

(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-3 β -ol-7,11-dione benzoate,¹ m.p. and mixed m.p. with previous sample 197-199°.

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A more detailed report of the results will be published.

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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 11 β -hydroxy steroids² 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 3 α -acetoxy- $\Delta^9(11)$ -etiocolanate³ (I) prepared from a sample of 3 α -hydroxy-11-ketoetiocolanic acid kindly supplied by Dr. Max Tishler (Merck & Co.), with perbenzoic acid to the oxide, needles from methanol, m.p. 166.9-167.4°, $[\alpha]_D +66.4^\circ$ Chf (Anal. Calcd. for $C_{23}H_{34}O_3$: C, 70.74; H, 8.77. Found: C, 70.47; H, 8.74), and by methoxide-catalyzed methanolysis obtained the 3 α -hydroxy oxide II, m.p. 149.8-151.0°, $[\alpha]_D +48.9^\circ$ 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°, $[\alpha]_D +29.4^\circ$ 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 3 β -hydroxy-3 α ,9 α -oxido-11-ketoetiocolanate (III), m.p. 174.6-176.0°, $[\alpha]_D +134.6^\circ$ Chf, λ_{Max}^{Chf} 2.92, 5.83, 5.86 μ (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°, $[\alpha]_D +135^\circ$ 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-12 α -bromoetiocolanate⁴ (IV), which was debrominated⁴ to methyl 3,11-diketoetiocolanate⁴ (V) m.p. 183.8-186.2°, $[\alpha]_D +92.4^\circ$ Chf; mixed m.p. determination with an authentic sample and

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-perfluoroolefins in good yield. This reaction appears to be unique with the salts of the perfluoro acids.



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 perfluorocaprato, 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 perfluoroolefins 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.			
	Found	Calcd.		Fluorine, %		Carbon, %	
			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 $C_nF_{2n+1}CF=CF_2$.

comparison of infrared spectra and rotations indicated identity.

(1) L. F. Fieser, H. Heymann and S. Rajagopalan, *THIS JOURNAL*, **73**, 2307 (1950).

(2) H. Heymann and L. F. Fieser, *ibid.*, **73**, in press (1951).

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

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