by the following features: λ_{sh} 230μ (log ϵ = 3.87), λ_{min} 263mμ (log ϵ = 3.63), λ_{max} 288mμ (log ϵ = 3.69) and λ_{sh} 355 (log ϵ = 2.99).

Anal. Calcd. for $C_{13}H_{12}FeO_3$: C, 57.38; H, 4.45; Fe, 20.53. Found: C, 57.29; H, 4.58; Fe, 20.31.

Preparation of a 2,4-dinitrophenylhydrazone of methoxaylferrocene was achieved by adding 20 ml. of the reagent solution (*6*) to the keto-ester (0.544 grams, 2.00×10^{-3} mole) and allowing the reaction to take place at room temperature with stirring for one hr. The accumulated black, crystalline precipitate was collected by suction filtration and washed and dried. Three recrystallizations from hot benzene-hexane gave 0.728 grams (80% yield) of the crystalline, black-colored 2,4-dinitrophenylhydrazone of methoxalylferrocene, m.p. 226–227°.

Anal. Calcd. for $C_{19}H_{16}FeN_4O_6$: C, 50.47; H, 3.57; Fe, 12.35; N, 12.39. Found: C, 49.88; H, 3.73; Fe, 12.35; N, 12.40.

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Radical Addition of Perfluoroalkyl Iodides and Diiodides to Allyl Monomers

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The addition of perfluoropropyl iodide and symmetrical diiodohexafluoropropane to allyl alcohol and allyl chloride has produced intermediates from which a number of novel fluorine-containing compounds have been prepared. Synthesis methods are described, and physical properties of the resultant compounds are tabulated.

THE FREE radical-catalyzed addition of perfluoroalkyl iodides to olefins has been reported by numerous authors (*5*). The work presently reported successfully extends this reaction to the use of a typical perfluoroalkyl diiodide. In addition, this work uses the iodide-addition reaction to prepare several new mono- and difunctional entities containing fluorine. The fluorinated compounds prepared during the course of this work are presented in Table I, and the properties of these compounds are presented in Table II.

Perfluoropropyl iodide was prepared by the Hunsdiecker reaction on perfluoropropionic acid and subsequently was added to allyl alcohol or allyl chloride using ultraviolet irradiation. The adducts thus prepared were reacted further using conventional organic synthesis techniques to produce the mono-functional fluorine-containing entities described in Tables I and II.

In a similar manner, 1,3-diiodohexafluoropropane was prepared from perfluoroglutaric acid. The yield of this diiodide was greatly improved over the 18% reported in the literature (*2*) by the use of a large excess of iodine during the Hunsdiecker reaction. This diiodide subsequently was added to allyl alcohol or allyl chloride. However, despite long periods of irradiation, monoadducts were obtained as the principal reaction products. Yields of diadducts were considerably improved by adding mercury to the irradiated solution. In this manner, the diadducts were obtained as the principal products and were reacted further to produce the difunctional fluorine-containing entities described in Tables I and II.

Many of the compounds listed in Table I have not previously been reported in the literature. In addition to reporting these new compounds, the work presently reported presents an overall reaction scheme capable of inserting methylene groups between a perfluorinated cluster and a functional group as demonstrated by the conversion of hexafluoroglutaric acid to symetrical hexafluoroazelaic acid, etc.

EXPERIMENTAL

Silver Heptafluorobutyrate. This compound was prepared by the method of Hauptschein and Grosse (*2*) from commercially available heptafluorobutyric acid in yields of 96–98%.

