d^{25}_{4} 2.0826, MR_D 38.12, AR_F 1.11.

Anal. Calcd. for $C_3H_3OF_2ClBr_2$: C, 12.49; H, 1.05; F, 13.17; Cl, 12.29; Br, 55.43; total Cl + Br, 67.72. Found: C, 13.04, 13.19; H, 1.30, 1.14; F, 13.05; Cl + Br, 65.25.

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[13] See, *e.g.*, (a) A. Magnani and S. M. McElvain, THIS JOURNAL, **60**, 2210 (1938); (b) S. M. McElvain and W. R. Davie, *ibid.*, **74**, 1816 (1952); (c) F. Beyerstadt and S. M. McElvain, *ibid.*, **59**, 2266 (1937).

[14] K. Auwers and K. Heymann, *Ber.*, **27**, 2795 (1894).

[15] *Cf.* $CCl_2{=}CClOEt \xrightarrow{NaOEt} CHCl_2COOEt + (EtO)_2CHCOONa$ (A. Geuther and G. Brockhoff, *J. prakt. Chem.*, [2] **7**, 102 (1865)).

[16] J. A. Young and Paul Tarrant, THIS JOURNAL, **72**, 1860 (1950).

Autoxidation of $CH_3OCFBrCFClBr$.—A small amount of the dibromide in an open flask at room temperature soon evolved acidic vapors. On standing overnight, colorless crystals were deposited which were shown to be oxalic acid dihydrate.

Thermal Decomposition of $CH_3OCFBrCFClBr$. a. No Catalyst.—Ten grams of dibromide was gradually heated in nitrogen under a 30-plate column which was in turn connected to a −80° trap. At a bath temperature of 110° there was no observable decomposition, at 160° decomposition was slow, and at 170° was occurring at an appreciable rate. The product from the column was 6.5 g. (95% yield) of CFClBrCOF, b.p. 51° (760 mm.) (reported[9] b.p. 51°), d^{20}_{4} *ca.* 1.83. The product reacted readily and exothermically with water, yielding a clear acidic solution containing chloride, fluoride, bromide and oxalate ions. Reaction with cold concd. aq. ammonia gave the amide, purified by sublimation, m.p. 137.5–138.5° (reported[9] m.p. 131.5°); and reaction with aniline gave the *anilide*, purified by crystallization from aq. alcohol and vacuum sublimation, m.p. 98–98.6°.

Anal. Calcd. for $C_8H_6ONFClBr$: N, 5.25. Found: N, 5.34. The −80° trap contained a colorless, volatile condensate (*ca.* 3 g.). Washing with water and drying on a gas washing manifold gave 1.2 g. of methyl bromide, b.p. 4–5° (759 mm.) (micro-column), which was confirmed by conversion to the α-naphthalide, m.p. 159–160°, *via* the Grignard reagent.

b. In the Presence of Zinc Chloride.—Ten grams of the dibromide and 1 g. of slightly moist zinc chloride were gradually heated together under nitrogen. At 170° the decomposition rate was still slow, but became appreciable at 180°, yielding 4.5 g. (67% yield) of CFClBrCOF, b.p. 51°.

c. In the Presence of Zinc.—A mixture of 10 g. of the dibromide and 10 g. of zinc dust was gradually heated under nitrogen. At 110–115°, there was a brisk evolution of CFClBrCOF, yield 4.35 g. (65%). The residue was treated with methanol. When the vigorous reaction subsided, the methanol solution was filtered, concentrated and distilled to give 0.5 cc. of a colorless liquid of pleasant odor, b.p. 78–80° (micro-column). This product was moderately soluble in water, giving a small amount of fluoride and chloride/bromide ions, gave a positive iodoform reaction and reacted with 2,4-dinitrophenylhydrazine reagent. This material was probably $CFClBrCOCH_3$.

