2. Reaction of Phenyl Selenobenzoate[9] at 80° with Raney Nickel.—To a suspension of 35 g. of degassed Raney nickel in benzene was added 1.20 g. of phenyl selenobenzoate. The mixture, protected from light, was refluxed for 15 hr. with continuous stirring. The nickel was extracted several times with hot benzene, the combined benzene solutions evaporated, and the residue distilled *in vacuo*. There was obtained 0.57 g. (yield 54%) of a yellowish liquid, b.p. 135–140° (3 mm.). The liquid was dissolved in ether, cooled and some drops of bromine added. The mixture was left in the ice-box overnight, the reaction product filtered off and recrystallized from carbon disulfide. The red needles obtained decomposed at 145°.

3. Reaction of Diphenyl Selenide at 180° with Raney Nickel.—A suspension of 60 g. of Raney nickel in benzene was dried *in vacuo* and then in a nitrogen atmosphere, 6.16 g. of diphenyl selenide was added and a current of nitrogen was then passed over the mixture which was heated at 180° for 8 hr. Then it was extracted thoroughly with benzene; the combined benzene solutions were distilled over a Widmer column and the solid residue fractionated. It boiled at 243–246° and the distillate solidified and melted after recrystallization from alcohol at 69.5–70.5°. This m.p. was not changed by admixture of authentic biphenyl; yield 3.13 g. (77%).

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[9] Prepared by reduction of diphenyl diselenide with glucose (H. Lecher and K. Simon, *ibid.*, **55**, 2423 (1922), and esterification of the resulting selenophenol with benzoyl chloride (H. Rheinboldt and E. Giesbrecht, Bol.n° 129, *Univ. São Paulo, Faculdade Filosofia, Ciências e Letras, Quimica*, n° **3**, 156 (1951); *C. A.*, **46**, 7555e (1952); white needles, m.p. 37.5–38.5°, yield 13% (from the diselenide).

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The Reaction of Ethyl Perfluorobutyrate with Sodium. An Improved Synthesis of Perfluoroheptan-4-one

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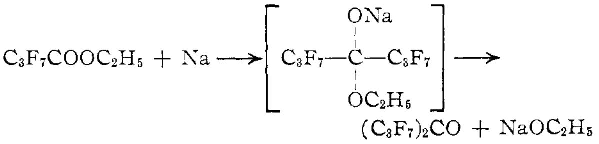
The only reported attempts to prepare perfluorinated acyloins were unsuccessful. Ethyl trifluoroacetate reacted with an ethereal solution of metallic sodium to give ethyl γ,γ,γ-trifluoroacetoacetate and polymeric material.[2,3] Since ethyl butyrate is known to undergo the acyloin reaction with much greater facility than ethyl acetate, it was thought that perhaps esters containing the larger perfluoropropyl group might give an acyloin reaction.

Accordingly, a study was made on the reactions of ethyl and methyl perfluoro-*n*-butyrate with sodium. It was quite a surprise to find, however, that this reaction represented the most convenient method yet reported for the synthesis of perfluoroheptan-4-one. The perfluoro ketone was isolated in up to 60% conversion. The known methods for preparing perfluoroheptan-4-one involve the reaction of C_3F_7MgI with C_3F_7COCl or $C_3F_7COOC_2H_5$[4,5] and the reaction of C_3F_7Li with $C_3F_7COOC_2H_5$.[6] The highest yield reported was 31%.[5] The distinct advantage of the present method is that, in addition to improved yields, it does not involve the critically precise conditions necessary for the preparation of perfluoropropylmagnesium iodide. The synthesis of perfluoroheptan-4-one now can be carried out with commercially available reactants.

The precise stoichiometry of the reaction of the esters of perfluorobutyric acid with sodium could not be ascertained. The perfluoro ketone is not formed until after the reaction mixture is acidified. The initial product is undoubtedly a sodium salt.



$$C_3F_7COOC_2H_5 + Na \longrightarrow \left[C_3F_7-\overset{\displaystyle ONa}{\underset{\displaystyle OC_2H_5}{C}}-C_3F_7 \right] \longrightarrow (C_3F_7)_2CO + NaOC_2H_5$$

Some side reaction or decomposition with loss of fluoride ion was observed in all runs. It was noted also in most of the experiments conducted that a small fraction boiling slightly above 100° gave a bright-red coloration (in the organic layer) with ferric chloride solution, which may indicate the presence of traces of a perfluorinated ene-diol. The highest yields of ketone were obtained when the reaction was carried out at room temperature. At higher temperatures two unidentified higher boiling fractions were produced.

Two unsuccessful attempts were made to prepare the perfluorinated acyloin by slightly modified routes. From the reaction of the acid chloride and sodium[7] in ether, the perfluorobutyric acid etherate, $2C_3F_7COOH{\cdot}(C_2H_5)_2O$,[8] was the product isolated. The reaction of ethyl perfluorobutyrate with sodium in liquid ammonia at −50° did not give any acyloin despite the fact that this method was quite successful for the preparation of aliphatic acyloins.[9] The sole product isolated was perfluorobutyramide.

