[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER AND THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

Fluorinated Esters. II. Diesters of Perfluorocarboxylic Acids with Alcohols and Glycols[1]

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RECEIVED JULY 24, 1952

A series of diesters of perfluorofatty acids has been prepared by condensation of fluorocarbon acids and acid chlorides with α,ω-polymethylene glycols and by the reaction of the silver salts of these acids with α,ω-polymethylene diiodides. A number of new diesters and polyesters of perfluorodicarboxylic acids with unfluorinated alcohols and diols are described. Various physical and chemical properties of these compounds and of certain intermediates are given.

In the first paper of this series,[2] a number of almost completely fluorinated esters and diesters were reported as part of a program correlating various properties with molecular structure of different series of fluorine-containing diesters. The present paper describes the preparation and properties of partially fluorinated diesters and polyesters derived from perfluorinated mono- and dicarboxylic acids and unfluorinated alcohols and glycols.

In Table I is listed a number of new diesters of general formula $C_nF_{2n+1}CO_2(CH_2)_xO_2CC_nF_{2n+1}$. These compounds were prepared in yields of 42–93% by three methods, (A) condensation of monocarboxylic acids with α,ω-polymethylene glycols, (B) reaction of perfluorinated monocarboxylic acid chlorides with an α,ω-glycol, and (C) reaction of the silver salts of fluorocarbon acids with α,ω-polymethylene diiodides.[3] Method A could be employed with or without mineral acid catalysts. Due to their high acid strength, the fluorocarbon acids effectively catalyzed the reaction to give good yields of diesters. As might be expected, these compounds exhibit physical properties intermediate between those of the highly fluorinated diesters[2] and the unfluorinated analogs. All of the esters are insoluble in water and are not appreciably hydrolyzed in 10% carbonate or bicarbonate solution. This is in contrast to the observation that methyl perfluorocaproate reacted rapidly with dilute bicarbonate at room temperature.[4] However, the esters are readily saponified in hot 5% alcoholic sodium hydroxide solution. In general, these esters are more stable toward alkaline hydrolysis than the almost completely fluorinated esters, but are saponified much more rapidly than the corresponding unfluorinated compounds. This can be attributed to the greater susceptibility of the carbonyl carbon atom to nucleophilic attack resulting from the strong electron-withdrawing effect exerted by the adjacent perfluoroalkyl group of the acid portion. This effect is increased, though to a lesser extent, by the presence of a perfluoroalkyl group in the alcohol portion.

TABLE I

Compound	Method[a] of prepn.	Yield, %	B.p. °C.	B.p. Mm.	$n^{25}D$	d^{25}_4	AR_F[b]	Analyses, %[c] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Fluorine Calcd.	Fluorine Found
$C_3F_7CO_2(CH_2)_3O_2CC_3F_7$	Ag–I	84	79	3.6	1.3225[d]	1.5856[d]	1.29	28.22	28.63	1.29	1.30	56.82	57.32
$C_3F_7CO_2(CH_2)_4O_2CC_3F_7$	DE	83	97	6.5	1.3288	1.5443	1.28	29.89	29.72	1.67	1.96		
$C_3F_7CO_2(CH_2)_5O_2CC_3F_7$	DE	93	102	3.5	1.3350	1.5015	1.29	31.46	31.43	2.03	2.36		
$C_3F_7CO_2(CH_2)_6O_2CC_3F_7$	Ag–I	88	111.5	4.0	1.3392[e]	1.4670[e]	1.29	32.95	33.18	2.37	2.35	52.13	52.06
$C_3F_7CO_2(CH_2)_{10}O_2CC_3F_7$	Ag–I	83	110.2	0.5	1.3568[e]	1.3576[e]	1.29	38.17	38.41	3.56	3.30	46.97	47.15
$CF_3CO_2(CH_2)_5O_2CCF_3$	DE	81	75	4.0	1.3530	1.3286	1.30	36.50	36.38	3.40	3.77		
$C_5F_{11}CO_2(CH_2)_5O_2CC_5F_{11}$	AC	86	126–127	5.0	1.3305	1.6156	1.29	29.32	29.27	1.45	1.48		
$C_7F_{15}CO_2(CH_2)_5O_2CC_7F_{15}$	AC	59	159–160	7.0	1.3284	1.6846	1.28	28.14	28.20	1.12	1.51		
$C_9F_{19}CO_2(CH_2)_5O_2CC_9F_{19}$	AC	42	164	4.0	1.3286	1.735	1.29	27.39	27.58	0.92	1.27		
$C_3F_7CO_2C_5H_{11}$	Ag–I	80	144	763	1.3334[e]	1.2471[e]	1.31	38.04	38.22	3.90	3.80	46.80	46.88

