(*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°.

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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. Found	Molecular wt. Calcd.	B.p., °C. 730–745 mm.	Anal. Fluorine, % Calcd.	Anal. Fluorine, % Found	Anal. Carbon, % Calcd.	Anal. Carbon, % 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.

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RECEIVED JULY 2, 1951

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.

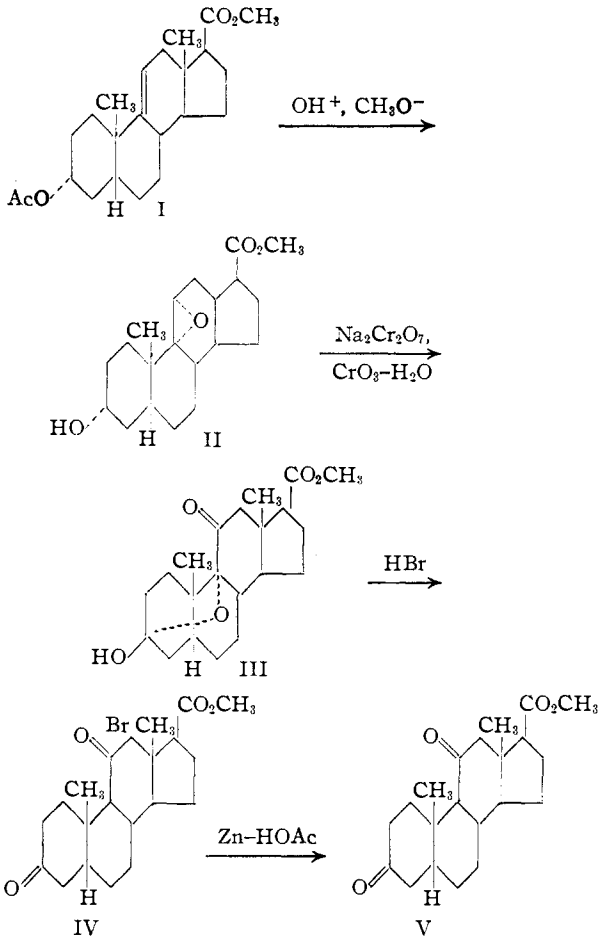
We hence converted methyl 3α-acetoxy-$\Delta^{9(11)}$-etiocholanate[3] (I) prepared from a sample of 3α-hydroxy-11-ketoetiocholanic acid kindly supplied by Dr. Max Tishler (Merck & Co.), with perbenzoic acid to the oxide, needles from methanol, m.p. 166.9–167.4°, $[\alpha]_D$ +66.4° Chf (*Anal.* Calcd. 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, $\lambda_{Max.}^{Chf}$ 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.

(1) L. F. Fieser, H. Heymann and S. Rajagopalan, THIS JOURNAL, **72**, 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).



After completion of this work, Dr. Woodward kindly informed us of the two-stage reduction and acetylation of synthetic methyl *d*-3-keto-$\Delta^{4,9(11),16}$ etiocholatrienate[5] to our starting material I, as reported in a parallel Communication. Our product V has been transformed by reactions reported by Reichstein[4,6] into an intermediate of Sarett's synthesis of cortisone.[7]

(5) R. B. Woodward, F. Sondheimer and D. Taub, THIS JOURNAL, **73**, 4057 (1951).

(6) J. v. Euw, A. Lardon and T. Reichstein, *Helv. Chim. Acta.*, **27**, 1287 (1944).

(7) L. H. Sarett, THIS JOURNAL, **70**, 1454 (1948); **21**, 2443 (1949).

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STEROIDS. XXV.[1] SYNTHESIS OF CORTISONE

Sir:

There was recorded recently the partial synthesis of allopregnane-11,20-dione-3β-ol from a number of ring C unsubstituted plant steroids such as diosgenin,[1,2] ergosterol,[2] and two degradation products (Δ^5-3β-hydroxybisnorcholenic acid[2] and Δ^5-pregnen-3β-ol-20-one[3]) of stigmasterol. Since allopregnane-3β,17α,21-triol-11,20-dione 21-monoacetate (monoacetate of Reichstein's compound D[4]) has already been transformed[5] into cortisone, there remains only the interconversion of allopregnane-11,-20-dione-3β-ol into Reichstein's compound D monoacetate in order to complete the partial synthesis of cortisone from readily available plant steroids. The present report is concerned with the successful completion of these missing steps.