Little is known about the chemistry of perfluoroheptan-4-one. The tendency of fluorinated ketones to form hydrates has been noted before,[5,10,11] but the pure hydrates have not been obtained. Fukuhara and Bigelow[10] observed that hexafluoroacetone was soluble in water but was completely volatile at low pressures. The slightly water-soluble crystalline hydrate of perfluoroheptan-4-one, m.p. 35–35.5°, which is only slightly volatile *in vacuo*, now has been isolated, and the dihydroxy structure, *i.e.*, perfluoroheptane-4,4-diol, was characterized by elemental analysis and infrared spectral examination.

Perfluoroheptane-4,4-diol was found to form a 1:1 adduct with several tertiary aliphatic amines. The triethylamine adduct, m.p. 88°, was very stable and could be sublimed at 100° at atmospheric pressure. A solid adduct also was obtained

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[1b] Based on a portion of the thesis presented by R. A. Braun to Temple University in partial fulfillment of the requirement for the Masters degree.

[2] E. T. McBee, O. R. Pierce, *et al.*, THIS JOURNAL, **75**, 4090 (1953).

[3] R. N. Haszeldine, *Nature*, **168**, 1028 (1951).

[4] A. L. Henne and W. C. Francis, THIS JOURNAL, **75**, 992 (1953).

[5] R. N. Haszeldine, *J. Chem. Soc.*, 1748 (1953).

[6] O. R. Pierce, E. T. McBee and G. F. Judd, THIS JOURNAL, **76**, 474 (1954).

[7] Egorova, *J. Russ. Phys. Chem. Soc.*, **60**, 1199 (1928).

[8] M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 5139 (1951).

[9] M. S. Kharasch, *J. Org. Chem.*, **5**, 362 (1940).

[10] N. Fukuhara and L. A. Bigelow, THIS JOURNAL, **63**, 788 (1941).

[11] A. L. Henne, *ibid.*, **72**, 3577 (1950).

with 2-ethylhexyldimethylamine, m.p. 57–57.5°. Other tertiary amines such as benzyldimethylamine, dimethylaniline and pyridine reacted vigorously, but no attempt was made to isolate the liquid reaction products.

We have found also that a similar type adduct, m.p. 48–49°, was formed from the reaction of hexachloroacetone hydrate with triethylamine at Dry Ice–acetone temperature. This adduct was much less stable than the perfluoroheptane-4,4-diol·triethylamine compound. It decomposed after standing for only one hour at room temperature, but could be stored at 0° without change.

With certain primary and secondary amines, *i.e.*, ethanolamine, diisobutylamine and dicyclohexylamine, cleavage of the perfluoro ketone or ketone hydrate occurred with formation of the corresponding amides of perfluorobutyric acid and C_3F_7H. The less basic aromatic amines such as aniline and *p*-chloroaniline failed to react with the ketone. Anhydrous ammonia formed a crystalline adduct thought to be perfluoroheptan-4-amino-4-ol which, however, decomposed on standing at room temperature to the amide and C_3F_7H.

A related reaction was carried out involving the synthesis of $C_3F_7COCH_2COOC_2H_5$ by the condensation of ethyl perfluorobutyrate and ethyl acetate in the presence of sodium ethoxide.

Experimental[12]

Perfluoroheptan-4-one.—In an atmosphere of dry nitrogen, 109.0 g. (0.45 mole) of ethyl perfluorobutyrate (Columbia Organic Chemicals) was added over a period of two hours with stirring to sodium shot (10.36 g., 0.45 mole) in 150 ml. of anhydrous ether. Reaction was indicated by the immediate change in color to yellow (later dark red). After stirring overnight at room temperature there was no unreacted sodium. The reaction mixture was acidified with 3 *N* sulfuric acid, the ether layer separated and the aqueous layer exhaustively extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate. The ether was removed by distillation and the residue was fractionated in a Podbielniak column. Perfluoroheptan-4-one (49 g., 60%) boiled at 73–76° (lit. 75°[4-6]). A central cut, b.p. 75°, was warmed with P_2O_5; mol. wt., calcd. for $C_7F_{14}O$: 366; found (gas density balance) 364. The infrared spectrum[13] was identical to that reported by Henne[4] for $C_3F_7COC_3F_7$.

The temperature of this reaction is critical, since at higher temperatures (*ca.* 60° bath temp.) the yield of ketone was considerably lower and two other products were formed in significant amounts. In a 0.3-mole run, 13 g. of product I (b.p. 83°, $n^{26}\mathrm{D}$ 1.3030; C, 30.93; H, 2.00) was obtained along with 7.5 g. of product II, b.p. 147°, $n^{28}\mathrm{D}$ 1.3252; C, 31.76; H, 2.96. Compound I contained perfluoroheptan-4-one and II, which reduced cupric acetate, was not characterized further.

The use of sodium dispersion in toluene is not recommended since the perfluoro ketone forms a homogeneous azeotrope containing approximately 20% by weight of toluene, b.p. *ca.* 80°, $n^{23}\mathrm{D}$ 1.3540.

