hydrocarbon. A little less than 50% of the bromine in the reacting halide appears as sodium bromide. The tars were found by sodium fusion to contain large quantities of bromine. Bromobenzene falls between these two groups of compounds with respect to bromine distribution in the products. Conversion and hydrocarbon yields for bromobenzene were low.

Hydrogen was evolved slowly over periods of 10 to 15 hours in all the reactions studied. Blank runs made at room temperature with halide and sodium hydride gave no hydrogen evolution. Blank runs made with Nujol and sodium hydride at 180° evolved 10 to 15 ml. of hydrogen over a period of one hour after which hydrogen evolution ceased.

A careful examination failed to give any evidence for the formation of di- or polyphenyl derivatives in these reactions.

Attempts were made to force these reactions by grinding the sodium hydride during the course of the reactions. Seven 15-mm. glass balls and a Hershberg stirrer were employed for this purpose. The grinding action was sufficiently severe to score the reaction flask but the effects were uncertain since they were very close to the limits of experimental error in the analysis of the products.

Rates of stirring from 0 to 7000 r.p.m. in unbaffled flasks had no measurable effect on these reactions.

Attempts were made to employ Nujol, N,N-diethylaniline and eicosane as high boiling solvents for these reactions. These substances were found to be inert to sodium hydride at 200°. When employed as solvents, however, large quantities of tar resulted and the only identifiable products found in the reaction mixture were unreacted halide and residual solvent. No reaction occurred below 150°.

The results obtained in this study are apparently consistent with the general mechanism proposed by Morton for the action of sodium alkyls on chlorobenzene. Part of the hydrogen which should be produced if Morton's[5] mechanism applies is probably absorbed by the polymeric materials produced as tar.

Acknowledgments.—The authors wish to thank the E. I. du Pont de Nemours and Co., Inc., who furnished the sodium hydride used in this investigation, and the Office of Naval Research for the financial support which made the work possible.

[5] A. A. Morton, This Journal, **64**, 2242 (1942); *Chem. Revs.*, **35**, 1 (1944).

CHEMISTRY DEPARTMENT
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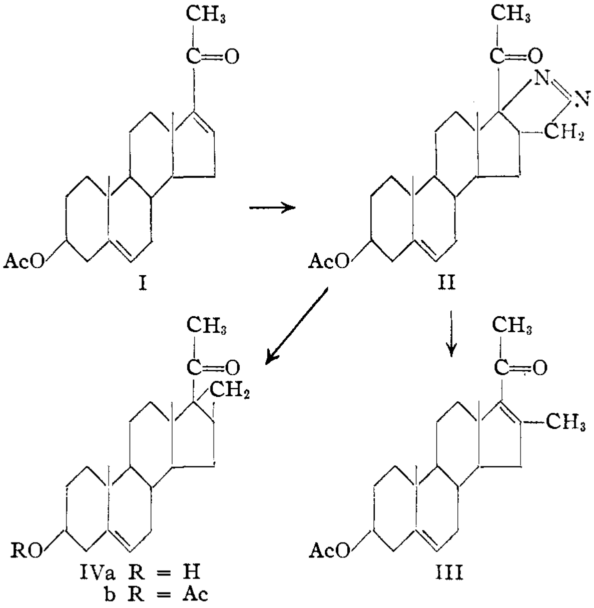
RECEIVED DECEMBER 26, 1950

Steroids. XVII.[1] A Steroidal Cyclopropyl Ketone

BY A. SANDOVAL, G. ROSENKRANZ AND CARL DJERASSI

During the thermal decomposition of the pyrazoline (II) arising from the action of diazomethane upon $\Delta^{5,16}$-pregnadien-3β-ol-20-one 3-acetate (I), Wettstein[2] observed the formation of two substances. The principal product was an α,β-unsaturated ketone, provisionally formulated as the 16-methyl-Δ^{16}-20-ketone III, but in addition there was isolated in poor, though unspecified yield an isomer which exhibited no absorption in the ultraviolet and by exclusion was tentatively assumed to be the cyclopropyl ketone IV. In connection with other experiments, we had occasion to carry out the large scale decomposition of this pyrazoline II and to accumulate enough of the by-product to establish its constitution.



