mole) of 4-*t*-butyl-2-(β-methoxy)ethyl-6-methylbenzyl chloride in 100 ml. of ether was allowed to drop upon 0.7 g. (0.03 g.-atom) of magnesium over a period of 2 hr. The 4-*t*-butyl-2-(β-methoxy)ethyl-6-methylphenylacetic acid, isolated in the usual way, melted at 81–83°, yield 1.0 g. (28%). Further recrystallization of this compound from low-boiling petroleum ether–methylcyclohexane raised the melting point to 83–84°.

Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69: H, 9.15. Found: C, 73.01; H, 9.36.

Treatment of 4-t-butyl-2,6-di(methoxymethyl)bromobenzene with magnesium. Various attempts to effect a reaction between 4-*t*-butyl-2,6-di(methoxymethyl)bromobenzene and magnesium were made. Such solvents as ether, benzene, toluene, and tetrahydrofuran as well as ether-benzene and ether-toluene solvent pairs were used. Catalysts employed were iodine, ethyl bromide, mercuric chloride, and aluminum chloride. In all cases only starting material was recovered.

4-t-Butyl-2,6-di(methoxymethyl)iodobenzene. To a flask containing a solution of 6.0 g. (0.02 mole) of 4-*t*-butyl-2,6-di(methoxymethyl)bromobenzene in 100 ml. of ether was added 60 ml. of 0.68*N* (0.04 mole) *n*-butyllithium. The orange-brown mixture was heated, with stirring, for 1 hr. and then cooled in an ice bath. The addition of a solution of 15.2 g. (0.060 mole) of iodine in 75 ml. of ether to the cold mixture was begun. The mixture was stirred for an additional hour in the cold and decomposed with crushed ice. The ether layer, after separation from the water layer, was washed successively with 50 ml. of a 5% sodium sulfite solution and water and dried over magnesium sulfate. After the ether had been removed the residue crystallized readily. The iodide, recrystallized from 95% ethanol, melted at 76–77°, yield 4.8 g. (69%).

Anal. Calcd. for $C_{14}H_{21}O_2I$: C, 48.28; H, 6.03. Found: C, 48.34; H, 5.98.

Treatment of 4-t-butyl-2,6-di(methoxymethyl)iodobenzene with magnesium. A mixture of 1.5 g. (0.0043 mole) of 4-*t*-butyl-2,6-di(methoxymethyl)iodobenzene and 0.94 g. (0.0086 mole) of ethyl bromide in 50 ml. of ether was added dropwise during 0.5 hr. to a flask containing 0.42 g. (0.017 g.-atom) of magnesium. After the addition, the mixture was stirred under reflux for 7 hr. and filtered through glass wool on solid carbon dioxide. The mixture failed to yield any acidic product.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Applicability of the Arndt-Eistert Reaction to Fluorinated Acids and Their Derivatives[1]

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Perfluorinated acids containing three or more carbon atoms failed to undergo the Arndt-Eistert reaction in a normal fashion. At least two methylene groups must be present in order to obtain satisfactory yields from this reaction. In all cases, it appears that the intermediate diazo ketone is formed and that it is the second stage of the reaction, the Wolff rearrangement, that fails to take place normally, resulting in the formation of α-halo ketones.

The following ketones, $C_2F_5COCH_2Cl$, $C_3F_7COCH_2Cl$, and $C_3F_7COCH_2Br$ were prepared and characterized, and the physical properties of a number of new compounds were determined and tabulated.

This investigation reports on the applicability of the Arndt-Eistert reaction[2] to perfluorinated acids and their homologs and to the preparation of ketones of the type R_FCOCH_2X (where X is any halogen and R_F is a perfluorinated group) from perfluorinated acids and diazomethane. Since perfluorinated acids are now commercially available, it seemed the easiest and most direct way of preparing the higher acids and ketones containing the perfluorinated group.

