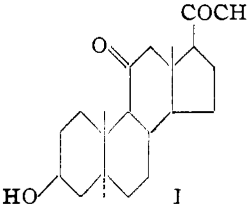
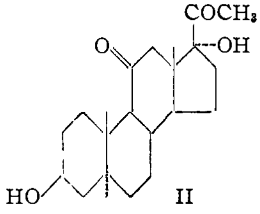
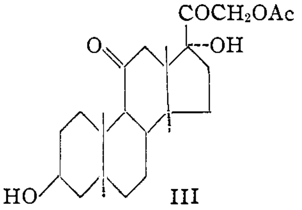
11,20-dione(II); m.p. 290–292° (all m.p.s. are uncorrected); found: C, 72.98; H, 9.74; $(\alpha)^{24}\mathrm{D}$ +43 (dioxane). Bromination of II in chloroform and subsequent treatment of the 21-bromo derivative (m.p. 238–240°; found: Br, 18.39) with sodium acetate afforded *allo*pregnane-3β,17α,21-triol-11,20-dione-21-acetate, III; m.p. 233–235°. The latter on oxidation with N-bromoacetamide in methanol was transformed into *allo*pregnane-17α,21-diol-3,11,20-trione (IV); m.p. 229–233°; $(\alpha)^{24}\mathrm{D}$ +100° ($CHCl_3$); found: C, 68.46; H, 7.68 which proved to be identical with a sample prepared by the hydrogenation of cortisone acetate with palladium in methanol containing potassium hydroxide. Bromination and dehydrobromination of the *allo*-dihydrocortisone acetate by a procedure to be described in detail later produced cortisone acetate characterized by its melting point, optical rotation, ultraviolet and infra-red absorption spectra.



I



II



III

Complete details for the conversion of ergosterol, diosgenin, stigmasterol and cholesterol to cortisone acetate will be published in this Journal.

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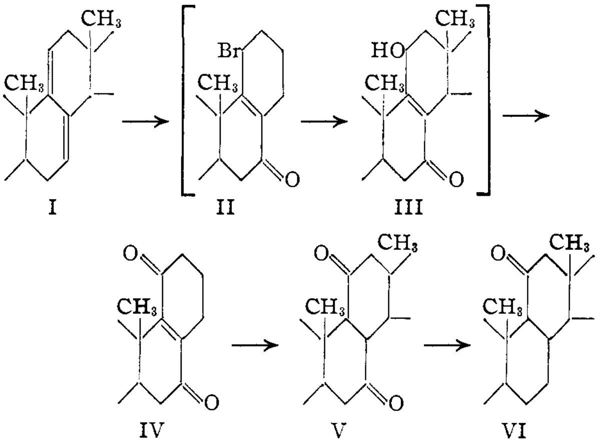
Received July 13, 1951

A FURTHER METHOD FOR PRODUCTION OF 11-KETOSTEROIDS FROM $\Delta^{7,9(11)}$-DIENES

Sir:

Three methods have been recorded for conversion of $\Delta^{7,9(11)}$-dienes into the corresponding 11-ketosteroids.[1,2,3] The first method[1] was shown to be applicable in both the cholestane and coprostane series; the third, demonstrated with sterol derivatives, is not applicable in the bile acid series, since we have found that methyl $\Delta^{7,9(11)}$-lithocholadienate reacts with performic acid to give methyl 3α-formoxy-7-keto-Δ^{8}-cholenate, m.p. 164–166°, $[\alpha]_{\mathrm{D}}$ −1.6° Di, λ^{EtOH} 255 mμ, log ϵ 3.85 (*Anal.* Calcd. for $C_{26}H_{38}O_5$: C, 72.52; H, 8.90. Found: C, 72.22; H, 9.12) in 63% yield; the hydroxy acid melts at 209–210°, $[\alpha]_{\mathrm{D}}$ −38° Di, (*Anal.* Calcd. for $C_{24}H_{36}O_4$: C, 74.19; H, 9.34. Found: C, 74.57; H, 9.33).