The *a priori* assumption that the by-product of the pyrazoline decomposition is the cyclopropyl ketone IV is not unjustified, since *substituted* pyrazolines yield cyclopropanes in addition to the ethylene.[3] Wettstein[2] characterized the substance only by its m.p. (202.5–205°) and analysis which was consistent with the expression IVb. In our hands, the substance had m.p. 195–197°, $[\alpha]^{20}\text{D}$ +33[4] and could be saponified to the free alcohol IVa. The latter was stable to boiling methanolic potassium hydroxide or hydrochloric acid and could be reacetylated to the original product IVb, thus indicating the absence of a 20-ketopregnane structure with an enolizable hydrogen atom at C-17. In contrast to the 16-methyl-Δ^{16}-20-ketone III it was impossible to prepare a ketonic derivative and even forcing conditions[5] failed which had served successfully for the formation of the semicarbazone of the unsaturated ketone I. Similarly, the substance appeared in the non-ketonic fraction during a Girard separation. Nevertheless, the presence of a carbonyl group could be demonstrated in IV by both chemical and spectroscopic means. The infrared spectrum[6] (carbon disulfide) of the alcohol IVa exhibited a band at 1688 cm.$^{-1}$ and

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[1] Paper XVI, St. Kaufmann, This Journal, **73**, 1779 (1951).

[2] A. Wettstein, *Helv. Chim. Acta*, **27**, 1803 (1944).

[3] For a recent review, see L. I. Smith, *Record of Chem. Progress*, **11**, 65 (1950).

[4] The 16-methyl-Δ^{16}-20-ketone III has $[\alpha]^{20}\text{D}$ −105.7°.

[5] R. Fischer, G. Lardelli and O. Jeger, *Helv. Chim. Acta*, **33**, 1335 (1950).

[6] We are grateful to Dr. K. Dobriner and Mrs. P. Humphries, Sloan-Kettering Institute for Cancer Research, New York, for these measurements.

the acetate IVb bands at 1736 cm.$^{-1}$ (acetate carbonyl) and 1685 cm.$^{-1}$, typical of a conjugated ketone.[7] This observation appears consistent with a 16,17-methylene-20-ketone structure as in IV, since the carbonyl band lies in between that for the saturated 20-ketone at 1708 cm.$^{-1}$[7] and the 16-methyl-Δ^{16}-20-ketone III at 1658 cm.$^{-1}$.[6] Furthermore, *i*-cholestenone (VII), the only other known steroidal cyclopropyl ketone exhibits a band at 1691 cm.$^{-1}$[6] and the ultraviolet absorption spectra (Fig. 1) of VII and the 16,17-methylene-20-ketone IV are characteristic[8] of cyclopropyl ketones with strong terminal absorption near 220 mμ. By contrast Δ^5-16-methylpregnen-3β-ol-20-one[2] exhibits relatively low absorption (log ϵ *ca.* 2.0) in that region. The presence of a carbonyl group in IV was established further by lithium aluminum hydride reduction to the alcohol Va, which formed a diacetate (Vb); the dextrorotatory shift on acetylation would indicate the β-configuration for the C-20 hydroxyl group.[9]

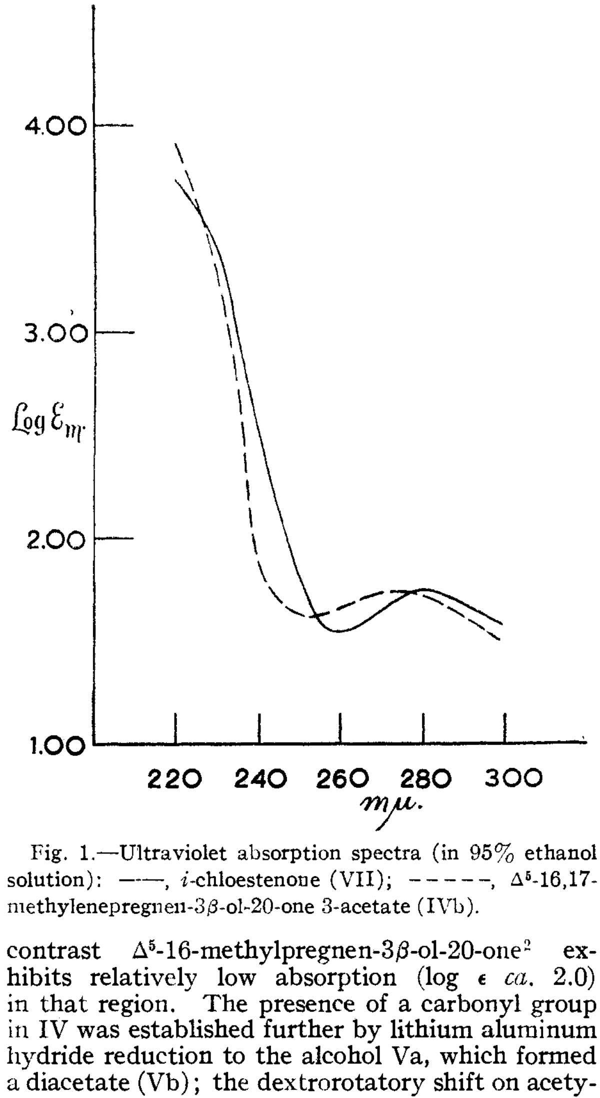
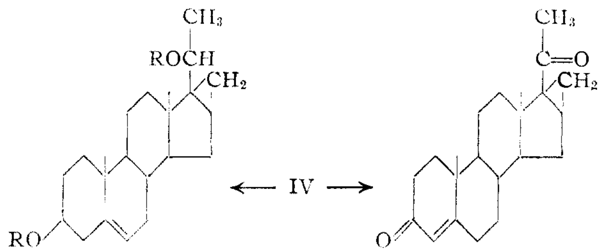
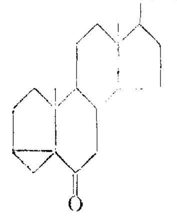