The acids, C_2F_5COOH, C_3F_7COOH, $C_3F_7CH_2COOH$, $C_3F_7CH_2CH_2COOH$, and C_4F_9COOH, were converted to their respective acid chlorides, and added to an excess of cold ethereal diazomethane to form the corresponding diazo ketone. In each case, the diazo ketone was isolated but not purified, before the attempted rearrangement. The presence of the $-COCHN_2$ group was shown by the evolution of nitrogen when the compound was treated with concentrated hydrochloric acid.

The diazo ketones derived from C_2F_5COOH, C_3F_7COOH and C_4F_9COOH failed to undergo the Wolff rearrangement and the diazo ketone from $C_3F_7CH_2COOH$ appeared to give only negligible amounts of $C_3F_7(CH_2)_2COOCH_3$. The diazo ketone derived from $C_3F_7(CH_2)_2COOH$ underwent the rearrangement in a normal fashion in good yield.

The acids, *n*-$C_3F_7CH_2COOH$ and $C_3F_7CH_2CH_2COOH$ were prepared from C_3F_7COOH through the following sequence of previously known reactions.

$$R_FCOOH \xrightarrow{AgOH} R_FCO_2Ag^{3} \xrightarrow{I_2} R_FI^{4} \xrightarrow{CH_2=CH_2}$$

$$R_FCH_2CH_2I^{5} \xrightarrow{Mg} R_FCH_2CH_2MgI \xrightarrow{O_2}$$

$$R_FCH_2CH_2OH^{6} \xrightarrow{[O]} R_FCH_2COOH^{6}$$

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(1) Presented before the Fluorine Subdivision of the Division of Industrial and Engineering Chemistry, 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 20, 1956. This paper represents part of the thesis submitted by E. R. Larsen to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the Ph.D. degree.

(2) W. E. Bachmann and W. S. Struve, *Org. Reactions*, **I**, 38–62 (1942).

(3) Minnesota Mining and Mfg. Co., pamphlet, *Preparation of Silver Heptafluorobutyrate.*

(4) R. N. Haszeldine, *J. Chem. Soc.*, 584 (1951).

(5) R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949).

(6) A. L. Henne, R. L. Pelley, and R. M. Alm, *J. Am. Chem. Soc.*, **72**, 3370 (1950).

Musgrave and Brown[8] have recently shown that CF_3CO_2H and CCl_3CO_2H undergo the Arndt-Eistert reaction normally and in good yield when the ester of the next higher homologous acid is formed, but give unsatisfactory yields of the acid, amide, or anilide. The reaction of CF_3CO_2H to give $CF_3CH_2CO_2C_2H_5$ has been verified by us.

It is concluded that perfluorinated acids, with the exception of CF_3COOH, fail to undergo the Arndt-Eistert reaction in a normal fashion, and that at least two insulating methylene groups must be present between the R_F and COOH groups in order to obtain satisfactory yields from this reaction. In all cases it appears that the intermediate diazo ketone is formed and that it is the second stage of the reaction, the Wolff rearrangement, that fails to take place normally.

The ketones, $C_2F_5COCH_2Cl$, $C_3F_7COCH_2Cl$ and $C_3F_7COCH_2Br$, were obtained by treating the respective acid halide with diazomethane. In the case of the α-chloroketone, the yield obtained by first forming the diazo ketone and treating this with anhydrous hydrogen chloride was essentially the same as that obtained by treating the acid chloride with diazomethane directly. The α-haloketones are strongly lachrymatory.

Attempts to prepare $C_3F_7COCH_2F$ and $C_3F_7COCH_2I$ failed. In the case of $C_3F_7COCH_2I$ various attempts were made, but the reaction was uncontrollable. Attempts to prepare $C_3F_7COCH_2F$ were confined to the treatment of C_3F_7COF with diazomethane. In general, it was found that the preparation of ketones of the type R_FCOCH_2X by this means is of little practical value, except in cases where only small amounts are desired by a rapid procedure.