Polymerization of $CH_3OCF{=}CFCl$.—The monomer showed no signs of polymerization when heated for 72 hours at 60° with either benzoyl peroxide or boron trifluoride etherate. Stannic chloride (12% by wt.) on heating for 16 hours at 60° (sealed, under prepurified nitrogen) gave a 20% yield of light yellow, viscous, liquid polymer after precipitation of a methanol solution into water and vacuum drying. Heating with 1.1% stannic chloride at 60° for 45 hours and purification in the same manner gave a 31.5% yield of an amber, tacky semi-solid polymer which did not flow under its own weight at room temperature. The latter polymer, on standing in the air for 3 months, had darkened to brown and had a slight acyl halide odor. The polymer was dissolved in ethanol and precipitated into water. The water was acidic and contained chloride and fluoride ions. The polymer was precipitated again and dried.

Anal. Calcd. for $(C_3H_3OF_2Cl)_n$: F, 29.8; Cl, 27.7. Found: F, 22.26 (loss 25%); Cl, 25.20 (loss 9%).

Addition of Phenol to $CF_2{=}CFCl$: $C_6H_5OCF_2CHFCl$.—Reaction of 0.74 mole of phenol, 0.095 mole of potassium phenoxide and 0.95 mole of $CF_2{=}CFCl$ for 3 hours at 180° gave on fractional distillation through a 30-plate column a 75 to 80% yield of $C_6H_5OCF_2CHFCl$, 5–7% of $C_6H_5OCF{=}CFCl$, and 0 to 4% of the diphenoxy ether mixture (see below). The alkaline aq. wash contained large amounts of chloride and fluoride ions. The purified $C_6H_5OCF_2CHFCl$ had b.p. 87.5° (30.4 mm.), n^{24}_{D} 1.4444, d^{25}_{4} 1.3672 (reported[2] b.p. 50.0° (4 mm.), n^{25}_{D} 1.4454, d^{25}_{4} 1.3294).

Anal. Calcd. for $C_8H_6OF_2Cl$: C, 45.62; H, 2.87; F, 27.07. Found: C, 45.85; H, 2.73; F, 27.39.

An attempt to hydrolyze $C_6H_5OCF_2CHFCl$ to $CHClFCOOC_6H_5$ with concd. sulfuric acid[16] under mild conditions resulted in recovery of *ca.* 66% of the unchanged ether, whereas more drastic conditions gave complete conversion to water soluble products—apparently phenol, the acid, CHFClCOOH, and further hydrolysis products. The marked accelerating effect of finely divided silica (powdered glass or Celite) was noteworthy.

The unsaturated ether was difficult to separate from the saturated ether by distillation, but mixtures were readily analyzed by aid of a linear refractive index-composition graph.

Reaction of $C_6H_5OCF_2CHFCl$ with Alkali: $C_6H_5OCF{=}CFCl$.—Reaction of $C_6H_5OCF_2CHFCl$ with 2 moles of solid potassium hydroxide and fractionation by washing with alkali, then distillation gave (a) from reaction at 100° for 20 hours, 50–53% $C_6H_5OCF{=}CFCl$, no diphenoxy-ethers and no diphenoxyacetic acid; (b) from reaction at 135° for 40 hours, 20–30% $C_6H_5OCF{=}CFCl$, 8–40% of the diphenoxy-ether mixture, and 9–18% of diphenoxyacetic acid (see below). In both cases, *ca.* 20% of $C_6H_5OCF_2CHFCl$ was recovered. The use of excess potassium carbonate or quinoline gave essentially no reaction, but potassium *t*-butoxide at 80° gave 0–40% of $C_6H_5OCF{=}CFCl$ and no other products. Fractionation of the monophenoxy fraction through a 30-plate column gave purified $C_6H_5OCF{=}CFCl$, b.p. 79.0° (30.5 mm.), n^{24}_{D} 1.4764, d^{24}_{4} 1.2940, MR_D 41.62, AR_F 1.12 (reported[2] b.p. 160° (760 mm.), n^{25}_{D} 1.4725, d^{25}_{4} 1.297, AR_F 1.0).

Anal. Calcd. for $C_8H_5OF_2Cl$: C, 50.43; H, 2.64; F, 19.95; Cl, 18.51. Found: C, 50.46; H, 2.59; F, 19.57; Cl, 18.52.

The ether had a pleasant, anisole-like odor, did not reduce bromine in carbon tetrachloride, but very rapidly decolorized dil. aq. permanganate. Both the saturated and unsaturated ethers were apparently completely stable to autoxidation—after standing for one week open to the air at room temperature, no HCl or HF was detected and the refractive indices had not changed.