Fig. 1.—Ultraviolet absorption spectra (in 95% ethanol solution): ——, *i*-chloestenone (VII); - - - - -, Δ^5-16,17-methylenepregnen-3β-ol-20-one 3-acetate (IVb).



Va R = H
b R = Ac

VI



VII

Oppenauer oxidation of IVa afforded 16,17-methyleneprogesterone (VI), which exhibited a high maximum at 240 mμ and a strongly positive rotation usually associated with Δ^4-3-ketosteroids. The progestational activity of VI and several other methylated progesterones will be reported elsewhere.

Experimental[10]

Δ^5-16,17-Methylenepregnen-3β-ol-20-one (IV).—A total of 695 g. of the pyrazoline II[2] was decomposed in 100-g. lots by heating at 0.02 mm. in an oil-bath initially at 135° and finally at 175° until gas evolution ceased. Crystallization from ethyl acetate afforded 455 g. (71%) of **Δ^5-16-methylpregnen-3β-ol-20-one 3-acetate (III)** with m.p. 171–174°, which was raised on further recrystallization to m.p. 176–178°, $[\alpha]^{20}$D −105.7° (chloroform), −76° (ethanol), ultraviolet maximum at 250 mμ (log ϵ 4.06). Wettstein[2] obtained this substance in unspecified yield as needles with m.p. 177–178°, $[\alpha]^{23}$D −83° (ethanol). From the mother liquors, there was obtained by direct crystallization 10.3 g. of material with m.p. 194–195° and an additional 21.7 g. (m.p. 187–194°) from the non-ketonic fraction of a Girard separation of the final oil, making a total yield of 5%. The analytical sample of **Δ^5-16,17-methylenepregnen-3β-ol-20-one 3-acetate (IVb)** crystallized from ethyl acetate as colorless crystals with m.p. 194–196°, $[\alpha]^{20}$D +33°, ultraviolet spectrum in Fig. 1, infrared carbonyl bands[6] at 1736 cm.$^{-1}$ and 1685 cm.$^{-1}$ (carbon disulfide).

Anal. Calcd. for $C_{24}H_{34}O_3$: C, 77.79; H, 9.25. Found: C, 77.56; H, 8.92.

Saponification of the acetate IVb with boiling methanolic potassium hydroxide or carbonate led in nearly quantitative yield to **Δ^5-16,17-methylenepregnen-3β-ol-20-one** (IVa), which after recrystallization from ethanol exhibited m.p. 211–213°, $[\alpha]^{20}$D +44°, infrared band at 1688 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{32}O_2$: C, 80.42; H, 9.83. Found: C, 80.54; H, 9.62.

Acetylation with pyridine–acetic anhydride regenerated the acetate IVb. Both the alcohol IVa and the acetate IVb were recovered unchanged on treatment with Girard's reagent P, 2,4-dinitrophenylhydrazine in ethanol-sulfuric acid, and either hydroxylamine or semicarbazide hydrochloride in ethanol–pyridine or ethanol–sodium acetate.

Δ^5-16,17-Methylenepregnen-3β,20β-diol (Va).—A solution of 1.0 g. of the cyclopropyl ketone IVa in 40 cc. of tetrahydrofuran was boiled for one hour with 0.4 g. of lithium aluminum hydride in 25 cc. of the same solvent. After decomposing the excess reagent with acetone, acid was added and the product was extracted with ether. Recrystallization from dilute ethanol followed by hexane–

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[7] R. N. Jones, P. Humphries and K. Dobriner, THIS JOURNAL, **72**, 956 (1950).

[8] I. M. Klotz, *ibid.*, **66**, 88 (1944).

[9] W. Klyne and D. H. R. Barton, *ibid.*, **71**, 1500 (1949). The unknown effect of an adjacent cyclopropane ring in our case makes evidence based on rotation data somewhat uncertain, but the 20β-configuration is supported by analogy to the lithium aluminum hydride reduction of Δ^5-pregnen-3β-ol-20-one (Klyne and Miller, *J. Chem. Soc.*, 1972 (1950)) which also afforded the 20β-isomer.

