

and the lower layer, 3.4 g. of colorless liquid, was separated. After drying with Drierite, there was obtained by distillation in a small Vigreux still 2.7 g. (0.0062 moles, 92%) of the ethyl ester $\text{CF}_3\text{CF}_2\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{CH}_2\text{COOC}_2\text{H}_5$, b.p. $77-81^\circ$ (ca. 0.1 mm.) (main fraction b.p. $80-81^\circ$ (ca. 0.1 mm.), n_D^{20} 1.345). A band at 5.73μ in the infrared is attributed to the $\text{C}=\text{O}$ stretching vibration of the ester.

Reaction of $\text{CF}_2\text{ClCF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_{4.5\text{av}}\text{I}$ with Chlorosulfonic Acid.—To 18 g. (0.0299 mole) of $\text{CF}_2\text{ClCF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_{4.5\text{av}}\text{I}$ in a 3-necked flask cooled in an ice-bath and equipped with stirrer, thermometer, addition funnel and gas inlet tube for purging and maintaining a nitrogen atmosphere, there was added very slowly 25 g. (0.215 mole) of chlorosulfonic acid. Crystalline iodine was liberated and sulfur dioxide was evolved during the addition. The reaction mixture was stirred at 0° for 2 hr. and hydrolyzed by addition of water. The lower organic layer was taken up in 1,1,2-trichlorotrifluoroethane, washed with dilute $\text{Na}_2\text{S}_2\text{O}_3$ solution, dried with Drierite and distilled to remove solvent. From the residue there was separated by distillation 12 g. (0.0256 mole) (85% yield and conversion) of a liquid, b.p. 64 to $>126^\circ$ (ca. 0.1 mm.), shown by infrared spectra to consist entirely of a mixture of fluorocarbon acid and acid fluoride, $\text{CF}_2\text{ClCF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_{3.5\text{av}}\text{CH}_2\text{COOH}$, characterized as the amide (see below) and $\text{CF}_2\text{ClCF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_{3.5\text{av}}\text{CH}_2\text{COF}$ with the acyl fluoride carbonyl absorption at 5.39μ decreasing progressively and the acid carbonyl absorption at 5.78μ increasing progressively with increasing boiling point of the fractions.

$\text{CF}_2\text{ClCF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_{3.5\text{av}}\text{CH}_2\text{CONH}_2$.—Anhydrous ammonia was passed through a solution of 7 g. (0.149 mole) of $\text{CF}_2\text{ClCF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_{3.5\text{av}}\text{CH}_2\text{COF}$ in 50 ml. of anhydrous ether for 0.25 hr. The solution was filtered, and the filtrate was distilled. After removal of the solvent there was obtained as the sole product 5.3 g. (76% conversion) of the amide, $\text{CF}_2\text{ClCF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_{3.5\text{av}}\text{CH}_2\text{CONH}_2$, b.p. $156-162^\circ$ (ca. 0.1 mm.), m.p. $49-50^\circ$ after one recrystallization from 1,1,2-trichlorotrifluoroethane.

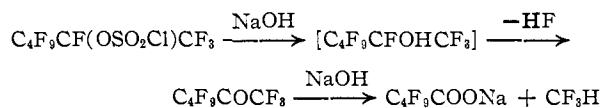
Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{OF}_{13}\text{ClN}$: C, 30.8; H, 2.4; N, 3.0. Found: C, 31.3; H, 2.7; N, 3.1.

Thermal Reaction of 2-Iodoperfluorohexane with Chlorosulfonic Acid.—Twenty grams (0.17 mole) of chlorosulfonic acid and 5 g. (0.0112 mole) of 2-iodoperfluorohexane were sealed in a heavy-walled Pyrex ampule and heated at 148° for 112 hours. A mass of orange crystals of iodine trichloride formed at the bottom of the tube. The tube was then cooled and opened and the top layer, a clear yellow oil, was decanted. On warming to room temperature, sulfur dioxide gas was evolved. A small amount of

additional oil was collected on hydrolysis of the iodine trichloride-acid layer, combined with the main fraction (total 4 g., 100%), washed with dilute potassium carbonate solution, dried with Drierite, and distilled to give entirely 2-chloroperfluorohexane, b.p. $83-84^\circ$, n_D^{20} 1.2826.

