of its 3,4-dihydro derivative[3] prompted us to synthesize the corresponding 6-fluoro compounds. Treatment of *m*-fluoroaniline with chlorosulfonic acid in the presence of sodium chloride gave the amorphous 1,3-bissulfonylchloride which on treatment with ammonia yielded crystalline 6-amino-4-fluorobenzene-1,3-disulfonamide (I). Cyclization with boiling formic acid[2] produced 6-fluoro-7-sulfamyl-1,2,4-benzothiadiazine-1,1-dioxide (II) reduced[3] by sodium borohydride to 6-fluoro-7-sulfamyl-3,4-dihydro-1,2,4-benzothiadiazine-1,1-dioxide (III). I, II, and III were potent diuretic agents in the saline-loaded female dog.[4]

## EXPERIMENTAL[5]

*6-Amino-4-fluorobenzene-1,3-disulfonamide* (I). *m*-Fluoroaniline (28.2 g.) was added slowly to a cooled suspension of 0.5 g. sodium chloride in chlorosulfonic acid (50 g.) and the mixture then heated for 2.5 hr. by means of an oil bath held at 150–160°. The solution was cooled and poured with stirring into a mixture of ice and water. The gummy bissulfonyl chloride (9 g.) was collected by filtration, washed, dried, and added to 80 ml. of 30% ammonium hydroxide. The solution was heated for 1 hr. at 90°, concentrated at atmospheric pressure to a small volume and cooled yielding 4.65 g. of I. m.p. 220–223°. Recrystallization from water gave the analytical specimen, m.p. 233–235°, $\lambda_{max}$ 261, 301 m$\mu$, log $\epsilon$ 4.32, 3.53.

*Anal.* Calcd. for $C_6H_8FN_3O_4S_2$: C, 26.79; H, 2.99; F, 7.05; S, 23.78; N, 15.62. Found: C, 26.71; H, 2.88; F, 6.80; N, 15.16; S, 23.27.

*6-Fluoro-7-sulfamyl-1,2,4-benzothiadiazine-1,1-dioxide* (II). A mixture of I (4.47 g.) and 85% formic acid (100 ml.) was boiled for 2 hr. and then concentrated to dryness *in vacuo*. The residue was taken up in hot water and a small amount of insoluble material removed. Concentration of the solution and cooling yielded 3.23 g. of II, m.p. 285–290°. Further recrystallization from water raised the melting point to 309–310°, $\lambda_{max}$ 271 m$\mu$, log $\epsilon$ 4.08.

*Anal.* Calcd. for $C_7H_6FN_3O_4S_2$: C, 30.11; H, 2.16; F, 6.80; N, 15.05; S, 22.96. Found: C, 30.24; H, 2.30; F, 6.26; N, 14.83; S, 22.85.

*6-Fluoro-7-sulfamyl-3,4-dihydro-1,2,4-benzothiadiazine-1,1-dioxide* (III). A solution of 1.4 g. of II in 200 ml. of methanol was cooled to 0° and treated with a cold solution of sodium borohydride (3 g.) in 30 ml. of water. After standing for 1 hr. at 0° and for 14 hr. at 10° the solution was treated dropwise with acetic acid to destroy the excess hydride and then concentrated *in vacuo*. Extraction with ethyl acetate gave crude III which was crystallized from water yielding 0.67 g. of 3,4-dihydro compound, m.p. 218–220°. Pure III melted at 218–221°, $\lambda_{max}$ 266, 305 m$\mu$, log $\epsilon$ 4.35, 3.56.

*Anal.* Calcd. for $C_7H_8FN_3O_4S_2$: C, 29.89; H, 2.87; F, 6.75; N, 14.94; S, 22.80. Found: C, 30.03; H, 2.88; F, 6.32; N, 14.62; S, 22.39.

*6-Propionylamino-4-fluorobenzene-1,3-dipropionylsulfonamide* (IV). A solution of 0.81 g. of I in 100 ml. of propionic anhydride was boiled for 2 hr. The solvent was removed *in vacuo* and the residue crystallized from methanol yielding 0.58 g. of tripropionate (IV), m.p. 238–240°, $\lambda_{max}$ 222, 268 m$\mu$, log $\epsilon$ 4.21, 4.13.

*Anal.* Calcd. for $C_{15}H_{20}FN_3O_4S_2$: C, 41.18; H, 4.60; F, 4.34; N, 9.60; S, 14.66. Found: C, 41.58; H, 4.53; F, 4.10; N, 9.40; S, 14.39.