I. I was prepared by the method of Hauptschein and Grosse (*2*) in yields of 78–82%.

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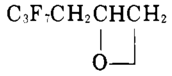
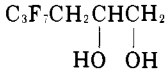
Table I. Description of Fluorinated Compounds

Key	Compound	Formula
I	Heptafluoropropy Iodide	C_3F_7I
II	2-Iodo-4,4,5,5,6,6,6-heptafluoro-1-hexanol	$C_3F_7CH_2CHICH_2OH$
III	4,4,5,5,6,6,6-Heptafluoro-1-hexanol	$C_3F_7(CH_2)_3OH$
IV	4,4,5,5,6,6,6-Heptafluorohexanoic Acid	$C_3F_7(CH_2)_2COOH$
V	1-Chloro-2-iodo-4,4,5,5,6,6,6-heptafluorohexane	$C_3F_7CH_2CHICH_2Cl$
VI	4,4,5,5,6,6,6-Heptafluoro-1-hexene	$C_3F_7CH_2CH=CH_2$
VII	4,4,5,5,6,6,6-Heptafluoro-1,2-epoxyhexane	 $C_3F_7CH_2\underset{\lfloor\text{O}\rfloor}{CHCH_2}$
VIII	4,4,5,5,6,6,6-Heptafluoro-1,2-hexanediol	 $C_3F_7CH_2\underset{HO}{CH}\underset{OH}{CH_2}$
IX	1,3-Diiodo-1,1,2,2,3,3-hexafluoropropane	$I(CF_2)_3I$
X	2,6-Diiodo-4,4,5,5,6,6-hexafluoro-1-hexanol	$I(CF_2)_3CH_2CHICH_2OH$
XI	2,8-Diiodo-4,4,5,5,6,6-hexafluoro-1,9-nonanediol	$CF_2(CF_2CH_2CHICH_2OH)_2$
XII	4,4,5,5,6,6-Hexafluoro-1,9-nonanediol	$CF_2(CF_2CH_2CH_2CH_2OH)_2$
XIII	4,4,5,5,6,6-Hexafluoroazelaic Acid	$CF_2(CF_2CH_2CH_2COOH)_2$
XIV	4,4,5,5,6,6-Hexafluoroazelayl Chloride	$CF_2(CF_2CH_2CH_2COCl)_2$
XV	Diethyl 4,4,5,5,6,6-Hexafluoroazelate	$CF_2(CF_2CH_2CH_2COOC_2H_5)_2$
XVI	1-Chloro-2,6-diiodo-4,4,5,5,6,6-hexafluorohexane	$ICF_2CF_2CF_2CH_2CHICH_2Cl$
XVII	1,9-Dichloro-2,8-diiodo-4,4,5,5,6,6-hexafluorononane	$CF_2(CF_2CH_2CHICH_2Cl)_2$
XVIII	4,4,5,5,6,6-Hexafluoro-1,8-nonadiene	$CF_2(CF_2CH_2CH=CH_2)_2$

II. I (148 grams, 0.5 mole) and allyl alcohol (58.grams, 1.0 mole) were placed in a 250 ml., 1-necked flask fitted with reflux condenser and irradiated for 120 hours with a 100 watt mercury arc lamp from a distance of approximately 2 cm. The excess allyl alcohol was removed by distillation at 100 mm. of Hg pressure. The residual material was distilled to give 143.5 grams (81%) of II.

III. Lithium aluminum hydride (41.7 grams, 1.10 moles) was added with 500 ml. anhydrous ethyl ether to a dry 2 liter, 3-necked flask fitted with stirrer, reflux condenser, and addition funnel containing II (160 grams, 0.45 mole) in 150 ml. ethyl ether. The ethereal solution of II was slowly added to the well-stirred $LiAlH_4$ suspension at such a rate that a gentle ethereal reflux occurred. The resultant solution was stirred and refluxed for an additional 3 hours. Sulfuric acid (180 grams in 500 ml. water) was placed in the addition funnel and carefully added drop-wise to the well-stirred ethereal solution. The resultant ether layer was separated from the aqueous layer and the aqueous layer extracted with ethyl ether. The ethereal extracts were combined, dried, and distilled to give 92.8 grams (90.5%) of III.

