

nection other ions of oxidation number three are of particular interest. Of these, aluminum, chromium and rare earths have been tested to date and they all were found to be practically not adsorbed from strong HCl solutions. To illustrate the effectiveness of the method an iron impurity (30 mg./l.) was separated from a 2 *M* aluminum chloride solution in 3 *M* HCl using a 10 cm. column of 0.024 sq. cm. cross-section. After passage of 30 ml. of solution (flow rate *ca.* 0.25 ml. cm.⁻² min.⁻¹), when the experiment was interrupted, iron could be detected (visually) only in the first 0.6 cm. of the column. Thus large volumes of solution could be processed with small amounts of resin.

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THE CRYSTAL STRUCTURE OF A SIGMA PHASE, FeCr¹

Sir:

Despite the importance of the sigma phase in transition group alloys, the crystal structure of the phase has not heretofore been determined, primarily because the materials, prepared by solid-state transition, are microcrystalline and not well suited for single crystal work, while powder photographs have proved too complicated for satisfactory interpretation.

However, we have succeeded in isolating from a specimen of σ -FeCr (46.5 at. % Cr) two single crystals roughly 0.1 mm. in size. Single crystal and powder photography gave a 30-atom primitive tetragonal cell (Laue symmetry D_{4h}), with $a_0 = 8.799 \text{ \AA}$. and $c_0 = 4.546 \text{ \AA}$.

The only observable ($hk0$) reflections (aside from a few faint ones at large Bragg angles) within the $\text{CuK}\alpha$ limit are uniformly strong, and are those ($\{410\}$, $\{330\}$, $\{550\}$, $\{720\}$, $\{820\}$, $\{660\}$, $\{960\}$, $\{11\cdot1\cdot0\}$, and $\{10\cdot5\cdot0\}$) which would result from fifteen atoms at the points of a slightly distorted hexagonal net (with the following typical (x,y) coordinates with respect to a vertical two-fold axis: I (1) (0, 0); II (2) (1/5, 1/5); III (2) (2/5, 2/5); IV (2) (2/3, 1/3); V (4) (7/15, 2/15); VI (4) (11/15, 1/15)) plus fifteen others in an equivalent net rotated 90° with respect to the first. The relative positions of the two nets are as in an "ideal" structure with space group $D_{4h}^{14} - P4/mnm$, as indicated by n -glide extinctions in ($0kl$) Weissenberg data ($\text{CuK}\alpha$).

That "ideal" structure is ruled out by the general (hkl) intensities. However, atoms IV in the second layer have (x,y) coordinates (1/6, 1/6, etc.) very close to those of II in the first layer, and if the eight atoms II and IV are moved to new positions $8(j)$ with $x = 11/60$, $z = 1/4$, a structure with space group D_{4h}^{14} is obtained which

(1) Work done in part under a contract with the Office of Naval Research and in part under a program sponsored by the Carbide and Carbon Chemicals Corporation.

gives a satisfactory qualitative accounting for the ($hk0$), ($hk1$), ($hk2$), and ($hk3$) Weissenberg intensities ($\text{CuK}\alpha$), including a prediction of weak ($hk0$) reflections which are perhaps not altogether inconsistent with those observed. Until intensity work (now in progress) has yielded quantitative data, a choice between this space group and $D_{2d}^8 - P4n2$ (obtainable with small distortions of the above structure) or $C_{4v}^4 - P4nm$ (permitting a closely related structure derived from the "ideal" structure by shifting II and IV about 1/4 in z) cannot be made. All other space groups have been ruled out.

The identities of the atoms are not yet known. They may be very difficult to determine because iron and chromium have nearly the same scattering factors.

This work is being continued. We are indebted to Professor Pol Duwez and Mr. Paul Pietrokowsky of this Institute for the sample of σ -FeCr. We are grateful to Professor Linus Pauling for helpful discussions, and to Miss Linda Pauling and Mrs. Nan Arp for computational assistance.