The aq. alkali wash of one run was found to contain a 3.8% yield of phenol, separated from the diphenoxyacetic acid by insolubility in aq. bicarbonate, and identified as the 2,4,6-tribromo derivative, m.p. 94–95°.

Diphenoxyacetic Acid.—Partition of the aq. washes from the potassium hydroxide dehydrofluorinations with diethyl ether yielded oily diphenoxyacetic acid as the aq. bicarbonate-soluble, aq. acid-insoluble fraction. Extraction of 5.8 g. of oily crude acid with hexane plus a little chloroform and cooling of the extract gave 3.43 g. of pale yellow acid, m.p. 89–91°, and left the remainder undissolved as a brown gum. Two crystallizations from hexane-chloroform gave 2.5 g. of the pure acid. The m.p.'s of the acid, amide and bis-*p*-bromo acid were the same as those reported,[14] but all are nearly the same as those of the mono-phenoxyacetic acid. Therefore an authentic sample of the diphenoxy-acid was prepared, m.p. 92.2–92.8° (reported[14] 91°); mixed m.p. with the acid from the dehydrofluorination, 92.2–93.0°.

Diphenoxy Ethers.—The high boiling neutral fraction from both the synthesis of $C_6H_5OCF_2CHFCl$ and its reaction with alkali proved inseparable on fractional distillation. Two consecutive simple distillations of the mid-cuts under nitrogen gave material, b.p. 123–124° (1.5 mm.), which instantly decolorized dilute bromine in carbon tetrachloride with evolution of some HBr and decolorized dilute aq. permanganate, but more slowly than $C_6H_5OCF{=}CFCl$. It was initially practically odorless, but on standing exposed to the air at room temperature for 3–4 days, it turned light pink, evolved fuming, acidic vapors, and smelled strongly of phenol. More impure samples turned deep red in 24–48 hours of exposure. This reddening was found to occur rapidly also with the purer material in the presence of a trace of free phenol or of free sulfuric acid.

Anal. Found: C, 60.43; H, 3.79; Cl, 12.07; F, 11.41. Calcd. for $(C_6H_5O)_2CFCHFCl$, $C_{14}H_{11}O_2F_2Cl$: C, 59.06; H, 3.90; Cl, 12.46; F, 13.35. Calcd. for $(C_6H_5O)_2C{=}CFCl$, $C_{14}H_{10}O_2FCl$: C, 65.53; H, 3.81; Cl, 13.40; F, 7.18. Assuming this binary mixture, calculation based on the found value for C gave wt. % $(C_6H_5O)_2C{=}CFCl$, 31.2; based on the found value for F gave wt. % $(C_6H_5O)_2C{=}CFCl$, 31.4.

Bromination of 10.0 g. of this material at 0–5° until no further uptake of bromine was observed (2.1 g. of bromine) resulted in some evolution of HBr. Treatment at 25° gave uptake of 1.3 g. more bromine. Distillation under nitrogen gave 4.98 g. of oily, colorless, lachrymatory oil, b.p. 130–137° (2 mm.), which could not be further separated by fractional distillation. All of the fractions autoxidized fairly rapidly, with evolution of large amounts of HF, and finally set to red gels.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LEHIGH UNIVERSITY]

Additions to Pyridinium Rings. II. Charge-Transfer Complexes as Intermediates

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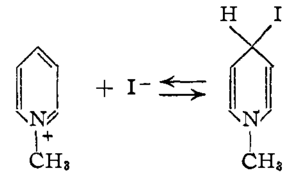
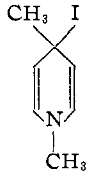
Investigation of the spectra of aqueous solutions of substituted 1-methylpyridinium iodides provides evidence that the new species, previously shown to be present in solutions of 1-methylpyridinium iodide itself, is a *charge-transfer complex*. Other cases where a charge-transfer complex may be present and where complex formation is essentially due to the "transfer" of an electron to a π-electron system containing a unit positive charge are discussed.