IV. III (22.8 grams, 0.1 mole), potassium dichromate (35.4 grams, 0.12 mole), 96% sulfuric acid (49 grams, 0.48 mole), and water (100 ml.) were placed in a 500 ml., 3-necked flask fitted with stirrer and reflux condenser. The resultant solution was stirred and refluxed for 6 hours, cooled, and extracted with ethyl ether. The ether extracts were combined and extracted with 10% aqueous sodium hydroxide. The aqueous extracts were combined, carefully acidified with 40% aqueous sulfuric acid, and extracted with ethyl ether. The ether extracts were combined, dried, and distilled to give 18.4 grams (76%) of IV.

V. I (88 grams, 0.3 mole) and allyl chloride (91.2 grams, 1.2 moles) were placed in a 250 ml. flask fitted with a reflux condenser. A 100 watt mercury arc lamp was placed approximately 1 cm. from the reaction mixture which was irradiated for 88 hours. The irradiation was stopped and the low-boiling materials were distilled from a steam bath. The residue was distilled in vacuo to give 48.7 grams (43.6% conversion, 91.8% yield) of V.

VI. From V. Zinc dust (40 grams, 0.61 mole) and diethylene glycol (80 ml.) were placed in a 300 ml., 3-necked flask fitted with stirrer, addition funnel, and total reflux distilling head. V (74.5 grams, 0.2 mole) was placed in the addition funnel. The diethylene glycol-zinc dust mixture was heated on a steam cone. V was added drop-wise to the heated, well-stirred zinc suspension at such a rate that the volatile olefin completely distilled from the reaction mixture. The collected liquid was redistilled to give 35.3 grams (84%) of VI.

VI. From III. Phosphorus pentoxide (11.4 grams, 0.08 mole) was placed in a 200 ml., 1-necked flask fitted with a total-reflux head. III (22.8 grams, 0.1 mole) was added to the phosphorus pentoxide in one portion. The resultant mixture was heated. A cloudy liquid distilled out of the reaction mixture at head temperatures of 80–90°. Distillation of this liquid gave 15.84 grams (75.5%) of VI.

VII. II (35.4 grams, 0.1 mole) was placed in a 200 ml., 3-necked flask fitted with stirrer and reflux condenser and cooled to 20°. An aqueous solution of sodium hydroxide (6.0 grams in 54 ml. of water) was added to II. The resultant two layer system was stirred vigorously for 1 hour at 20°. The resultant layers were separated and the upper (aqueous) layer extracted with ethyl ether. The ethereal extracts were combined and added to the original organic layer. The resultant solution was dried and distilled to give 17.44 grams (77.3%) of VII.

VIII. VII (11.5 grams, 0.051 mole) and 100 ml. of 1% sulfuric acid were placed in a 200 ml. flask fitted with a reflux condenser and refluxed for 6 hours. The resultant solution was cooled and extracted with ethyl ether. Distillation gave 9.2 grams (74.1%) of VIII.

Perfluoroqlutaric Acid was prepared by the method of Henne and Zimmerscheid (*3*) in yields of 88–90%.

Silver Perfluoroglutarate was prepared by the method of Hauptschein and Grosse (*2*) in yields of 95–97%.

IX. Silver perfluoroglutarate (353 grams, 0.78 mole) was ground to a fine powder, thoroughly mixed with finely powdered iodine (950 grams, 7.48 gram atoms), and placed in a 3 liter, 1-necked flask which was connected to a cold trap cooled with dry ice. The connecting tubing was at least 15 mm. in diameter to prevent clogging by the sublimed iodine. The cold trap was connected to a bubble counter so that the reaction could be followed by the evolution of carbon dioxide. The flask was heated with an open flame at such a rate that a smooth, steady evolution of carbon dioxide was maintained. When the evolution diminished, a vacuum system including an extra dry ice trap replaced the bubble counter and the entire system was slowly reduced to 1 mm. of Hg pressure while heat was applied to the flask. This removal procedure was repeated three times during the