Similarly, from two reactions of 17.8 g. (0.0399 mole) of 2-iodoperfluorohexane with 50 g. (0.429 mole) of chlorosulfonic acid in sealed tubes at 75° for 4.25 hours and 95° for 2 hours, respectively, mainly unreacted iodide was recovered, and small amounts of 2-chloroperfluorohexane and perfluoro-2-hexyl chlorosulfate were detected by infrared spectroscopic analyses.

Hydrolysis of Perfluoro-2-hexyl Chlorosulfate.—Several fractions of the product from the reaction of 2-iodoperfluorohexane and chlorosulfonic acid carried out at 75° and 95° (see above) were combined (total weight 28 g.) and shaken exhaustively with water. The water-insoluble lower layer (27 g.) was removed and the aqueous part was neutralized with dilute aqueous sodium hydroxide solution. A small amount of gas (probably fluorocarbon) was liberated. After evaporation of the water, the residual solid salts were extracted in a Soxhlet apparatus with anhydrous ether. From the ether extract there was obtained after evaporation of the solvent a small amount of a sodium salt of a perfluorocarboxylic acid, as shown by the infrared spectrum, probably $\text{C}_6\text{F}_{13}\text{COOH}$. These chemical observations may be ascribed to a transformation of the type



Thermal Reaction of 2-Iodoperfluorohexane with Sulfuryl Chloride.—A mixture of 8.9 g. (0.0199 mole) of 2-iodoperfluorohexane and 29 g. (0.215 mole) of sulfuryl chloride was sealed in an 80-cc. heavy-wall Pyrex ampule. The tube was heated at $100-115^\circ$ with shaking for 11 hours. There was recovered from this reaction only $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CFClCF}_3$ shown spectroscopically to contain a trace of $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CFClCF}_3$. No $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}(\text{OSO}_2\text{Cl})\text{CF}_3$ was detected.

Acknowledgment.—We wish to thank Messrs. Fred P. Curtis and John J. Mullaney for technical assistance, Miss Ruth A. Kossatz and co-workers for infrared spectroscopic determinations, and Mr. Howard Francis and co-workers for various analytical determinations.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, PENNSALT CHEMICALS CORP., PHILADELPHIA 18, PA.]

Fluorocarbon Halosulfates and a New Route to Fluorocarbon Acids and Derivatives. II. Polyfluoroalkyl Fluorosulfates

BY MURRAY HAUPTSCHIN AND MILTON BRAID

RECEIVED DECEMBER 30, 1960

Novel reactions of fluorosulfonic acid with fluorocarbon iodides have been discovered by which fluorocarbon fluorosulfates are prepared. The syntheses of $\text{CF}_3\text{CF}_2\text{CF}_2\text{OSO}_2\text{F}$, $\text{CF}_2\text{ClCFClOSO}_2\text{F}$ and $\text{CF}_3\text{CF}_2\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{OSO}_2\text{F}$ and their one-step conversions to $\text{CF}_3\text{CF}_2\text{CONH}_2$, $\text{CF}_2\text{ClCONH}_2$ and $\text{CF}_3\text{CF}_2\text{CF}(\text{CF}_3)\text{CH}_2\text{CF}_2\text{CH}_2\text{CONH}_2$ by ammonolysis of the respective fluorosulfates are described.