A study of the spectra of aqueous solutions of 1-methylpyridinium iodide[2] revealed that a new species was present to an extent dependent upon the square of the concentration of the quaternary salt. It was suggested that this new species might be the product of addition of the iodide ion to the pyridinium ring.[2,3] In an effort to substantiate this proposal, substituted 1-methylpyridinium iodides were investigated. The prediction was made that replacement of a hydrogen by a methyl group would prevent addition at that particular position, so that the concentration of the new species would be reduced or made to disappear altogether. If we examine the formula for a possible product of addition, I, on the right-hand side of equation 1, we see that I is a reactive secondary iodide and that dissociation to the 1-methylpyridinium and iodide ions represents its solvolysis. It would be expected that replacement of the hydrogen at the 4-position by a methyl group would yield the far more reactive tertiary iodide, II.[5] Thus, the equilibrium position for dissociation and association of II should lie much farther over on the side of the separated ions. Since the amount of new species present in any solution is not too large in any case,[2] serious displacement of the equilibrium toward the dissociated ions should preclude the observation of addition at the methyl-substituted position.


(I) (1)


II

A second argument in support of the proposition that methyl groups will prevent addition is based upon the report of König[6] that, although 1-cyanopyridinium bromide and 1-cyano-2-methylpyridinium bromide reacted with amines to give glutacondialdimine derivatives, a reaction which no doubt proceeds through preliminary addition, 2,4,6-trimethylpyridine (*sym*-collidine), cyanogen bromide and aniline in ether did not react.[7]

Experimental

The quaternary salts were prepared by refluxing reagent grade substituted pyridines with the appropriate halide in absolute ethanol.

1,2-Dimethylpyridinium iodide was obtained as white crystals by the addition of acetone to an aqueous solution of the crude product, m.p. 229–231°[10] (reported 224°[11,12]).

1,4-Dimethylpyridinium iodide was crystallized by the slow addition of ether to a solution prepared by diluting a very concentrated aqueous solution with a large volume of acetone. It was recrystallized by dissolving in a large volume of boiling acetone, cooling and adding ether; white plates or needles, m.p. 153.3–154.3° (reported 157–158°[13]).

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[1] A portion of this paper is drawn from a thesis submitted by P. E. K. in partial fulfillment of the requirements for the degree of Bachelor of Science, June, 1955.

[2] E. M. Kosower, THIS JOURNAL, **77**, 3883 (1955).

[3] In a paper previously overlooked, Hantzsch and Burawoy[4] have written formulas corresponding to 2-addition and 4-addition, probably to "modernize" the earlier formulations of Hantzsch. No new experimental evidence was presented. They also stated that triiodide ion could not be responsible for the yellow color of chloroform solutions of 1-methylpyridinium iodide because the yellow color disappears upon dilution with alcohol. This statement must be considered insufficient in the absence of spectral data and the objection[2] to the "new absorption maxima" in chloroform solution must stand.

[4] A. Hantzsch and A. Burawoy, *Ber.*, **65**, 1059 (1932).

[5] A quantitative evaluation of the rate effect to be expected for α-methyl substitution on solvolyses which involve ionization of the leaving group is given by S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1120 (1952).

[6] W. König, *J. prakt. Chem.*, **69**, 105 (1904).

[7] Since no particular difficulty is associated with the conversion of 2,4,6-trimethylpyridine to the 1-methyl quaternary iodide, the lack of reaction should not be attributed to failure to form a 1-cyanopyridinium salt. H. C. Brown[8] has found that pyridine reacts with methyl iodide in nitrobenzene at 60° almost 17 times faster than 2,6-dimethylpyridine (2,6-lutidine), but 2,4,6-trimethylpyridine should be more reactive than the 2,6-derivative because a 4-methyl group doubles the rate over that for the unsubstituted case.[9]

[8] H. C. Brown and D. Gintis, footnote 37 in H. C. Brown, *et al.*, THIS JOURNAL, **75**, 1 (1953).

[9] H. C. Brown and A. Cahn, *ibid.*, **77**, 1715 (1955).

[10] All melting points were taken with a Hershberg apparatus using Anschütz thermometers.

[11] P. Murill, THIS JOURNAL, **21**, 828 (1899).

[12] H. O. Jones, *J. Chem. Soc.*, **83**, 1415 (1903).

[13] E. D. Bergmann, F. E. Crane, Jr., and R. M. Fuoss, THIS JOURNAL, **74**, 5979 (1952).