Research Laboratories
Syntex, S. A.
Apdo. Postal 2679
Mexico, D. F.

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(1) This material represents part of the professional thesis submitted by Srta. Carmen Pelayo to the Facultad de Química, Universidad Nacional Autónoma de México.

(2) F. C. Novello and J. M. Sprague, *J. Am. Chem. Soc.*, **79**, 2028 (1957).

(3) G. De Stevens, *Experientia*, **14**, 463 (1958).

(4) We wish to thank Mr. R. H. Tust of the Pharmacology Dept. of Eli Lilly for these assays.

(5) Melting points are uncorrected and ultraviolet absorption spectra were determined in 96% ethanol.

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## Preparation of Fluorocarbon α-Olefins

R. N. Griffin and M. I. Bro

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Previous workers have shown that thermal decomposition of the alkali metal salts of perfluorocarboxylic acids produces high yields of olefins containing one less carbon atom.[1] When small

$$R_fCF_2—CF_2CO_2M \longrightarrow R_f—CF=CF_2 + MF + CO_2$$

amounts of the salt are used, α-olefin of high ($\geq$ 90%) isomeric purity is obtained. As the bed depth of the salt is increased, the isomeric purity of the olefinic product decreases. The α-olefin of highest purity is produced early in the pyrolysis, and as the reaction progresses the product contains larger amounts of isomeric internal olefins. Since their boiling points generally differ by only a few degrees, the separation of the terminal and internal olefins is tedious.

Contrary to previous reports,[2] perfluorocarboxylic acids also undergo a similar general reaction to yield fluorocarbon olefins having one less carbon.

$$R_f—CF_2—CF_2—CO_2H \xrightarrow[\Delta]{} R_f—CF=CF_2 + CO_2 + HF$$

We have prepared olefins in good yield from linear and branched aliphatic perfluorocarboxylic acids, as well as linear ω-hydroperfluorocarboxylic acids.

The reaction is carried out by passing an anhydrous mixture of the acid and an inert gaseous diluent through a heated tube at temperatures of 400–650°. The flow rate of the inert gas is adjusted so that residence time of the acid in the hot zone of the tube is about five seconds. Decarboxylation appears to occur most readily when the acids are in vaporized form. Little or no isomerization of terminal to internal olefin is observed in the pyrolysis. This may be due to differences in catalytic activity of hydrogen fluoride and alkali metal fluorides, or to the low concentration of fluoride in the hot reaction zone, or both.

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(1) J. D. LaZerte, U. S. Patent **2,601,536** issued June 24, 1952; L. J. Hals, T. S. Reid, and G. H. Smith, U. S. Patent **2,668,864**, issued Feb. 9, 1954; J. D. LaZerte, L. J. Hals, T. S. Reid, and G. H. Smith, *J. Am. Chem. Soc.* **75**, 4525 (1953).

(2) T. S. Reid, G. H. Smith, and W. H. Pearlson, U. S. Patent **2,746,997**, issued May 22, 1956.

### EXPERIMENTAL

*Pyrolysis of perfluoropropionic acid.* Perfluoropropionic acid (16.4 g., 0.10 mole) was passed through a quartz tube heated to 650° using nitrogen as carrier gas. The residence time in the tube was about 3 seconds. The products contained 85–90% tetrafluoroethylene, about 10% of pentafluoroethane, and traces of hexafluoropropylene and perfluorocyclobutane; all determined by mass spectrographic analysis. In other experiments, Monel tubes with either nitrogen or carbon dioxide as the carrier were used with similar results.

*Pyrolysis of perfluorobutyric acid.* Perfluorobutyric acid (21.4 g., 0.10 mole) was passed through a Monel tube under the same conditions as those used with perfluoropropionic acid. The product contained 86% hexafluoropropylene, about 10% hexafluoroethane, and 4% octafluoropropane.

*Pyrolysis of ω-hydroperfluorononanoic acid.* Dropping 20 g. ω-hydroperfluorononanoic acid through a Vycor tube at 586–613° produced 12 g. of nearly pure ω-hydroperfluorooctene-1 as well as an undetermined amount of unchanged acid.