[a] Ag–I, silver salt–iodide method; DE, direct esterification; AC, acid chloride + glycol. [b] AR_F is the atomic refraction for F, obtained from *MR*(Found) by subtracting the customary increments for C, H and O. [c] Analyses by Clark Microanalytical Laboratory, Urbana, Illinois, and Jack V. Fenner, Materials Laboratory. [d] At 27.5°. [e] At 27°.

The kinematic viscosities of several diesters mentioned above are shown in Table II.

TABLE II

VISCOSITY DATA

Compound	t, °C.	Kinematic viscosity, centistokes	ASTM slope
$C_3F_7CO_2(CH_2)_3O_2CC_3F_7$	0.5	9.22	
	20.0	4.46	1.05
	62.4	1.54	
$C_3F_7CO_2(CH_2)_5O_2CC_3F_7$	0.5	11.8	
	20.25	5.60	0.95
	62.5	1.96	
$C_3F_7CO_2(CH_2)_6O_2CC_3F_7$	0.5	13.4	
	20.25	6.35	0.91
	62.5	2.23	
$C_3F_7CO_2(CH_2)_{10}O_2CC_3F_7$	0.5	21.8	
	19.75	10.1	0.81
	62.5	3.19	

The perfluorofatty acid chlorides used in method B were prepared in 59–90% yields from the corresponding acids and phosphorus pentachloride.

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[1] Opinions expressed are those of the authors and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

[2] M. Hauptschein, J. F. O'Brien, C. S. Stokes and R. Filler, THIS JOURNAL, **75**, 87 (1953).

[3] M. Hauptschein and A. V. Grosse, *ibid.*, **73**, 5139 (1951).

[4] W. H. Pearlson in Simons' "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 486, pp. 500–505.

TABLE III

Di-2-ethylhexyl octafluoroadipate, b.p. 190–195° at 5.0 mm., $n^{25}\text{D}$ 1.3990, rapidly decomposed on heating above 200°; impure di-*t*-butyl octafluoroadipate, b.p. 100–110° at 8.0 mm., readily decomposed on standing; di-*n*-butyl hexafluoroglutarate, b.p. 128° at 8.0 mm., $n^{25}\text{D}$ 1.3741.

Compound	Yield, %	B.p., °C.	Mm.	$n^{25}\text{D}$	$d^{25}{}_4$	AR_F[a]	Analyses, %[b] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-$C_4H_9O_2C(CF_2)_4CO_2C_4H_9$	86	126	8.5	1.3725	1.2711	1.29	41.80	41.67	4.51	4.33
i-$C_4H_9O_2C(CF_2)_4CO_2C_4H_9$	87	118	8.0	1.3697	1.2671	1.29	41.80	41.76	4.51	4.64
s-$C_4H_9O_2C(CF_2)_4CO_2C_4H_9$	57	111	5.0	1.3680	1.2643	1.28	41.80	41.94	4.51	4.44
n-$C_6H_{13}O_2C(CF_2)_4CO_2C_6H_{13}$	58	155–156	3.5	1.3888	1.2038	1.26	47.16	47.20	5.72	5.58
n-$C_6H_{13}O_2C(CF_2)_3CO_2C_6H_{13}$	74	158–159	5.0	1.3938	1.1447	1.30	50.00	50.34	6.42	6.55

[a] See Table I for meaning of AR_F. [b] Microanalyses by Jack V. Fenner, Materials Laboratory.