Table II. Properties of Fluorinated Compounds

		B.P.[a]		M.P.,[a]			Analysis[a]							
							Calculated				Found			
Key	Yield, %	°C.	Mm. Hg	°C.	n^{20}_D	d^{20}_4		%H	MR$_D$	Other	%C	%H	MR$_D$	Other
I	78–82	40 41	750	...	1.3275[b]	...	...	...	...	...	...	...	...	...
II	81	50	0.7	...	1.4148	1.976[c]	20.34	1.69	44.53	...	20.51	1.96	44.82	...
III	91(44[d])	137	745	...	1.3348	1.492	31.58	3.07	31.67	...	31.35	2.89	31.58	...
IV	76	101–102	25	38.5[e]	...	...	...	...	...	242[f]	...	...	...	242[f]
V	92	64–65	7	...	1.4201	1.974	19.35	1.35	47.82	...	19.31	1.37	47.83	...
VI	84	57–58	752	...	1.2986	1.308	34.28	2.38	29.65	...	33.99	2.37	29.89	...
VII	77	109	754	...	1.3173	1.384[c,g]	31.86	2.11	29.76	...	32.00	2.20	29.82	...
VIII	74	84–86	3	...	1.3510	1.581[c]	29.51	2.89	33.22	...	29.38	2.64	33.31	...
IX	75	130–131	750	...	1.4520[b]	..	...	...	...	...	...	...	...	...
X	26	107–109	0.5	...	...	...	...	...	...	...	...	...	...	...
XI	(Not isolated)													
XII	45–62	129	0.5	...	1.4094	1.404	40.30	5.22	47.08	...	40.39	5.07	47.24	...
XIII	86	...	...	155	...	...	36.49	3.40	...	296[f]	36.34	3.45	...	296.5[f]
XIV	86	107–108	0.5	...	1.4146	1.557	32.45	2.42	53.66	21.29[h]	32.22	2.42	53.52	21.41[h]
XV	84	120	0.7	...	1.3943	1.275	44.32	5.15	66.04	...	44.72	4.79	66.13	...
XVI	19(16[d])	88–90	0.5											
XVII	52(45[d])													
XVIII	72	139	752	...	1.3670	1.205	46.54	4.34	43.04	...	46.80	4.54	43.26	...

[a] All temperatures are corrected. Analyses were made by C.S. Yeh and Mrs. I.D. Groten of the Department of Chemistry, Purdue University. Calculated molecular refractions were obtained by addition of the bond refractions of K.G. Denbigh (*1*). [b] Checks with reported constants (*2*). [c] After completion of this work, the preparation of this compound was described by J.D. Park and coworkers (*5*). [d] This figure represents conversion. [e] Checks with reported physical constants (*4*). [f] Neutralization equivalent. [g] See footnote *c*. No explanation can be offered for the discrepancy in measured density since all other physical constants agree well. [h] This figure represents % Cl.

4 hour reaction period. The portions of dark liquid in the cold traps were combined and distilled from copper powder (5 grams) to give 236 grams (75.2%) of IX.

X, XI and XII. IX (404 grams, 1.0 mole) and allyl alcohol (464 grams, 8.0 moles) were placed in a 1 liter, 3-necked flask fitted with stirrer and reflux condenser. A heating mantle was added and a 100 watt mercury arc lamp placed about 2 cm. from the reaction mixture which was stirred, irradiated, and refluxed for 110 hours. The excess allyl alcohol was removed by distillation at 100 mm. of Hg pressure. Further distillation gave 118.4 grams (25.7%) of X. The residue (principally XI) was dissolved in 400 ml. of anhydrous ethyl ether and added drop-wise to a well-stirred solution of lithium aluminum hydride (67.5 grams, 1.8 moles) in ethyl ether (800 ml.). After the addition was complete, the resultant solution was stirred and refluxed for 3 hours, cooled, and carefully hydrolyzed by the drop-wise addition of 1200 ml. of 40% sulfuric acid. The organic layer was separated and the aqueous layer extracted with ethyl ether. The ether extracts and organic layer were combined, dried, and distilled to give 121 grams (45%) of XII.

