11-dione prepared previously by Sarett[6] in connection with the synthesis of Cortisone.

This cyanopregnene in the form of its 3-diethyl ketal was reduced with lithium borohydride[7] 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° $[\alpha]^{25}D$ +24.4° (1.03, acetone); $\lambda_{max.}^{CH_3OH}$ 2230 Å., $E_{1cm.}^{1\%}$ 387; *Anal.* Found: C, 74.12; H, 8.73. Acetylation of (I) afforded the 21-acetate (Ia): m.p. 170–171.5°; $[\alpha]^{25}D$ +32.4° (1.02, acetone): *Anal.* Found: C, 71.93; H, 8.37. Hydroxylation of (Ia) with osmium tetroxide[6] yielded 4,5-dihydro-17(α)-hydroxycorticosterone-21-acetate; m.p. 217.6–219.8; $[\alpha]^{25}D$ + 86.6 (1.05, acetone); *Anal.* Found: C, 68.20; H, 8.19. Bromination of the latter followed by dehydrobromination with semicarbazide acetate[8] afforded 17(α)-hydroxycorticosterone acetate (II); m.p. 218.5–220.5°; $[\alpha]^{25}D$ + 150.7 (0.5, acetone) $\lambda_{max.}^{CH_3OH}$ 2420 Å., $E_{1cm.}^{1\%}$ 371; *Anal.* Found: C, 68.47; H, 8.11. A mixed melting point of synthetic (II) with an authentic sample[9] 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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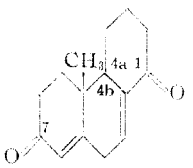
TRICYCLIC INTERMEDIATES FOR THE SYNTHESIS OF NON-AROMATIC STEROIDS

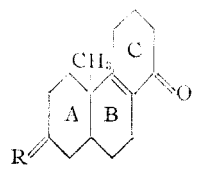
Sir:

The synthesis by Cornforth and Robinson[1] 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 difficulty 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.



I



II, R = O; III, R = H_2

Dihydroresorcinol was alkylated with 1-diethylamino-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 mμ (log E = 3.84) and 345 mμ (3.89). *Anal.* Calcd. for $C_{11}H_{14}O_2$: 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^{1a-8a}-octalin-1,6-dione (V), m.p. 142.5–143° max. 246 mμ (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 mμ (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 mμ (4.38). *Anal.* Calcd. for $C_{15}H_{18}O_2$: 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 mμ (4.14). *Anal.* Calcd. for $C_{15}H_{20}O_2$: 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 Dreiding[2] 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 mμ (4.40); found: C, 78.38; H, 8.41.

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

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

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

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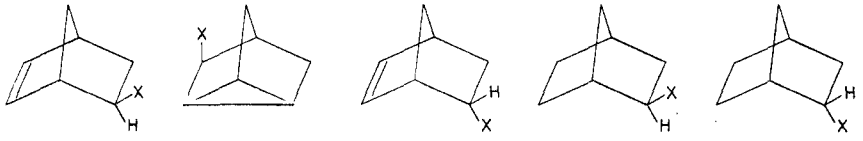
DRIVING FORCE OF THE HOMOALLYLIC REARRANGEMENT IN ACETOLYSIS OF *exo*-DEHYDRONORBORNYL *p*-BROMOBENZENESULFONATE[1]

Sir:

Roberts, Bennett and Armstrong[2] have very recently reported the relative solvolysis rates of *exo*-dehydronorbonyl (I), nortricyclyl (II), and *endo*-dehydronorbornyl (III) halides (X = Cl or Br) in 80% ethanol as *ca.* 5:1:1. Solvolysis of I and III gives mainly the homoallylic rearrangement product with the structure II; I is not much more reactive than III, and I and III are slower, if anything, than the saturated analogs IV and V. These workers conclude that the double bonds in I and III exert no very substantial driving force of the type postulated for cholesteryl compounds,[3] presumably because the geometry is less favorable for participation of the olefinic linkage in the ionization process. On the other hand, on the prediction that conditions in I were very favorable for substantial participation of the olefinic linkage in the ionization process, we had been studying the acetolysis of the corresponding *p*-bromobenzenesulfonates, I, m.p. 78.4–79.8° (still heavily contaminated with isomeric material; prepared from alcohol derived by stereoisomerization of *endo*-dehydronorborneol), II, m.p. 80.2–81.8° (pure material prepared from hydrolysis product from III), and III, m.p. 87.4–89.0° (pure material prepared from *endo* alcohol), all three of which yield acetate in *ca.* 80% yield, largely with the structure II from infrared and hydrogenation data.



I II III IV V

The first order rates of acetolysis obtained give the sequence I:II:III of 7000:2000:1 at 25°. This indicates a very substantial driving force in isomer I which has the proper configuration for delocalization of the neighboring electron cloud in the rate-determining ionization, whereas in III this must occur essentially subsequent to ionization. Also, it indicates considerable reactivity of the structure II.

V and cholestanyl benzenesulfonates (with no neighboring group participation in the rate-determining ionization) have rates nearly identical with cyclohexyl.[4] III has a rate reduced somewhat (by *ca.* one power of ten) by the polar effect due to an unsaturated group (e.g., K_A for phenylacetic or vinylacetic acid). These facts make it clear that in acetolysis of *p*-bromobenzenesulfonates the driving force in I (I:III = 7000:1) is at least as large and probably somewhat larger than in cholesteryl. Also, as would be expected, it is larger than in IV, the latter being measured by the factor[4a] of 360 for IV:V.

The essential difference between our results on sulfonates and those of Roberts and co-workers[2] on halides lies in the high reactivities they report for III and V.

(1) Research supported by the Office of Naval Research.

(2) Roberts, Bennett and Armstrong, THIS JOURNAL, **72**, 3329 (1950).

(3) Winstein and Adams, *ibid.*, **70**, 838 (1948).

(4) (a) Winstein and Trifan, *ibid.*, **71**, 2953 (1949); (b) A. H. Schlesinger, unpublished work.

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THE EXCHANGE REACTION BETWEEN HYDROGEN AND LITHIUM HYDRIDE. THE PREPARATION OF LITHIUM HYDRIDE-*t* AND LITHIUM ALUMINUM HYDRIDE-*t*

Sir:

The exchange of hydrogen between hydrogen gas and lithium hydride (solid), traced with both deuterium and tritium, occurs under unexpectedly mild conditions. At high temperatures lithium hydride exhibits a measurable degree of dissociation[1] and should therefore exhibit exchange through a mechanism of dissociation and recombination. However, the following observations indicate that exchange involves a surface reaction and a slower diffusion process occurring at rates such that exchange can be observed at room temperature and is substantially complete at 200° within twenty-four hours.

Rate measurements were made on a sample of lithium hydride-*t* which had been prepared by heating 200-mesh lithium hydride (Maywood Chemical Co.) with hydrogen gas containing tritium in a Pyrex flask at 350°. The hydride was then brought into contact with inactive hydrogen gas and the uptake of tritium in the gas phase was followed by means of ion-current measurements[2] on samples of the gas. Between runs the hydride was heated with hydrogen gas for sixteen hours at 230° to ensure uniform distribution of tritium throughout the solid phase. The measurements extend over the range from 25 to 200° and are shown in the accompanying figure as a plot of log $(1 - F)$ with time, where F is the ratio of specific

(1) Hurd and Moore, THIS JOURNAL, **57**, 332 (1935).

(2) Wilzbach and Van Dyken, to be published.