EXPERIMENTAL

The acids, CF_3COOH, C_3F_7COOH and C_4F_9COOH were obtained from the Minnesota Mining and Mfg. Co., St. Paul, Minn. The acid chlorides were prepared by conventional methods using PCl_5 or $SOCl_2$ and purified before use by distillation. The diazomethane[9] was prepared from *N*-nitrosomethylurea as described by Bachmann *et al.*[2]

3,3,4,4,5,5,5-Heptafluoro-1-pentanol. Method I. A dry 2-l. three-neck flask was equipped with a Herschberg stirrer, reflux condenser, dropping funnel, and a gas inlet tube for passing dry nitrogen through the system. The condenser outlet was connected to a calcium chloride drying tube and a bubbler. The nitrogen was dried by passing it through a train consisting of a concentrated sulfuric acid scrubber and a drying tube filled with potassium hydroxide pellets.

Twelve grams (0.5 mole) of reagent grade magnesium was introduced into the flask and the apparatus was flamed. A nitrogen atmosphere was maintained by passing a slow stream of dry nitrogen through the apparatus during the reaction.

Ten ml. of ethereal methyl iodide (2 g.) was added to start the reaction, and then 126 g. (0.39 mole) of n-$C_3F_7CH_2CH_2I$, dissolved in 1 l. of sodium-dried ether, was added at a rate sufficient to maintain reflux. When the addition was complete the mixture was refluxed on a steam bath for 0.5 hr.

The mixture was cooled to −78° in a Dry Ice–acetone bath and dry oxygen was passed into the reaction flask along with the nitrogen for about 10 hr., during which time a gray salt precipitated. The mixture was allowed to warm and 200 ml. of water was added dropwise, followed by the addition of 40 ml. of concentrated hydrochloric acid.

The ether layer was removed and the aqueous layer extracted with three 50-ml. portions of ether. The combined ether layers were dried over anhydrous magnesium sulfate, the ether stripped off and the residue distilled. The fraction boiling at 116–117°/630 mm., was collected. The yield of heptafluoropentanol was 64 g. (77%).

Method II. About 0.055 mole (14 g.) of $C_3F_7CH_2CH_2OCOCH_3$ was mixed with 10 ml. of β,β-dihydroxyethyl ether and 0.07 mole (4 g.) of potassium hydroxide in a stoppered 25-ml. flask. The mixture was allowed to stand, with occasional shaking, at room temperature for 48 hr. The alcohol was distilled directly from the reaction mixture through a 10-theoretical plate, platinum spiral Todd column, and the fraction (10.5 g., 91%) boiling at 116–117°/632 mm. was collected; n_{D}^{20} 1.3151; d_4^{20} 1.506.

Anal. Calcd. for $C_5H_5F_7O$: C, 28.05; H, 2.35; F, 62.12. Found: C, 28.32; H, 2.6; F, 61.9.

3,3,4,4,5,5,5-Heptafluoro-1-pentyl acetate. Fifty grams (0.17 mole) of $C_3F_7CH_2CH_2I$, 50 g. (0.3 mole) of silver acetate and 100 ml. of glacial acetic acid were placed in a 300-ml. flask fitted with a reflux condenser and a calcium chloride drying tube. The mixture was refluxed for 48 hr. with occasional shaking. The solid became yellow, almost immediately, due to the formation of silver iodide.

The reaction mixture was cooled and slowly poured into 300 g. of cracked ice. The solution was filtered and the precipitate washed with 50 ml. of ether. The filtrate was extracted three times with 50-ml. portions of ether and the combined ether layers washed with a saturated solution of sodium bicarbonate to remove any dissolved acid and dried over anhydrous sodium sulfate.

The ether was stripped off and the residue was rectified on a 10-theoretical plate, platinum spiral Todd column. The fraction boiling at 132.5–133.0°/630 mm. was collected. The yield of ester was 24.0 g. (55%); n_{D}^{20} 1.3283, d_4^{20} 1.4135.