In another experiment, IX (162 grams, 0.4 mole), allyl alcohol (47.4 grams, 0.82 mole), and mercury (8 grams, 0.04 gram-atom) were placed in a 500 ml., 3-necked flask fitted with stirrer and reflux condenser. A 100 watt, mercury arc lamp was placed about 2 cm. from the reaction mixture which was stirred and irradiated for 22 hours. An additional portion of allyl alcohol (29 grams, 0.5 mole) was added and the stirring and irradiation continued for an additional 26 hours. No IX or X was obtained by distillation. The residual, crude XI was reduced by lithium aluminum hydride and distilled to give 66 grams (61.6%) of XII.

XIII. XII (67 grams, 0.25 mole) was placed in a 1 liter, 3-necked flask fitted with stirrer and reflux condenser. A solution of potassium dichromate (160 grams, 0.545 mole), 95% sulfuric acid (225 grams, 2.18 moles), and water (500 ml.) was added. The resultant solution was stirred and refluxed for 4 hours, cooled, and filtered. The precipitate was recrystallized from water to give 63.6 grams (86%) of XIII.

XIV. XIII (29.6 grams, 0.1 mole) and an excess (100 grams, 0.84 mole) of thionyl chloride were allowed to react at room temperature for 2 hours, and heated under reflux for an additional 2 hours. The excess thionyl chloride was removed by distillation at 100 mm. of Hg, and the residue was rectified to give 28.6 grams (86%) of XIV.

XV. XIV (16.7 grams, 0.05 mole) and absolute ethyl alcohol (30 ml.) were placed in a 100 ml. flask and refluxed for 2 hours. Distillation gave 14.8 grams (84%) of XV.

XVI and XVII. IX (130 grams, 0.32 mole), allyl chloride (49 grams, 0.64 mole), and mercury (5 grams, 0.25 gram-atom) were placed in a 500 ml., 3-necked flask fitted with stirrer and reflux condenser. A 100 watt mercury arc lamp was placed about 2 cm. from the reaction mixture which was stirred and irradiated for 24 hours. Allay chloride (49 grams, 0.64 mole) and mercury (5 grams, 0.25 mole) were added. The stirring and irradiation were continued for an additional 24 hours. The resultant solution was filtered and distilled from a steam bath to give recovery of the excess allyl chloride. Further distillation gave 18 grams (13.8% recovery) of IX, 25 grams (18.6% yield, 16.1% conversion) of XVI and 80 grams (52% yield, 44.5% conversion) of crude XVII (undistilled residue).

In another experiment, IX (150 grams, 0.372 mole) and allyl chloride (190 grams, 2.50 moles) were stirred and irradiated for 88 hours without the mercury catalyst. Distillation gave 100 grams (66.7% recovery) of IX, 46 grams (77.3% yield, 25.8% conversion) of the monoadduct (XVI) and 8 grams (11.6% yield, 3.9% conversion) of the crude, undistilled diadduct (XVII).

XVIII. Crude XVII (80 grams, 0.144 mole) and diethylene glycol (30 ml.) were placed in an addition funnel with a pressure-equalizing side arm. Zinc dust (44 grams, 0.695 mole) and diethylene glycol (100 ml.) were placed in a 300 ml., 3-necked flask fitted with stirrer, total reflux head, and the addition funnel mentioned above. The solution of XVII was added drop-wise to the well-stirred suspension of zinc dust in diethylene glycol and allowed to stir for 1 hour after the addition was complete. The resultant solution was stirred and heated at such a rate that the volatile products distilled smoothly at head temperatures of less than 150°. After most of the volatile materials had been removed, the temperature slowly was raised until diethylene glycol distilled over. The collected liquid was washed with water, separated, and distilled to give 24 grams (72%) of XVIII.

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