The novel reactions of chlorosulfonic acid with fluorocarbon iodides and other polyfluoroalkyl iodides to produce the corresponding chlorosulfates have been described.¹ The present report deals with the extension of this work to the reaction of fluorosulfonic acid with these fluorinated iodides to form the corresponding fluorocarbon and fluoroalkyl fluorosulfates, and also describes their con-

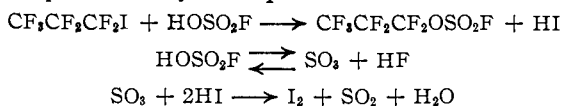
versions to fluorocarbon carboxylic acids and derivatives.

A typical primary fluorocarbon iodide, 1-iodoheptafluoropropane, reacted with an excess of fluorosulfonic acid in a sealed tube at 150° for 5 hr. to produce the novel perfluoropropyl fluorosulfate in high yield. The fluorination product, perfluoropropane, was formed in only trace amounts.

In a manner analogous to the formation of the

(1) M. Hauptschein and M. Braid, *J. Am. Chem. Soc.*, **83**, 2500 (1961).

chlorosulfates, the formation of fluorosulfates may be represented by the equations

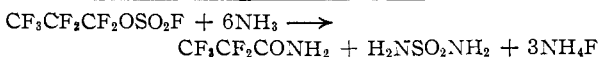
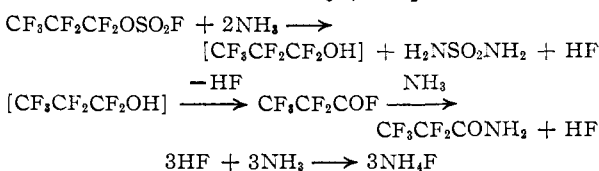


This reaction was extended to perfluorochloroalkyl iodides. Thus, $\text{CF}_2\text{CICFCII}$, prepared by the low temperature (iron-free) addition of ICl to chlorotrifluoroethylene,² was converted to the corresponding fluorosulfate $\text{CF}_2\text{CICFCIOSO}_2\text{F}$ by reaction with fluorosulfonic acid at 70° .

The fluorosulfonic acid reaction also was applied to iodides of the type $\text{R}_f(\text{CH}_2\text{CF}_2)_n\text{I}$ (where R_f is a perfluoroalkyl group) which can be obtained by thermal telomerization of 1,1-difluoroethylene with a telogen iodide such as $\text{C}_2\text{F}_5\text{CFICF}_3$.³ As was also the case for the chlorosulfonic acid reactions,¹ the $-\text{CH}_2\text{CF}_2\text{I}$ group was more reactive than the $-\text{CF}_2\text{CF}_2\text{I}$ group and a temperature of 40° was sufficient to give a high conversion of the iodide $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{I}$ to the fluorosulfate $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{OSO}_2\text{F}$.⁴

The reactivity of the fluorocarbon fluorosulfates is similar to that of the corresponding chlorosulfates.¹ Carboxylic acid salts, amides and esters are readily produced by alkaline hydrolysis, ammonolysis and alcoholysis of the fluorosulfates.

The ammonolysis of each of the series of fluorosulfates is described (see Experimental) by the scheme illustrated for the $\text{C}_3\text{F}_7\text{OSO}_2\text{F}$ reaction.



The fluorocarbon fluorosulfates are relatively stable to acid or neutral hydrolysis. Even in the presence of cold 10% aqueous sodium bicarbonate used to remove the hydrofluoric acid coproduced in the fluorosulfonic acid reaction only a minor amount of hydrolysis occurred.

It is of interest to compare the position of the "sulfone" $-\text{SO}_2$ asymmetric stretching vibrations of the $-\text{OSO}_2\text{F}$ group with that of the corresponding $-\text{OSO}_2\text{Cl}$ group¹ in the infrared. Thus, in

(2) M. Hauptschein, M. Braid and A. H. Fainberg, *J. Am. Chem. Soc.*, **83**, 2495 (1961).

(3) M. Hauptschein, M. Braid and F. E. Lawlor, *ibid.*, **80**, 846 (1958).