Anal. Calcd. for $C_7H_7F_7O_2$: C, 32.82; H, 2.76; F, 51.93. Found: C, 32.7; H, 2.9; F, 51.71.

3,3,4,4,5,5,5-Heptafluoropentanoic acid. Twenty-one grams (0.1 mole) of n-$C_3F_7CH_2CH_2OH$ was dissolved in 140 ml. of technical grade acetone in a 250-ml. three-neck flask fitted with a mechanical stirrer, dropping funnel, condenser, and thermometer. The mixture was cooled to 0° in an ice-salt bath maintained at −5° and 14 g. (0.14 mole) of powdered chromium trioxide was added portionwise. The addition took about 0.5 hr., during which time the temperature of the mixture was not allowed to exceed 15°. The mixture was again cooled to 0° and 15 ml. (0.35 mole) of concentrated sulfuric acid was added dropwise. The addition took about 1 hr., during which the temperature was not allowed to exceed 15°. The mixture was kept at 15° for 1 hr. after the addition was completed. The ice-salt bath was removed and the temperature allowed to rise. The temperature spontaneously reached 35° and then fell to room temperature. The reaction mixture was filtered through Filter-Cel, dried over Drierite, and the acetone was stripped off. The residue was distilled in a modified Claisen distilling flask and the fraction boiling between 50–70° at 6 mm. was collected and redistilled through a 10-theoretical plate, platinum spiral Todd column. The fraction boiling at 62–63°/6 mm. was collected. The yield was 13 g. (57%); b.p. 170–172°/630 mm.; m.p. 10°, n_{D}^{20} 1.3202; d_4^{20} 1.604.

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[7] E. T. McBee and A. Truchan, *J. Am. Chem. Soc.*, **70**, 2910 (1948).

[8] F. Brown and W. K. R. Musgrave, *J. Chem. Soc.*, 2087 (1953).

[9] F. Arndt, *Org. Syntheses*, **15**, 48 (1935).

Anal. Calcd. for $C_5H_3F_7O_2$: C, 26.34; H, 1.33; F, 58.31. Found: C, 26.5; H, 1.51; F, 58.6.

The method described by Henne *et al.*[6] for the oxidation of $CF_3CH_2CH_2OH$ resulted in only 4% yield of $C_3F_7CH_2$-COOH when applied to the alcohol $C_3F_7CH_2CH_2OH$.

Oxidation of $C_3F_7CH_2CH_2OH$ with CrO_3 in glacial acetic acid resulted in about a 10% yield of the corresponding acid. The procedure described by Powell[10] for the oxidation of CH_2Cl—CH_2CH_2OH with concentrated HNO_3, when applied to this study resulted in total destruction of the alcohol.

4,4,5,5,6,6,6-Heptafluorohexanoic acid. Four grams (0.17 mole) of dry magnesium turnings were placed in a dry 500-ml. flask fitted with a reflux condenser and dropping funnel. The whole apparatus was then heated with an open flame. The reaction was started by adding 10 g. of $C_3F_7CH_2CH_2I$ and 10 ml. of sodium-dried ether, and warming on a water bath. The reaction started immediately. An additional 40 g. (to make 0.154 mole) of $C_3F_7CH_2CH_2I$ in 200 ml. of ether was added at a rate sufficient to maintain reflux. The mixture was refluxed for an additional hour after the addition was completed to insure completeness of reaction. The reaction mixture was poured slowly onto approximately 100 g. of finely crushed Dry Ice in a 1500-ml. beaker. When the excess Dry Ice had evaporated the mixture was poured into 250 g. of cracked ice in a 500-ml. beaker and 30 ml. of concentrated hydrochloric acid was added. The mixture was poured into a separatory funnel and the beaker was rinsed with 50 ml. of benzene. The water layer was removed and extracted with two 50-ml. portions of benzene. The benzene and ether layers were combined and dried for 1 hr. over anhydrous sodium sulfate. The ether and benzene solvents were distilled through an 8-inch Vigreux column. The residue was placed in a sublimation apparatus and the remaining benzene removed under vacuum. The residue was sublimed at 4 mm. pressure to yield 20 g. of acid (55%); m.p. 36–37° (literature[11] m.p. 37°).