*Pyrolysis of perfluorooctanoic acid.* Perfluorooctanoic acid (3.4 g., 0.0082 mole) was dropped through a Vycor tube at 620° with a residence time of about 5 seconds, using carbon dioxide as a carrier. The yield of olefin was 89%. Since the starting material was a mixture of isomers, no attempt was made to determine the isomeric purity of the products.

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POLYCHEMICALS DEPARTMENT
E. I. DU PONT DE NEMOURS & CO.
DU PONT EXPERIMENTAL STATION
WILMINGTON, DEL.

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## Inner Complexes. I. Copper and Beryllium Chelates of 4-Acetyl-5-ketohexanoic Esters

RUDOLPH W. KLUIBER, FREDERICK G. OBERENDER, AND CARL J. ROSSI

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Although the properties of inner complexes depend largely on the nature of the ring system, such physical constants as solubility and melting point can be modified by varying the substituents attached to the chelate ring. In a study of these effects and potential commercial uses of inner complexes, we have prepared a series of metal derivatives of various esters of 4-acetyl-5-ketohexanoic acid (I). The ethyl and methyl esters and their copper derivatives have previously been reported by March[1] who prepared them by basic condensation of the corresponding β-chloropropionic ester and 2,4-pentanedione. Because of the availability of various acrylic esters, their monoaddition to 2,4-pentanedione presented a potentially more attractive synthesis. Analogous Michael reactions have been reported with malonic esters[2,3] and β-keto esters,[3,4] but no work has been reported on the monoaddition of acrylic esters to the active methylene of a β-diketone system.

$$CH_2 = CH{-}COOR + CH_3COCH_2COCH_3 \longrightarrow \underset{\text{I}}{(CH_3CO)_2CHCH_2CH_2COOR}$$

Ethyl 4-acetyl-5-ketohexanoate has now been prepared in 83% yield from ethyl acrylate and an excess of 2,4-pentanedione using a stoichiometric amount of sodium ethoxide in ethanol. This was converted to the copper chelate using ammoniacal copper sulfate and to the beryllium chelate using a sodium acetate–buffered beryllium nitrate solution. The use of a buffered solution eliminates the neutralization step and decreases the contamination of the product with beryllium oxide. In preparing the metal derivatives from the other esters, the distillation of the intermediate ester diketone was omitted and only the yields for the over-all conversion to the pure chelate were recorded. The solubility of these chelates in aliphatic and aromatic hydrocarbons increases with increasing chain branching. For the straight chain ester copper chelates the solubility rises to a maximum and decreases as the chain length increases. The solubility of *bis*(2,4-pentanediono) copper II in benzene was found to be 1.0 mg./ml. at 27°, whereas for the copper chelates of the *n*-alkyl 5-keto-4-acetyl hexanoates, the solubility was: ethyl, 2.0 mg./ml.; butyl, >7 mg./ml.; lauryl, 2.3 mg./ml. These are given in Table I along with other characterization data.

In three cases, the *n*-decyl, lauryl, and isoamyl esters, about 10% of a crystalline *bis*-adduct separated from the crude Michael addition product. These 4,4-diacetylpimelic esters are characterized in Table II.

### EXPERIMENTAL

*Alkyl 4-acetyl-5-keto-hexanoate.* The following preparation of the ethyl ester illustrates the general procedure used in the preparation of the other alkyl esters. However, except for the ethyl ester, the crude residual product was converted directly to the metal derivatives. Metallic sodium (12 g., 0.52 mole) was dissolved in approximately 250 ml. of commercial absolute ethanol in a 500 ml. three necked flask equipped with a stirrer and a dropping funnel. 2,4-Pentanedione (100 g., 1.0 mole) was added to the stirred sodium ethoxide solution cooled by an ice bath. Ethyl acrylate 50 g. (0.5 mole) was added dropwise with stirring to the cooled reaction mixture, and the stirring was continued approximately 16 hr. at room temperature. The reaction was quenched with an excess of glacial acetic acid and the clear solution (*p*H 4–5) was evaporated under reduced pressure. The semisolid residue was treated with 20 ml. of water and extracted with four 100-ml. portions of ether. After drying the extracts over anhydrous magnesium sulfate, the ether was removed under reduced pressure and the residual product distilled, yielding 83 g. (83%) of a light yellow liquid, b.p. 124–128° (3 mm.) (reported[1] 154–155°, 15 mm.).

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(4) L. Ruzicka, *Helv. Chim. Acta*, **2**, 144 (1919).