(4) The partially fluorinated fluorosulfates $\text{CH}_2\text{CF}_2\text{OSO}_2\text{F}$ and $\text{CH}_2\text{CICF}_2\text{OSO}_2\text{F}$ have been prepared [J. D. Calfee and P. A. Florio, U. S. Patent 2,628,972 (1953)] by the reaction of fluorosulfonic acid with the olefins $\text{CH}_2=\text{CF}_2$ and $\text{CF}_2=\text{CHCl}$, respectively. After the present work had been completed, a paper was presented on related 2-hydroperfluoroalkyl fluorosulfonates (fluorosulfates) prepared by reaction of perfluoro- and ω -hydroperfluoroolefins with sulfuric or fluorosulfonic acid to give $\text{RCHF}-\text{CF}_2\text{OSO}_2\text{F}$ where $\text{R} = \text{C}_n\text{F}_{2n+1}$ or $\text{H}(\text{CF}_2)_n$; H. H. Gibbs, W. L. Edens and R. N. Griffin, Abstract of Papers presented at the 138th Meeting of the American Chemical Society, New York, N. Y., September 11 to 16, 1960, p. 11-M. Also W. P. Van Meter and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 6005 (1960), have just reported that a compound of probable structure $\text{CF}_3\text{OSO}_2\text{F}$ was isolated from the many products obtained from the reaction of CF_3OF with SO_2 .

the case of the vapor spectra: $n\text{-C}_3\text{F}_7\text{OSO}_2\text{F}$ with a maximum at 6.65μ is displaced 0.17μ farther to the visible than for $n\text{-C}_3\text{F}_7\text{OSO}_2\text{Cl}$ (6.82μ); $\text{CF}_2\text{-CICFCIOSO}_2\text{F}$ with a maximum at 6.71μ is displaced 0.13μ farther to the visible than for $\text{CF}_2\text{-CICFCIOSO}_2\text{Cl}$ (6.84μ). In the liquid infrared spectrum of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{OSO}_2\text{F}$ a maximum at 6.75μ is displaced 0.19μ farther to the visible than for $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{OSO}_2\text{Cl}$ (6.94μ).

Experimental

Reaction of 1-Iodoheptafluoropropane with Fluorosulfonic Acid.—Fifteen grams (0.0507 mole) of $n\text{-C}_3\text{F}_7\text{I}$ and 30 g. (0.3 mole) of fluorosulfonic acid were sealed *in vacuo* in a 70-cc. heavy-walled Pyrex ampule. The tube was shaken and heated at a temperature of 150° for 5 hr. The ampule was cooled in liquid nitrogen and opened. Approximately 0.5 g. of volatile products was collected on warming to room temperature, which were found by vapor liquid partition chromatography (v.l.p.c.) and infrared spectroscopic analyses to contain SO_2 , SiF_4 and C_2F_6 . In addition trace amounts of other fluorocarbon materials not further characterized were present.

The remaining liquid mixture was poured cautiously onto chipped ice. The lower organic layer was separated, washed once with cold 10% aqueous sodium bicarbonate solution, washed again with water, and dried with calcium sulfate and magnesium sulfate. By v.l.p.c. in a Perkin-Elmer Vapor Fractometer model 154, the reaction product mixture (10.5 g.) was shown to consist almost entirely of equimolar amounts of unreacted $n\text{-C}_3\text{F}_7\text{I}$ (5.5 g.) and n -perfluoropropyl fluorosulfate, $n\text{-C}_3\text{F}_7\text{OSO}_2\text{F}$ (5 g.). Complete separation of the close-boiling iodide from the fluorosulfate was not effected by distillation. An analytical sample of $\text{CF}_3\text{CF}_2\text{CF}_2\text{OSO}_2\text{F}$ was freed from contaminant $\text{CF}_3\text{CF}_2\text{CF}_2\text{I}$ chromatographically using a Perkin-Elmer "B" column at 30° . The characteristic v.l.p.c. elution time ratios $t_R/t_{\text{OC}_2\text{I}_4}$ at 30° are 0.012 for $n\text{-C}_3\text{F}_7\text{OSO}_2\text{F}$ and 0.14 for $n\text{-C}_3\text{F}_7\text{I}$. (Note that the corresponding ratio for $\text{C}_3\text{F}_7\text{OSO}_2\text{Cl}$ is 0.155.)