Preparation of 3,3,4,4,5,5,5-heptafluoropentanoyl chloride and the amide. Twenty-six grams (0.114 mole) of n-$C_3F_7CH_2$-CO_2H was placed in a 35-ml. flask fitted with a reflux condenser. The top of the condenser was attached to a calcium chloride drying tube and a dilute sodium hydroxide scrubber. Fifteen ml. (0.21 mole) of thionyl chloride was added and the mixture refluxed for 15 hr.

The reflux condenser was replaced by a 4-in. metal spiral distilling column and the excess thionyl chloride was stripped off. The acid chloride was distilled under reduced pressure and the fraction (12 g., 41.5%) boiling at 52–53°/140 mm., 94–95°/630 mm. was collected. (Approximately 10 g. of the acid was recovered, some decomposition took place during distillation.)

About 1 g. of the acid chloride was treated with dilute aqueous ammonia to yield the amide. The recrystallized and sublimed amide melted at 92.5–93.0°.

Anal. Calcd. for $C_5H_4F_7ON$: C, 26.44; H, 1.77; N, 6.17. Found: C, 26.80; H, 1.72; N, 6.18.

Preparation of 4,4,5,5,6,6,6-heptafluorohexanoyl chloride and amide. Eighteen grams (0.074 mole) of n-$C_3H_7(CH_2)_2$-CO_2H was treated under conditions similar to those used to prepare n-$C_3F_7CH_2COCl$. In this case, however, the mixture was refluxed for only 2 hr. The yield of acid chloride, b.p. 125–126°/627 mm., was 14 g. (73%).

About 1 g. of the acid chloride was treated with dilute aqueous ammonia. The precipitated amide, n-$C_3H_7(CH_2)_2$-$CONH_2$, was recrystallized from water and sublimed, m.p. 96.5–97.0°.

5,5,6,6,7,7,7-Heptafluoroheptanamide. Eighteen grams (0.074 mole) of $C_3F_7(CH_2)_2CO_2H$ was placed in a 50-ml. flask fitted with a condenser, an absorbent cotton drying tube, and an aqueous sodium hydroxide scrubber. Thirteen grams (0.11 mole) of redistilled thionyl chloride (b.p. 73–74°/628 mm.) was added and the mixture refluxed for 2 hr. The mixture was distilled in a modified Claisen distilling flask and the acyl chloride, b.p. 125–127°/627 mm. was collected.

The acyl chloride (14 g.) was dissolved in 100 ml. of sodium-dried ether and was added dropwise to a vigorously stirred solution of 0.3 mole of diazomethane in 500 ml. of ether. The mixture was kept below −10° for 2 hr. after the addition was complete. The mixture was allowed to warm to room temperature and the ether was removed under vacuum. The crude diazoketone was dissolved in 100 ml. of dioxane and placed into a 500-ml. three-neck flask. The flask was fitted with a dropping funnel, stirrer, and condenser. The outlet of the condenser was connected to an air-cooled trap, a water scrubber, a dilute sulfuric acid scrubber, and a bubbler. Approximately 150 ml. of aqueous ammonia (sp. gr. 0.90) was added to the mixture and heated to 60–70° on a water bath. To the mixture 30 ml. of 10% aqueous silver nitrate was added dropwise. The mixture was then heated to reflux for 2 hr., cooled, and the amide precipitated by the addition of 250 ml. of cold water. The precipitated amide was filtered, taken up in alcohol, and refiltered to remove the silver oxide. The alcohol was evaporated and the crude amide was sublimed from the tarry residue. The yield of the amide was 6.2 g. (33%); m.p. 101.5–102°.