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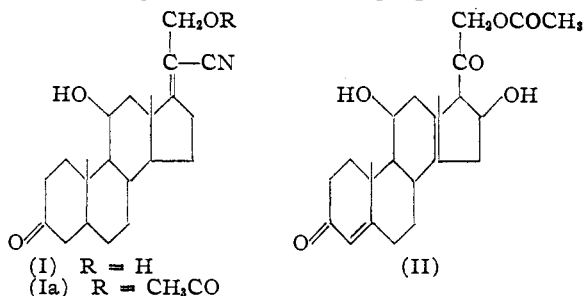
SYNTHESIS OF 11-HYDROXYLATED CORTICAL STEROIDS. 17(α)-HYDROXYCORTICOSTERONE

Sir:

We wish to report the synthesis of 17(α)-hydroxycorticosterone otherwise known as Reichstein's Compound M¹ or Kendall's Compound F,² a substance found by preliminary studies³ to have therapeutic activity similar to Cortisone.

The biosynthesis of 17(α)-hydroxycorticosterone from 11-desoxy-17(α)-hydroxycorticosterone has been demonstrated using techniques of perfusion in the isolated beef adrenal gland⁴ and of incubation with adrenal homogenates.⁵

We have synthesized 17(α)-hydroxycorticosterone starting with 20-cyano-17-pregnene-21-ol-3,-



- (1) Reichstein, *Helv. Chim. Acta*, **20**, 953 (1937).
- (2) Mason, Hoehn and Kendall, *J. Biol. Chem.*, **124**, 459 (1938).
- (3) Hench, Kendall, Stocumb and Polley, *Arch. Int. Med.*, **85**, 545 (1950).
- (4) Hechter, Jacobsen, Jeanloz, Levy, Marshall, Pincus and Schenker, *Arch. Biochem.*, **25**, 457 (1950).
- (5) McGinty, Smith, Wilson and Worrel, *Science*, **112**, 506 (1950).

11-dione prepared previously by Sarett⁶ in connection with the synthesis of Cortisone.

This cyanopregnene in the form of its 3-diethyl ketal was reduced with lithium borohydride⁷ selectively at position 11. After removal of the ketal grouping, 20-cyano-17-pregnene-11(β),21-diol-3-one (I) was obtained; m.p. 207–210°, solidifies and remelts at 217.5–221.5° [α]_D²⁵ + 24.4° (1.03, acetone); $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 2230 Å., $E_{1\text{cm}}^{1\%}$ 387; *Anal.* Found: C, 74.12; H, 8.73. Acetylation of (I) afforded the 21-acetate (Ia): m.p. 170–171.5°; [α]_D²⁵ + 32.4° (1.02, acetone); *Anal.* Found: C, 71.93; H, 8.37. Hydroxylation of (Ia) with osmium tetroxide⁸ yielded 4,5-dihydro-17(α)-hydroxycorticosterone-21-acetate; m.p. 217.6–219.8; [α]_D²⁵ + 86.6 (1.05, acetone); *Anal.* Found: C, 68.20; H, 8.19. Bromination of the latter followed by dehydrobromination with semicarbazide acetate⁹ afforded 17(α)-hydroxycorticosterone acetate (II); m.p. 218.5–220.5°; [α]_D²⁵ + 150.7 (0.5, acetone) $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 2420 Å., $E_{1\text{cm}}^{1\%}$ 371; *Anal.* Found: C, 68.47; H, 8.11. A mixed melting point of synthetic (II) with an authentic sample⁹ of 17(α)-hydroxycorticosterone acetate was not depressed; comparative *infrared* spectra of the two samples were identical in all respects.

(6) Sarett, *THIS JOURNAL*, **70**, 1454 (1948).

(7) Nystrom, Chaikin and Brown (*ibid.*, **71**, 3245 (1949)) have reduced carbonyl groups in the presence of ester functions with this reagent.

(8) Koechlin, Kritchevsky and Gallagher, *J. Biol. Chem.*, **184**, 393 (1950); also, Djerassi, *THIS JOURNAL*, **71**, 1003 (1949); Hershberg, *J. Org. Chem.*, **13**, 542 (1948).

(9) The authors are indebted to Dr. Arnold Ott of the Upjohn Co. for authentic samples of 17(α)-hydroxycorticosterone and its acetate for identification purposes.