A fourth method, applicable in both series, consists in reaction of a diene (I) with excess N-bromosuccinimide in aqueous *t*-butanol and addition of silver nitrate followed by chromic acid. The resulting Δ^{8}-ene-7,11-dione IV is convertible through V to VI as previously described[1]; alternately, at least with methyl 3α-acetoxy-7,11-diketocholanate, V is convertible to VI by Raney nickel reduction of the 7-cycloethylenemercaptol derivative, m.p. 162–163.5°, $[\alpha]_{\mathrm{D}}$ +27.6° Di (*Anal.* Calcd. for $C_{29}H_{44}O_5S_2$: C, 64.89; H, 8.26; S, 11.96. Found: C, 65.20; H, 8.49; S, 11.86).



Methyl 3α-acetoxy-$\Delta^{7,9(11)}$-lithocholadienate (430 mg.), processed as indicated, gave 152 mg. of crude IV, λ^{EtOH} 272 mμ (3.77), which on reduction gave 90 mg. of pure V, m.p. 161–162° (no depression with previous sample; identical IR spectra), $[\alpha]_{\mathrm{D}}$ + 26.7° Di (*Anal.* Calcd. for $C_{27}H_{40}O_6$: C, 70.40; H, 8.75. Found: C, 70.71; H, 8.96). The reaction with NBS results in development of strong absorption at about 255 mμ; when the excess reagent was destroyed and the crude bromo derivative extracted and debrominated, the product, m.p. 179–180°, λ^{EtOH} 254, 310 mμ (3.88, 2.84) corresponded closely to methyl 3α-acetoxy-7-keto-Δ^{8}-cholenate[1] (no depression) and not at all to the isomeric 11-ketone[4]; hence II is a probable intermediate.

As applied to $\Delta^{7,9(11),22}$-ergostatrienyl acetate, the reaction sequence afforded a crude enedione that on reduction with zinc and acetic acid gave 7,11-diketo-Δ^{22}-erogostenyl acetate, m.p. 197–199°, $[\alpha]_{\mathrm{D}}$ −29.5° Chf (*Anal.* Calcd. for $C_{30}H_{46}O_4$: C, 76.55; H, 9.85. Found: C, 76.47; H, 9.77), in agreement with the properties reported.[2] $\Delta^{7,9(11)}$-Cholestadiene-3β-ol benzoate was converted similarly to the Δ^{8}-ene-7,11-dione benzoate,[1] m.p. 155–158°, $[\alpha]_{\mathrm{D}}$ +46° Di, λ^{EtOH} 269 mμ, log ϵ 3.80

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(1) L. F. Fieser, J. E. Herz and W. Y. Huang, THIS JOURNAL, **73**, 2397 (1951). The by-product of the oxidation (no ultraviolet absorption) described as methyl 3α-acetoxy-7,8-oxido-$\Delta^{9(11)}$-cholenate, actually is methyl 3α-acetoxy-7-keto-$\Delta^{9(11)}$-cholenate, since on reduction with sodium borohydride it yields an alcohol, m.p. 111–115°, $[\alpha]_{\mathrm{D}}$ +57.5° Di, λ^{Chf} 2.91, 5.80μ (*Anal.* Calcd. for $C_{27}H_{42}O_5$: C, 72.61; H, 9.48. Found: C, 72.56; H, 9.45), that on dichromate oxidation is reconverted to the starting material. The by-product can be isomerized to the conjugated isomer and the latter converted into the starting diene for recycling, by reduction of the free acid with, sodium and amyl alcohol followed by acid dehydration.

(2) E. M. Chamberlain, 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) G. Stork, J. Romo, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 3546 (1951).

(4) H. Heymann and L. F. Fieser, THIS JOURNAL, **73**, 4054 (1951).

(*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.

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

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, $\lambda^{\text{Chf}}_{\text{Max.}}$ 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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[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).