The yield of fluorosulfate based on reacted iodide is $>95\%$ (including $\text{CF}_3\text{CF}_2\text{COONa}$ formed by hydrolysis of the fluorosulfate during isolation). At higher temperatures, higher conversions to fluorosulfate may be obtained. The pure n -perfluoropropyl fluorosulfate, a colorless liquid, b.p. 46° , $n_D^{20} < 1.290$, has a strong band in the vapor infrared spectrum at 6.65μ related to the asymmetrical stretching vibrations of the "sulfone" $-\text{SO}_2-$ function of the fluorosulfate group.

Anal. Calcd. for $\text{C}_3\text{F}_7\text{O}_2\text{S}$: C, 13.4; F, 56.7. Found: C, 13.7; F, 56.7.

The principal bands in the infrared (vapor) spectrum of $n\text{-C}_3\text{F}_7\text{OSO}_2\text{F}$ are at 6.65vs, 7.51vs, 7.90vssh, 8.02vvs, 8.24vs, 8.61vs, 8.85vs, 9.95vvs, 11.49s, 11.85vs, 12.97s and 13.39vs μ (vvs = very, very strong, vs = very strong, s = strong, sh = shoulder).

For comparison purposes, the principal bands in the infrared (vapor) spectrum of $n\text{-C}_3\text{F}_7\text{OSO}_2\text{Cl}$ are at 6.82vs, 7.36s, 7.53s, 8.00vvs, 8.21vs, 8.36ssh, 8.65vs, 8.91vs, 10.04vs, 11.82s and 13.5vs μ .

Ammonolysis of n -Perfluoropropyl Fluorosulfate.—Anhydrous ammonia was passed for 10 minutes into a solution of 0.24 g. (0.0009 mole) of $n\text{-C}_3\text{F}_7\text{OSO}_2\text{F}$ in 10 ml. of anhydrous ethyl ether cooled at 0° . The ether solution was filtered to remove ammonium salts, and the filtrate was evaporated. There remained 0.2 g. of white crystals from which after one recrystallization from 1,1,2-trichlorotrifluoroethane there was obtained 0.18 g. (100%) of the spectroscopically pure amide $\text{C}_2\text{F}_5\text{CONH}_2$.⁵

Reaction of 1,2-Dichloro-1,2,2-trifluoro-1-iodoethane with Fluorosulfonic Acid.—To 45 g. (0.449 mole) of fluorosulfonic acid stirred at 70° , there was added drop by drop during 0.5 hr. 40 g. (0.143 mole) of CF_2CICFCI . Iodine and SO_2 were liberated during the addition period and traces of 1,2-dichlorotetrafluoroethane were detected in the evolved volatiles spectroscopically. The reaction mixture was stirred

(5) D. R. Husted and A. H. Ahlbrecht, *ibid.*, **75**, 1605 (1953).