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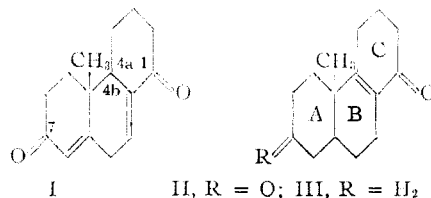
TRICYCLIC INTERMEDIATES FOR THE SYNTHESIS OF NON-AROMATIC STEROIDS

Sir:

The synthesis by Cornforth and Robinson¹ of a tricyclic diketone having rings ABC of the steroids and an appropriate configuration at the fixed asymmetric centers represents a notable advance toward total synthesis of non-aromatic steroids. The length of the synthesis, however, makes their intermediate difficultly accessible by that route, although it is more available through degradation of cholesterol.

We have developed a short synthetic route to similar tricyclic diketones which makes these more readily accessible and in which the stereochemical problems may be dealt with more selectively. In this way I, II and related compounds which should be suitable for attachment of ring D have been prepared.

(1) Cornforth and Robinson, *J. Chem. Soc.*, 1855 (1949).



Dihydroresorcinol was alkylated with 1-diethyl-amino-3-pentanone methiodide, the product (m.p. 84.5–85°; found: C, 67.07; H, 8.06) was cyclized as the isopropyl or methyl enol ether and hydrolyzed to the enol of 5-methyloctahydronaphthalene-1,6-dione (IV), m.p. 95–98°; max 242 m μ (log E = 3.84) and 345 m μ (3.89). *Anal.* Calcd. for C₁₁H₁₄O₂: C, 74.13; H, 7.92. Found: C, 73.98; H, 7.93. Alkali converted this in part to 6-hydroxy-5-methyl-1-tetralone. IV and methyl vinyl ketone led to 5- γ -ketobutyl-5-methyl- Δ^{4a-8a} -octalin-1,6-dione (V), m.p. 142.5–143° max. 246 m μ (3.93); found: C, 72.73; H, 8.14. With acid this was isomerized to the Δ^{8-8a} compound (VI), m.p. 195.5–197°, max. 240 m μ (3.97); found: C, 72.86; H, 8.11. Alkaline cyclization of each isomer led to the same tricyclic diketone formulated as I, m.p. 122–123.5°, max. 240.5 m μ (4.38). *Anal.* Calcd. for C₁₅H₁₈O₂: C, 78.22; H, 7.88. Found: C, 77.96; H, 7.94.

Alkaline palladium hydrogenation of I gave a mono-unsaturated diketone formulated as II, m.p. 61.5–63°, max. 245 m μ (4.14). *Anal.* Calcd. for C₁₅H₂₀O₂: C, 77.55; H, 8.68. Found: C, 77.51; H, 8.91. Formation of the 7-dibenzyl mercaptole of II and desulfurization with Raney nickel has given the ketone III synthesized by Bachmann and Dreiding² from *cis*-9-methyl-1-decalone; semicarbazone, m.p. 229–231°, 2,4-dinitrophenylhydrazone, m.p. 227.5–228°, oxime, m.p. 135–137°.

Further alkaline hydrogenation of I has given a mixture from which the Cornforth-Robinson isomer A of 4b-methylperhydrophenanthrene-1,7-dione (VII) could be isolated, m.p. 149–150.5°, bis-2,4-dinitrophenylhydrazone, m.p. 254–255°. While this isomer has the unnatural configuration at the C-4a-C-4b "backbone," the present transformations, nevertheless, complete a chain of intermediates linking the A:B ring configuration of desoxycholic acid with that of *cis*-9-methyl-1-decalone. In addition a new isomer C of VII (A:B ring probably *trans*) was obtained, m.p. 76.5–77.5° (found: C, 76.82; H, 9.68); bis-ethylene ketal, m.p. 150.5–151.5° (found: C, 70.64; H, 9.36) bis-2,4-dinitrophenylhydrazone, m.p. 262.5–263.5°.

I was converted via the 2-hydroxymethylene-7-ethylene ketal derivative, m.p. 110–113°, to 2,4b-dimethyl-1,2,3,4,4a,4b,5,6,7,9-decahydrophenanthrene-1,7-dione, m.p. 136.5–138°, max. 240 m μ (4.40); found: C, 78.38; H, 8.41.

We are indebted to Merck and Co., Inc., the

(2) Bachmann and Dreiding, *J. Org. Chem.*, **13**, 317 (1948).