Their boiling points are considerably lower than those of the unfluorinated analogs.[5]

A number of new diesters of general formula $RO_2C(CF_2)_xCO_2R$, where $x = 3$ or 4 and R is a straight or branched chain alkyl group, are listed in Table III. These compounds were prepared from the perfluorodicarboxylic acids[6,7] and unfluorinated alcohols either with or without mineral acid catalysts. Only a few diesters of this type have been reported previously.[4]

It will be noted that the di-*n*-butyl, diisobutyl and di-*s*-butyl octafluoroadipates show the expected similarity of properties, with the straight chain *n*-butyl isomer having the highest boiling point, refractive index and density. The yield of the *s*-butyl isomer was lower than those of the other two due to the formation of unsaturated by-products. When the preparation of di-*t*-butyl octafluoroadipate by direct esterification was attempted, only an impure diester could be isolated. This material rapidly decomposed on standing to form unsaturated substances which were not identified. This may be compared with the successful isolation of *t*-butyl heptafluorobutyrate[8] from the reaction of *t*-butyl chloride with silver heptafluorobutyrate.

These compounds also do not hydrolyze appreciably in dilute bicarbonate or carbonate solution, but are readily saponified in dilute alcoholic sodium hydroxide.

Two polyesters have been prepared by an extension of the silver salt–iodide method described earlier. These materials, of the type $Z[(-O_2C-(CF_2)_3CO_2-(CH_2)_x-)]_nZ$, (where Z = Ag or I and $x = 3$ or 6) are viscous oils or greases. A third similar polyester of higher molecular weight was obtained by condensation polymerization of perfluoroglutaric acid and trimethylene glycol.

Experimental

Diesters of Polymethylene Glycols and Heptafluorobutyric Acid by the Silver Salt–Diiodide Method.—The method is illustrated for the preparation of hexamethylene glycol diheptafluorobutyrate. However, the procedure is general and has been used for the preparation of several other esters (see Table I).

In a 250-ml. flask equipped with a reflux condenser and a dropping funnel was placed 49.9 g. (5% excess) of silver heptafluorobutyrate[9] suspended in 50 ml. of Freon 113 (1,1,2-trichlorotrifluoroethane). Over a period of half an hour, 25.0 g. (0.074 mole) of hexamethylene diiodide[10] dissolved in the mixed solvent of Freon 113 (20 ml.), and carbon tetrachloride (5 ml.) was added in small portions with shaking. Reaction was indicated by the formation of yellow silver iodide and the evolution of heat. The reaction mixture was refluxed for an additional two hours with intermittent stirring. The liquid product was then removed by decantation and several carbon tetrachloride washings of the silver iodide were added. After removal of the solvent the product was distilled under reduced pressure in a Vigreux column and there was obtained approximately 31 g. (82.4% yield) of the water-white liquid ester boiling at 110–111.5° (mostly 111.5°) at 4.0 mm. pressure. The theoretical amount of silver iodide was formed. An additional 2 g. of ester remained adsorbed in the silver iodide so that the total over-all yield of ester was 88%. Yields of 83–88% were obtained by this method.

Polyesters of Perfluorodibasic Acids with Polymethylene Glycols. A. Silver Salt-Iodide Method.—This is an extension of the method employed in the preparation of diesters. To 78.8 g. (1% excess) of silver hexafluoroglutarate[9] suspended in 50 ml. of Freon 113 and 10 ml. of carbon tetrachloride, 58.1 g. (0.172 mole) of hexamethylene diiodide in 50 ml. of Freon 113 and 10 ml. of carbon tetrachloride was added with shaking over a period of 15 minutes. The reaction mixture was refluxed with intermittent stirring for three hours. The liquid product was removed by decantation and the residue extracted 15 times with 10-ml. portions of anhydrous ether. The solvents were removed by distillation and the product subjected to a bath temperature of 138° at 0.5 mm. pressure to ensure complete removal of solvent. There remained in the flask 34.6 g. of a light brown, viscous, oily polyester. The silver iodide was further extracted with hot acetone and there was obtained about 12 g. of a greenish-brown, sticky, grease-like material. A small quantity of semi-transparent plastic-like solid was found adhering to the glass beaker after decanting the acetone. A similar result was obtained when trimethylene diiodide was used with silver hexafluoroglutarate.

