(*Anal.* Calcd for $C_{34}H_{46}O_4$: C, 78.72; H, 8.94. Found: C, 78.14; H, 8.98); this on reduction gave cholestane-3β-ol-7,11-dione benzoate,[1] m.p. and mixed m.p. with previous sample 197–199°.

LOUIS F. FIESER
CONVERSE MEMORIAL LABORATORY JOHN C. BABCOCK
HARVARD UNIVERSITY JOSEF E. HERZ
CAMBRIDGE 38, MASSACHUSETTS WEI-YUAN HUANG
WILLIAM P. SCHNEIDER

RECEIVED JULY 16, 1951

THE PREPARATION OF TERMINALLY UNSATURATED PERFLUORO OLEFINS BY THE DECOMPOSITION OF THE SALTS OF PERFLUORO ACIDS

Sir:

We have found that salts of the perfluorocarboxylic acids can be decarboxylated to give the 1-perfluoroölefins in good yield. This reaction appears to be unique with the salts of the perfluoro acids.

$$C_nF_{2n+1}CF_2CF_2CO_2M \longrightarrow C_nF_{2n+1}CF{=}CF_2 + CO_2 + MF$$

The sodium salts have been found to give the most satisfactory yields.

The salts were prepared by neutralizing an aqueous solution of the perfluoro acid with sodium hydroxide and were dried by heating in air at 100° for 8 hours. The decarboxylation reaction was carried out in a distilling flask heated in a furnace. Gaseous products were collected in traps cooled by liquid air or Dry Ice–acetone. Heat was gradually applied to the flask. Decomposition occurred at a controllable rate at a furnace temperature of 200–300°. The reactions were carried out at atmospheric pressure except where the product olefin boiled above room temperature, as in the case of C_9F_{18}-1 from sodium perfluorocaprate, when reduced pressure was used.

For example, in the pyrolysis of sodium perfluorobutyrate decomposition occurred at 245–253°. From 723 g. of salt, 590 g. of product was collected in the cold trap. Infrared analysis indicated this to consist of 50 mole % CO_2 and 50 mole % C_3F_6. After passage of the gases through aqueous base, 455 g. of C_3F_6 (99% yield) boiling at −29° was obtained. Terminally unsaturated perfluoro olefins containing 2, 3, 4, 5 and 9 carbon atoms, prepared by this procedure, are described in the table.

TABLE I

TERMINAL PERFLUORO OLEFINS

Compound	Molecular wt.		B.p., °C. 730–745 mm.	Anal.			
				Fluorine, %		Carbon, %	
	Found	Calcd.		Calcd.	Found	Calcd.	Found
$CF_2{=}CF_2$	99	100	−76 to −75	..	..	..	..
$CF_3CF{=}CF_2$	150	150	−29	..	..	..	..
$CF_3CF_2CF{=}CF_2$	201	200	− 2 to − 1	76.0	75.9	24.0	24.2
$CF_3(CF_2)_2CF{=}CF_2$	250	250	29 to 30	76.0	75.9	24.0	24.1
$CF_3(CF_2)_6CF{=}CF_2$	...	450	123 to 124	76.0	75.5	24.0	24.0

The olefins were identified by molecular weight, boiling point, infrared spectra, the preparation of chemical derivatives, or oxidation to perfluoro acids containing one less carbon atom than the olefin. They have in common an infrared absorption peak at 1795 cm.$^{-1}$ which is characteristic of the double bond in $C_nF_{2n+1}CF{=}CF_2$.

A more detailed report of the results will be published.

CENTRAL RESEARCH DEPARTMENT LYLE J. HALS
MINNESOTA MINING & MANUFACTURING
COMPANY THOMAS S. REID
ST. PAUL, MINNESOTA GEORGE H. SMITH, JR.

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CORRELATION OF A SYNTHETIC STEROID WITH AN INTERMEDIATE TO CORTISONE

Sir:

The method reported for the production of 11-keto[1,2] and 11β-hydroxy steroids[2] from 9,11-ethylenes is clearly inapplicable to natural (A/B *trans*) sterols but might, we thought, be useful in total synthesis if it could be shown applicable to compounds with shortened side chains.

We hence converted methyl 3α-acetoxy-$\Delta^{9(11)}$-etiocholanate[3] (I) prepared from a sample of 3α-hydroxy-11-ketoetiocholanic acid kindly supplied by Dr. Max Tishler (Merck & Co.), with perbenzoic acid to the oxide, needles from methanol, m.p. 166.9–167.4°, $[\alpha]_D$ +66.4° Chf (*Anal.* Calcd. for $C_{23}H_{34}O_5$: C, 70.74; H, 8.77. Found: C, 70.47; H, 8.74), and by methoxide-catalyzed methanolysis obtained the 3α-hydroxy oxide II, m.p. 149.8–151.0°, $[\alpha]_D$ +48.9° Chf (*Anal.* Calcd. for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.20; H, 9.50). Oxidation with sodium dichromate in glacial acetic acid furnished the 3-ketone, m.p. 128–130° and 138.0–139.8°, $[\alpha]_D$ +29.4° Chf (*Anal.* Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.62; H, 8.85), and chromic anhydride in aqueous acetic acid converted the keto oxide to methyl 3β-hydroxy-3α,9α-oxido-11-ketoetiocholanate (III), m.p. 174.6–176.0°, $[\alpha]_D$ +134.6° Chf, $\lambda^{\text{Chf}}_{\text{Max.}}$ 2.92, 5.83, 5.86μ (*Anal.* Calcd. for $C_{21}H_{30}O_5$: C, 69.58; H, 8.34. Found: C, 69.30; H, 8.44); acetate (acetic anhydride–boron fluoride), m.p. 123.8–125.3°, $[\alpha]_D$ +135° Chf (*Anal.* Calcd. for $C_{23}H_{32}O_6$: C, 68.29; H, 7.97. Found: C, 68.01; H, 8.09). Cleavage of III with dry hydrogen bromide gave the known methyl 3,11-diketo-12α-bromoethiocholanate[4] (IV), which was debrominated[4] to methyl 3,11-diketoetiocholanate[4] (V) m.p. 183.8–186.2°, $[\alpha]_D$ +92.4° Chf; mixed m.p. determination with an authentic sample and comparison of infrared spectra and rotations indicated identity.

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(3) A. Lardon and T. Reichstein, *Helv. Chim. Acta*, **28**, 1420 (1945).

(4) A. Lardon and T. Reichstein, *ibid.*, **26**, 705 (1943).