The reaction of sodium with methyl perfluorobutyrate gave $C_3F_7COC_3F_7$ in about 50% yield.

Perfluoroheptan-4,4-diol.—To a 1-g. sample of pure perfluoroheptan-4-one (b.p. 75°) a slight deficiency of water was added. The product was evacuated at 0.1 mm. A white crystalline solid, m.p. 35–35.5°,[14] $n^{20}\mathrm{D}$ 1.293 (for super-cooled sample), remained. The solid is $C_3F_7C(OH)_2C_3F_7$.

Anal. Calcd. for $C_7H_2F_{14}O_2$: C, 21.88; H, 0.52. Found: C, 21.70; H, 0.57.

The dihydroxy structure for the ketone hydrate was further confirmed by examination of its infrared spectrum. It has a broad band around 3.0 μ which is attributed to the associated hydroxyl group. The carbonyl band at 5.6 μ was only very slight, while in the ketone spectrum there is an intense carbonyl band at 5.6 μ.[15]

Reaction of Perfluoroheptan-4-one with Primary and Secondary Amines.—N-(2-Hydroxyethyl)-perfluorobutyramide, m.p. 56.5–57.5°; N,N-diisobutylperfluorobutyramide, m.p. 155°; and N,N-dicyclohexylperfluorobutyramide, m.p. 179.5–180° (all recryst. from benzene) were obtained in nearly quantitative yield by the reaction at room temperature of $C_3F_7COC_3F_7$ with excess ethanolamine, diisobutylamine and dicyclohexylamine, respectively. These amines also were prepared from $C_3F_7COOC_2H_5$.

Perfluoroheptane-4,4-diol–Triethylamine Adduct.—Perfluoroheptane-4,4-diol (2.34 g., 0.006 mole) was treated with an excess of anhydrous triethylamine (1.13 g., 0.01 mole). At room temperature there was a vigorous exothermic reaction and a white crystalline product formed immediately. The product may be purified by recrystallization from benzene or by sublimation at 100°. The yield of $C_3F_7C(OH)_2C_3F_7 \cdot N(C_2H_5)_3$ was 2.8 g. (95%), m.p. 87.5–88.5°.

Anal. Calcd. for $C_{13}H_{17}F_{14}NO_2$: C, 32.16; H, 3.50. Found: C, 32.06; H, 3.70.

The infrared spectrum showed a hydroxyl band at 2.85 μ. The carbonyl band at 5.6 μ is absent. It is of interest to note that there was no reaction between dry perfluoroheptan-4-one and dry triethylamine at room temperature. However when a drop of water was added there was a vigorous reaction resulting in the formation of the previously described adduct. The ketone hydrate was regenerated by treatment with sulfuric acid.

Ethyl *n*-Heptafluorobutyroacetate (By Charles S. Stokes).—$C_3F_7COCH_2COOC_2H_5$, b.p. *ca.* 150°, $n^{24}\mathrm{D}$ 1.355, was prepared by the method identical to that used by Henne[16] for the preparation of $CF_3COCH_2COOC_2H_5$.

Copper(II) Chelate of Ethyl *n*-Heptafluorobutyroacetate.—The chelate was prepared by treating a sample of $C_3F_7COCH_2COOC_2H_5$ with an aqueous solution of copper(II) acetate. After shaking at room temperature a crystalline solid was obtained. The product was recrystallized from ethanol to give bright blue-green crystals, m.p. 105–105.5° in nearly quantitative yield.

Anal. Calcd. for $C_{16}H_{12}F_{14}O_6Cu$: Cu, 10.1. Found: Cu (electrolytic), 10.3.

Acknowledgment.—The financial support of the Research Corporation is gratefully acknowledged.

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[12] Microanalyses by Clark Microanalytical Laboratory.

[13] Determined with a Baird Associates Infrared Recording Spectrophotometer of Samuel P. Sadtler and Sons, Inc., Phila., Pa.

[14] It "boiled" near 75° which indicates that the reaction of the ketone with water is probably an equilibrium reaction, and that at higher temperatures the equilibrium is shifted in the direction of the individual components.

[15] It is predicted that this small carbonyl band would disappear entirely at temperatures considerably below 30°, at which temperature the present spectrum was taken. At lower temperatures the equilibrium would be displaced entirely toward the hydrate.

[16] A. L. Henne, *et al.*, This Journal, **69**, 1819 (1947).

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The Treatment of Arachin with Terephthalyl Dichloride

By W. E. F. Naismith

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Mann[1] showed that the intrinsic viscosity of peanut protein (measured in 10 *M* urea solution) was increased by treatment of the protein with terephthalyl dichloride. It was suggested that the increase was the result of cross-linking of protein molecules.

Following Mann's method for the preparation of the modified protein (using the arachin fraction of peanut protein instead of the whole protein) an examination of the modified arachin has been made in the ultracentrifuge and by viscosity determina-

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[1] G. E. Mann, This Journal, **75**, 3526 (1953).