B. Condensation Polymerization of Perfluoroglutaric Acid and Trimethylene Glycol.—To 180 g. (0.747 mole) of hexafluoroglutaric acid was added 62.5 g. (10% excess) of trimethylene glycol. The mixture was stirred at a temperature of 130–170° over a period of four hours. As the reaction progressed, water distilled out and the reaction product became increasingly viscous and brown in color. The product was decolorized by treating an ethereal solution of the product with decolorizing charcoal. After the ether was evaporated, the product was subjected to a temperature of 150° at 0.5 mm. pressure to remove any volatile material present. There was obtained 197.5 g. of pure, clear, light amber-colored lubricant. The absolute viscosity of this polyester was higher than that obtained by method A.

Viscosity measurements were made in the usual manner with standard Ostwald–Cannon–Fenske type viscosimeters using the β oil standard of the American Petroleum Institute.

Diesters of Polymethylene Glycols and Perfluorofatty Acids by Direct Esterification.—The method is illustrated by the preparation of pentamethylene glycol diheptafluorobutyrate.

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[5] K. S. Markley, "Fatty Acids, Their Chemistry and Physical Properties," Interscience Publishers, New York, N. Y., 1947, p. 357.

[6] Perfluoroglutaric acid was prepared by permanganate oxidation of 1,2-dichlorohexafluorocyclopentene; E. T. McBee, P. A. Wiseman and G. B. Bachman, *Ind. Eng. Chem.*, **39**, 415 (1947).

[7] Perfluoroadipic acid was obtained as a gift from Minnesota Mining and Manufacturing Co., St. Paul, Minn.

[8] Minnesota Mining and Manufacturing Co., "Fluorochemicals—Heptafluorobutyric Acid," 1950.

[9] M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951).

[10] The diiodides were purchased from Columbia Organic Chemicals Co.

RESULTS OF VISCOSITY MEASUREMENTS

Compound	t, °C.	Kinematic viscosity, centistokes	ASTM slope
$[-O_2C(CF_2)_3CO_2(CH_2)_3-]_n$[11]	0.2	5365	
	19.0	934.3	0.68
	76.4	39.3	
	99.5	17.27	
After standing for 64 days	0.2	4346	
	25.6	464.0	0.68
$[-O_2C(CF_2)_3CO_2(CH_2)_3-]_n$[12]	18.2	5190	
	21.9	3519	0.68
	76.6	91.95	
$[-O_2C(CF_2)_3CO_2(CH_2)_6-]_n$	0.0	4480	
	23.4	748	0.59
	27.4	578	
	75.8	57.5	

In a 200-ml. round bottom flask equipped with a modified Dean and Stark apparatus used as a phase separator and a reflux condenser to which a drying tube containing Drierite was attached, was placed 42.8 g. (0.2 mole) of heptafluorobutyric acid (Minnesota Mining and Manufacturing Co.), 10.4 g. (0.1 mole) of 1,5-pentanediol (du Pont Electrochemical), 30 ml. of redistilled toluene and 0.5 g. of sodium bisulfate. The mixture was heated under reflux for four hours. The reaction was followed by the rate of formation of water, which was carried over into the phase separator as an azeotrope with toluene. The theoretical amount of water (3.6–3.65 ml.) was obtained. The reaction mixture was allowed to cool, washed with a 5% solution of potassium carbonate, dried over anhydrous sodium sulfate and distilled. There was obtained 46.0 g. (92.7%) of diester, b.p. 103–104° (4 mm.). This reaction was also carried out and with similar results without the use of the inorganic acid catalyst.

Perfluorofatty Acid Chlorides.—The method used was described in the previous paper of this series.[2] The acid was mixed with phosphorus pentachloride, the reaction mixture heated under reflux for three to four hours and the product separated by distillation from the phosphorus oxychloride formed in the reaction. Yields of 59–90% were thus obtained. Perfluorocapryl chloride distilled at 174–175° at 747 mm., m.p. 27–28°.

Anal. Calcd. for $C_{10}F_{19}OCl$: Cl, 6.66. Found: Cl, 6.53.

Crude perfluorocaproyl chloride distilled at 90–100°.