Anal. Calcd. for $C_7H_8F_7NO$: C, 32.9; H, 3.16; N, 5.5. Found: C, 33.1; H, 3.04; N, 5.5.

Attempted preparation of 3,3,4,4,4-pentafluorobutyric acid. About 20 g. of C_2F_5COCl (1.16 moles) in 75 ml. of anhydrous Et_2O was slowly added with stirring to a solution of approximately 0.3 mole diazomethane in 0.5 l. of ether cooled to 0° to −10°. After completion of the addition, the solution was kept cold and stirred for an hour and finally allowed to warm up to room temperature with stirring over a period of 6 to 7 hr. The excess ether was then removed under reduced pressure with a water aspirator at room temperature. A bright yellow, oily liquid was obtained which evolved nitrogen vigorously when treated with concentrated HCl, indicating the presence of the —CHN_2 group. This diazo ketone was dissolved in 100 ml. of dioxane and added dropwise to a solution of 2 g. of silver oxide, 3 g. of sodium thiosulfate and 5 g. of sodium carbonate in 200 ml. of H_2O at 50–60°. The mixture was stirred for an hour after completion of the addition and finally heated to reflux for an hour.

The solution was then cooled, acidified with dilute nitric acid, and extracted with ether. The dried ether solution upon distillation did not yield any of the expected product.

The attempted Wolff rearrangement carried out with the diazo ketone dissolved in alcohol or in the presence of dioxane and aqueous ammonia did not yield the expected amide or ester.

Attempted preparation of $C_4F_9CH_2COOEt$. C_4F_9COCl was treated with CH_2N_2 in a manner similar to that described for the attempted preparation of $C_2F_5CH_2COOH$. Although the corresponding diazoketone was formed, the normal Wolff rearrangement to $C_4F_9CH_2$ COOEt did not take place.

Preparation of heptafluoropropyl chloromethyl ketone. Method I. Twenty-three grams (0.1 mole) of perfluorobutyryl chloride was dissolved in 150 ml. of sodium-dried ether in a 1-l., three-neck flask fitted with a dropping funnel, stirrer, and calcium chloride drying tube. The mixture was cooled in an ice-salt bath to −15°, and ethereal diazomethane was added dropwise to the vigorously stirred solution. The addition was stopped when the solution became pale yellow showing the presence of excess diazomethane. The mixture was kept cold for an additional 2 hr. and then allowed to warm to room temperature. The ether was stripped off and the residue rectified on a micro Podbielniak glass concentric-tube column. The yield of α-chloroketone, b.p. 97–98° at 625 mm. was 7.0 g. (28.5%), n_D^{20} 1.3240 and d_4^{20} 1.580.

Anal. Calcd. for $C_5H_2ClF_7O$: C, 24.3; F, 54.0. Found: C, 24.6; F, 53.9.

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(10) S. G. Powell, *J. Am. Chem. Soc.*, **46**, 2879 (1924).

(11) Private communication from the Minnesota Mining & Mfg. Co., St. Paul, Minn.

TABLE I

SUMMARY OF PROPERTIES OF NEW COMPOUNDS

	B.P.					Molar Refraction		AR_F
Compound	°C.	Mm. Hg	M.P., °C.	n_D^{20}	d_4^{20}	Calcd.[a]	Found	Calcd.
n-$C_3F_7CH_2CH_2I$	112–113	628	−5	1.3771	1.918	38.10	38.89	1.21
	77.8	185						
	44.3	47						
n-$C_3F_7CH_2CH_2OCOCH_3$	132	633		1.3283	1.4135	35.49	36.8	1.24
n-$C_3F_7CH_2CH_2OH$	116–117	632		1.3151	1.506	26.83	27.81	1.24
	62–63	111						
n-$C_3F_7CH_2COOH$	170–172[b]	630	10	1.3202	1.604	26.84	28.21	1.31
	62.3	6						
n-$C_3F_7CH_2CONH_2$			92.5–93					
n-$C_3F_7(CH_2)_2CONH_2$			96.5–97					
n-$C_3F_7(CH_2)_3CONH_2$			102.5–103					
n-$C_3F_7COCH_2Cl$	97–98	625		1.3240	1.580	30.18	31.8	1.21
	61	178						
n-$C_3F_7COCH_2Br$	118	631		1.3436	1.818	33.08	33.88	1.22
	80.2	213						
$C_2F_5COCH_2Cl$	74	634		1.3088	1.348	26.55	27.8	1.34