Allopregnane-11,20-dione-3β-ol was converted (acetic anhydride–*p*-toluenesulfonic acid) into its 11,20-dienol acetate,[6] which without isolation was treated with excess perbenzoic acid in chloroform solution.[7] Brief saponification with 2 *N* sodium hydroxide solution afforded in good yield allopregnane-3β,17α-diol-11,20-dione (m.p. 270–272° (uncor.), $[\alpha]^{20}D$ + 76° (dioxane); found: C, 72.44; H, 9.46). Bromination in chloroform solution smoothly led to 21-bromoallopregnane-3β,17α-diol-11,20-dione (m.p. 243–245° (dec.), $[\alpha]^{20}D$ + 73° (dioxane)) which was treated with sodium iodide in acetone solution followed by refluxing with potassium acetate exactly as described recently[8] for the preparation of Reichstein's compound P. The resulting allopregnane-3β,17α,21-triol-11,20-dione 21-acetate (m.p. 235–237°, $[\alpha]^{20}D$ + 66° (acetone); found: C, 68.22; H, 8.73) was identified with Reichstein's compound D[4] by direct comparison of the 3,21-diacetates (m.p. 220°). We are grateful to Prof. T. Reichstein of the University of Basle for carrying out the mixed melting point determination.

Formally speaking the above sequence of reactions completes the total synthesis of cortisone. Androstan-3β-ol-17-one has been synthesized totally[9] and is convertible[10–13] into methyl 3-ketoetiocholanate, which has also been synthesized totally.[14] The latter substance has already been transformed[15] into methyl Δ^4-3-ketoetiocholenate and thence *via* methyl Δ^5-3β-acetoxyetiocholenate[16] and Δ^5-3β-acetoxyetiocholenic acid[17] into Δ^5-preg-

(1) Paper XXIV, G. Stork, J. Romo, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 3546 (1951).

(2) E. M. Chamberlin, W. V. Ruyle, A. E. Erickson, J. M. Chemerda, L. M. Aliminosa, R. L. Erickson, G. E. Sita and M. Tishler, *ibid.*, **73**, 2396 (1951).

(3) C. Djerassi, J. Romo and G. Rosenkranz, *J. Org. Chem.*, **16**, 754 (1951); J. Romo, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, in press (1951).

(4) J. v. Euw and T. Reichstein, *Helv. Chim. Acta*, **25**, 1009 (1942).

(5) G. Rosenkranz, C. Djerassi, R. Yashin and J. Pataki, *Nature*, **168**, 28 (1951). The reactions involve N-bromoacetamide oxidation to allopregnane-3,11,20-trione-17α,21-diol 21-acetate, dibromination and treatment with sodium iodide (*cf.* ref. 15).

(6) *Cf.* B. A. Koechlin, D. L. Garmaise, T. H. Kritchevsky and T. F. Gallagher, THIS JOURNAL, **71**, 3262 (1949), for the analogous reaction with pregnane-11,20-dione-3α-ol.

(7) General method of T. H. Kritchevsky and T. F. Gallagher (*J. Biol. Chem.*, **179**, 507 (1949); THIS JOURNAL, **73**, 184 (1951)) for the introduction of the 17α-hydroxy group.

(8) G. Rosenkranz, J. Pataki, St. Kaufmann, J. Berlin and C. Djerassi, *ibid.*, **72**, 4081 (1950).

(9) H. M. E. Cartwell, J. W. Cornforth, S. R. Duff, H. Holtermann and R. Robinson, *Chemistry and Industry*, 389 (1951).

(10) L. Ruzicka, P. A. Plattner, H. Heusser and J. Pataki, *Helv. Chim. Acta*, **29**, 936 (1946).

(11) P. A. Plattner, L. Ruzicka, H. Heusser, J. Pataki and K. Meier, *ibid.*, **29**, 943 (1946).

(12) M. Sorkin and T. Reichstein, *ibid.*, **29**, 1209 (1946).

(13) M. Steiger and T. Reichstein, *ibid.*, **20**, 1040 (1938); C. Djerassi and C. R. Scholz, THIS JOURNAL, **69**, 2409 (1947).

(14) R. B. Woodward, F. Sondheimer and D. Taub, *ibid.*, **73**, 3547 (1951).

(15) C. Djerassi and C. R. Scholz, *ibid.*, **69**, 2410 (1947); G. Rosenkranz, C. Djerassi and co-workers, *ibid.*, **72**, 1046, 4077 (1950).

(16) H. Reich and A. Lardon, *Helv. Chim. Acta*, **29**, 671 (1946).

(17) This step is carried out industrially (*cf.* F.I.A.T. Final Report No. 996, London, H. M. Stationery Office 1949, pp. 87–89).