Diesters from Perfluorofatty Acid Chlorides and Polymethylene Glycols.—In a 100-ml. round-bottom flask fitted with a water-cooled condenser vented through a drying tube containing Drierite was placed 43.3 g. (0.1 mole) of perfluorocaprylyl chloride and 6.2 g. (0.06 mole) of 1,5-pentanediol. There was no observed evolution of hydrogen chloride upon mixing. The reaction mixture was gently refluxed for six hours with evolution of hydrogen chloride. At first the reaction mixture consisted of two immiscible liquids which gradually formed a yellow, then finally a dark brown solution. After washing with 10% potassium carbonate solution until the upper, aqueous layer was free of chloride ion, the reaction mixture was washed with water, dried over anhydrous sodium sulfate and distilled. The yield of pure diester, b.p. 158–160° (mostly 159–160°) at 7 mm., was 26.4 g. (59%).

Diesters of Octafluoroadipic Acid and Hexafluoroglutaric Acid with Unfluorinated Alcohols.—This method is illustrated by the preparation of diisobutyl octafluoroadipate.

In a 200-ml. round bottom flask equipped with a modified Dean and Stark apparatus used as a phase separator and a water-cooled reflux condenser to which a drying tube was attached, was placed 29.0 g. (0.1 mole) of octafluoroadipic acid, 14.8 g. (0.2 mole) of isobutyl alcohol, 35 ml. of dry benzene and 0.5 g. of sodium bisulfate. The mixture was heated under reflux for two hours by which time the theoretical amount of water had been formed. After the benzene and excess alcohol had been removed by distillation, the crude ester was washed with 5% sodium bicarbonate, then with water, dried over anhydrous sodium sulfate and distilled, yielding 35.0 g. (87.1%) of diester, b.p. 117–118° at 8 mm.

Acknowledgment.—The authors wish to express their appreciation to Mr. Richard Sneed and Mrs. Lois Cook for technical assistance during this investigation, and to Minnesota Mining and Manufacturing Co. for their gift of some of the perfluorinated acids.

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[11] Prepared by the reaction of silver perfluoroglutarate and trimethylene diiodide.

[12] Prepared by condensation polymerization of perfluoroglutaric acid and trimethylene glycol.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

The Synthesis and Polymerization of Some Fluorinated Styrenes[1]

BY MAURICE PROBER

RECEIVED MAY 13, 1952

A series of fluorinated styrenes, α,β,β-trifluorostyrene, β,β-difluorostyrene, α,β-difluorostyrene and α-chloro-β-fluorostyrene, was prepared starting with sodium difluoroacetate. α,β,β-Trifluorostyrene was also prepared by the direct reaction of chlorotrifluoroethylene and benzene. Good conversion to a high softening polymer was obtained with α,β,β-trifluorostyrene.

Discussion

Interest in the properties of the fluorinated polymers prompted an investigation into the synthesis and polymerization of fluorinated styrenes in which the fluorine was substituted in the vinyl side chain. When the problem was begun in this Laboratory, the only styrenes of this class described in the literature were β-fluorostyrene[2] and dichlorofluorostyrene,[3] neither of which was fully characterized. Recently the preparation of α,β,β-trifluorostyrene, α-chloro-β,β-difluorostyrene[4] and β-chloro-α,β-difluorostyrene[5] has been described, but no information concerning polymerization has appeared.

This paper consists of three parts: the synthesis of α,β,β-trifluorostyrene, α-chloro-β-fluorostyrene, α,β-difluorostyrene and β,β-difluorostyrene by the following reaction sequence; the direct synthesis of α,β,β-trifluorostyrene; and the polymerization behavior of these olefins.

The difluoroacetophenone (I) was prepared in

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[1] Presented at the 120th Meeting of the American Chemical Society, New York, N. Y., September, 1951.

[2] F. Swarts, *Bull. soc. chim.*, [4] **25**, 145 (1919).

[3] V. Weinmayr, U. S. Patent 2,398,483 (June 19, 1945).

[4] S. G. Cohen, H. T. Wolosinski and P. J. Scheuer, THIS JOURNAL, **71**, 3439 (1949).

[5] S. G. Cohen, H. T. Wolosinski and P. J. Scheuer, *ibid.*, **72**, 3952 (1950).