[a] Calculated from the Lorenz-Lorentz formula with 1.1 as AR_f for fluorine. [b] With dec.

Method II. Twenty-three grams (0.1 mole) of C_3F_7COCl dissolved in 150 ml. of sodium-dried ether was added dropwise to 500 ml. of ethereal diazomethane (prepared from 35 g. of N-methylnitrosourea) contained in a 1-l. three-neck flask fitted with a dropping funnel and stirrer. The third neck was protected with a calcium chloride drying tube. The reaction mixture was kept cold (0° to −10°) during the addition of the acid chloride.

When the addition was completed the mixture was allowed to warm to room temperature and allowed to stand for 8 hr. The dropping funnel was replaced by a gas inlet tube, and a bubbler was attached to the drying tube outlet. Anhydrous hydrogen chloride, passed successively through a safety trap, a concentrated sulfuric acid scrubber, and a second safety trap, was passed slowly into the solution. When the evolution of nitrogen ceased, the flow of hydrogen chloride was discontinued. The solution was then worked up as described in Method I. The yield of $C_3F_7COCH_2Cl$ (b.p. 98.5–99.5°/632 mm.) was 7 g. (28.5%).

Preparation of heptafluoropropyl bromomethyl ketone. This reaction was carried out under conditions similar to that described for $C_3F_7COCH_2Cl$ (Method I). Twenty-eight grams (0.1 mole) of C_3F_7COBr was used. The fraction boiling at 80–81° at 213 mm. was collected. The yield of α-bromoketone was 6 g. (20%), n_D^{20} 1.3436; d_4^{20} 1.818.

Anal. Calcd. for $C_5H_2BrF_7O$: C, 20.64; H, 0.69; Br, 27.46. Found: C, 20.69; H, 0.80; Br, 27.80.

Pentafluoroethyl chloromethyl ketone was prepared in a manner similar to that used for the preparation of C_3F_7CO-CH_2Cl.

Acknowledgment. We wish to express our appreciation to the Office of Naval Research and to the Minnesota Mining and Manufacturing Co., St. Paul, Minn., for partial support of this work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Action of Aluminum Chloride on Hexafluoropropene

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Aluminum chloride has been found to react with hexafluoropropene to yield $CF_3CF{=}CFCl$, $CF_3CF{=}CCl_2$, $CF_2ClCF{=}CCl_2$, $CFCl_2CF{=}CCl_2$, $CCl_3CF{=}CCl_2$ and $CCl_3CCl{=}CCl_2$. A mechanism for the reactions involving replacement as well as rearrangement is postulated.

The reaction of aluminum chloride with chlorofluoroalkanes to replace fluorine by chlorine has been reported by Henne[2,3] and Miller and his co-workers.[4–6] In the present work, the action of aluminum chloride on hexafluoropropene was studied to ascertain the order of replacement of the organically bound fluorine atoms by chlorine and the de-

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(1) From the Ph.D. dissertation submitted to the University of Colorado, May 1953. E. I. du Pont de Nemours & Co., Inc., Pre-doctoral fellow: 1952–1953.

(2) A. L. Henne and H. M. Leicester, *J. Am. Chem. Soc.*, **60**, 864 (1938).

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(6) W. A. Miller, Jr., U. S. Patent Application **47,553**. *Chem. Abstr.*, **47**, 4895 (1953).