for 2 hr. at 70°, and after cooling, was hydrolyzed by pouring cautiously onto chipped ice. The lower organic layer was separated, washed once with cold 10% aqueous sodium bicarbonate solution, and again with cold water. The crude reaction mixture (38 g.) was dried with calcium sulfate and magnesium sulfate. By v.l.p.c. this liquid fraction was shown to consist of 8 g. (90%) of 1,2-dichloro-1,2,2-trifluoroethyl fluorosulfate, $\text{CF}_2\text{ClCFClOSO}_2\text{F}$, and 30 g. of unreacted iodide. The conversion to fluorosulfate would clearly be increased considerably at higher reaction temperatures. An analytical sample of $\text{CF}_2\text{ClCFClOSO}_2\text{F}$ was separated chromatographically from the $\text{CF}_2\text{ClCFClI}$ contaminants using a Perkin-Elmer "B" column at 75°. The characteristic v.l.p.c. elution time ratio t_R/t_{CCl_4} is 0.48 for $\text{CF}_2\text{ClCFClOSO}_2\text{F}$ as compared to 2.9 for $\text{CF}_2\text{ClCFClI}$.² Pure $\text{CF}_2\text{ClCFClOSO}_2\text{F}$ is a colorless liquid, b.p. 89°, n_D^{20} 1.3468. The vapor infrared spectrum of the fluorosulfate has a strong band at 6.71 μ characteristic of the -OSO₂F group. The principal infrared spectrum maxima for $\text{CF}_2\text{ClCFClOSO}_2\text{F}$ (vapor) are at 6.71vs, 7.98vs, 8.42vs, 8.74vs, 9.18vs, 9.71vs, 10.64s, 11.45sh, 11.77vs, 12.0ssh, 14.1msh and 14.45s μ .

Anal. Calcd. for $\text{C}_2\text{Cl}_2\text{F}_4\text{O}_3\text{S}$: C, 9.6; Cl, 28.3; F, 30.3; S, 12.8. Found: C, 9.8; Cl, 28.2; F, 30.3; S, 12.6.

Ammonolysis of 1,2-Dichloro-1,2,2-trifluoroethyl Fluorosulfate.—Anhydrous ammonia was passed for 15 minutes into a solution of 0.2 g. (0.0008 mole) of $\text{CF}_2\text{ClCFClOSO}_2\text{F}$ in 10 ml. of 1,1,2-trichlorotrifluoroethane cooled at 0°. The reaction mixture was filtered to remove ammonium salts and the filtrate was evaporated. There remained a small amount of white crystals, m.p. 76–77°, from which, after recrystallization from methylene chloride, there was obtained 0.1 g. (97%) of the amide $\text{CF}_2\text{ClCONH}_2$. The infrared spectrum of this amide matched that of $\text{CF}_2\text{ClCONH}_2$ prepared by ammonolysis of $\text{CF}_2\text{ClCOOC}_2\text{H}_5$, and the melting point of the known chlorodifluoroacetamide was not depressed on admixture with the amide derived from the fluorosulfate.

Reaction of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{I}$ with Fluorosulfonic Acid.—To 40 g. (0.4 mole) of fluorosulfonic acid stirred at 40° was added drop by drop during 15 minutes 10 g. (0.211 mole) of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{I}$ and stirring was continued

at 40° for 1.25 hr. longer. Crystalline iodine and SO_2 were formed during the reaction. After cooling, the reaction mixture was hydrolyzed by cautiously pouring onto chipped ice. The lower organic layer was separated, washed once with cold 10% aqueous sodium bicarbonate solution and again with water. The crude liquid reaction products (9.5 g.) were dried with calcium sulfate and magnesium sulfate and distilled in a small Vigreux unit. There was obtained 7 g. (75%) of the fluorosulfate $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{OSO}_2\text{F}$, middle cut b.p. 114° at 100 mm. The liquid infrared spectrum of this fluorosulfate has a strong absorption band at 6.75 μ characteristic of the -OSO₂F group.

Anal. Calcd. for $\text{C}_8\text{H}_4\text{F}_{14}\text{O}_3\text{S}$: C, 21.5; H, 0.90. Found: C, 21.1; H, 0.90.

A small amount of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)\text{CH}_2\text{CF}_2\text{CH}_2\text{COF}$ was detected by v.l.p.c. and infrared spectroscopy.

Ammonolysis of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{OSO}_2\text{F}$.—Anhydrous ammonia was passed for 15 minutes into a solution of 2 g. (0.00449 mole) of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{OSO}_2\text{F}$ in 10 ml. of anhydrous ethyl ether cooled at 0°. The reaction mixture was filtered to remove ammonium salt and the filtrate was evaporated. There remained 0.15 g. (98%) of an oil shown to be almost entirely pure $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{CONH}_2$ by the infrared spectrum. By distillation in a small Vigreux unit there was obtained a fraction of the pure amide, b.p. 85–86° at ca. 0.1 mm., for which there were absorption maxima in the infrared spectrum at 5.93 μ (carbonyl stretching vibration), 3.0 and 3.2 μ (NH stretching vibration) and 6.2 μ (probably NH bending). The spectrum had the general characteristic similarities expected for homologs to the spectrum of $\text{C}_2\text{F}_5\text{CF}(\text{CF}_3)(\text{CH}_2\text{CF}_2)_2\text{CH}_2\text{CONH}_2$ previously made by ammonolysis of the corresponding chlorosulfate.¹

Anal. Calcd. for $\text{C}_8\text{H}_5\text{F}_{11}\text{ON}$: C, 28.16; H, 1.77; N, 4.10. Found: C, 28.02; H, 1.78; N, 3.95.

Acknowledgment.—We wish to thank Dr. A. H. Fainberg for the vapor liquid partition chromatographic and infrared spectroscopic work and Mr. Howard Francis and co-workers for the elemental analyses.

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION, RICHMOND, CALIF.]

Oxidative Decarboxylation of Aromatic Acids to Isomeric Aryloxy Derivatives

BY WILLIAM G. TOLAND

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A convenient and highly selective method has been found for converting aromatic carboxylic acids to isomeric phenyl esters of the starting acids. Several new esters were prepared. Corresponding phenols are obtained by simple hydrolysis. A possible mechanism is proposed. Alternate paths are suggested to explain the other products observed when the reaction is allowed to proceed uncontrolled.

Introduction

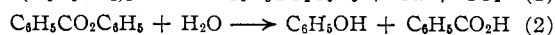
The pyrolysis of copper benzoate, described as early as 1845,¹ was the subject of several old papers.² Dry distillation reportedly gave a mixture of products, including benzene, biphenyl, phenol, diphenyl ether, benzoic acid, salicylic acid and phenyl benzoate. The subject remained dormant until relatively recently when a series of patents was issued. These showed that this reaction can be made highly specific to the formation of phenyl benzoate³ and/or phenol.^{3,4} They also demon-

strated that it can be applied to substituted aromatic carboxylic acids to obtain substituted phenyl esters and phenols.

The present paper is intended to present the experimental work undertaken in exploring the scope of this new reaction and to discuss some of the probable mechanisms involved.

Results

The over-all reactions are illustrated by eq. 1 and 2. They are effected in the temperature range



of 200–350° in a period of one to six hours by merely heating the cupric salt alone or in a solvent such as Patent 2,727,926, filed January 8, 1954; (c) R. D. Barnard and R. H. Meyer, U. S. Patent 2,852,567, filed January 8, 1954.

(1) Dr. Ettling, *Ann.*, **53**, 77 (1845).

(2) (a) J. Stenhouse, *ibid.*, **53**, 91 (1845); (b) K. List and H. Limpricht, *ibid.*, **90**, 190 (1854); (c) R. Fittig, *ibid.*, **125**, 328 (1863); (d) W. Hoffmeister, *ibid.*, **159**, 197, 204 (1871).

(3) (a) W. G. Toland, U. S. Patent 2,762,838, filed March 16, 1951; (b) W. G. Toland, U. S. Patent 2,766,294, filed May 19, 1952.

(4) (a) M. B. Pearlman, U. S. Patent 2,727,924, filed January 8, 1954; (b) W. W. Kaeding, R. O. Lindblom and R. G. Temple, U. S.