[10] All melting points are corrected and were determined on the Kofler block. Rotations were measured in chloroform and ultraviolet absorption spectra in 95% ethanol solution. We are indebted to Srta. Paquita Revaque for these measurements and to Srta. Amparo Barba for the microanalyses.

acetone gave the analytical sample (85% yield) of the **diol Va** with m.p. 177–179°, $[\alpha]^{20}\text{D}$ −51°, no selective absorption in the ultraviolet between 216–300 mμ.

Anal. Calcd. for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37. Found: C, 79.75; H, 10.23.

The diacetate Vb (acetic anhydride–pyridine, one hour, steam-bath) was isolated as colorless crystals with m.p. 180–182°, $[\alpha]^{20}\text{D}$ −28° after recrystallization from methanol.

Anal. Calcd. for $C_{26}H_{38}O_4$: C, 75.32; H, 9.24. Found: C, 75.18; H, 8.98.

16,17-Methyleneprogesterone (VI).—A solution of 5.0 g. of Δ^5-16,17-methylenepregnen-3β-ol-20-one (IVa) and 10 g. of aluminum *t*-butoxide in 100 cc. of toluene and 50 cc. of cyclohexanone was refluxed for one hour and then steam distilled. The residue was extracted with ether, washed with a saturated solution of Rochelle salt, dried and evaporated. Crystallization from ethyl acetate gave 3.9 g. of crystals with m.p. 180–187°. The analytical sample of the ketone VI crystallized as long, colorless prisms with m.p. 191–192°, $[\alpha]^{20}\text{D}$ +211°, ultraviolet maximum at 240 mμ (log ε 4.32). A sample was sublimed under high vacuum at 130° before analysis.

Anal. Calcd. for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26. Found: C, 80.74; H, 9.29.

JOINT CONTRIBUTION FROM THE INSTITUTO DE QUÍMICA
UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO
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MEXICO CITY, D. F.

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The Citronellol Problem and the Isolation of α-Citronellol

BY MAURICE D. SUTHERLAND

Despite continuing controversy[1,2] it has been proved,[3,4,5] and recently confirmed[6] that natural citronellol is virtually free from α-citronellol (I), nature offering only β-citronellol (II). Pure α-citronellol has never been isolated, though Doeuvre[7,3] reported that citronellol could be isomerized to a mixture containing about 30 to 50% of 1. This conclusion was based only on ozonolyses, no significant changes in physical properties being detected. Naves[8] also affirmed that "no physical difference, other than the Raman effect, has been demonstrated between citronellol (rhodinol) β-isomer and the mixtures of isomers."

I wish to report the isolation of I in approximately 95% purity by distillation. Citronellol (b.p. (10 mm.) 104.6°, $n^{25}\text{D}$ 1.4540, d^{25}_4 0.8515) from the reduction of citronellol, was obtained by fractional distillation (10 mm. pressure) in a 6-ft. Podbielniak column, and was saponified after heating with benzoyl chloride at 160° for 6 hours. The products were distilled using a reflux ratio of 100 and amongst others, a material of b.p. (10 mm.) 103.0°, $n^{25}\text{D}$ 1.4501 and d^{25}_4 0.8488 was obtained. This was followed by a long series of intermediate fractions leading to unchanged II. Redistillation of selected fractions yielded a purer product (A) of $n^{25}\text{D}$ 1.4494, d^{25}_4 0.8484 and $[\alpha]^{25}\text{D}$ −1.63°. A reflux ratio of 40 was found to be insufficient to produce any worthwhile separation.

β-Citronellol and A differ only in the site of unsaturation, since catalytic hydrogenation of either yields dihydrocitronellol identified as the phenylazophenylurethan,[9] m.p. 86.5–87.5°, clusters of orange plates from hexane (found: C, 72.7; H, 8.05). From the 73% yield of formaldehyde obtained from A by an oxidative procedure[10] and from its optical activity it follows that A is mainly α-citronellol. The proportion of II in A was measured by the Kuhn and Roth[11] ozonization technique, yields of only 5–6% of acetone being obtained, whereas II gave 93–98% yields.

The phenylazophenylurethan (found: C, 72.9; H, 7.51) from A formed clusters of orange plates of m.p. 64–65° from hexane and yielded 3.1% and 4.8% of acetone. The urethan (found: C, 72.6; H, 7.62) from II formed clusters of orange plates of m.p. 69–70° from hexane and yielded 96 and 97% of acetone. A mixture of these urethans, ground together in equal proportions, melted at 64–69° but after fusing or crystallizing together from hexane, the melting point was 66–67.5° indicating that solid solutions are formed by these derivatives of I and II.

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[1] Owen and Simonsen, *Endeavour*, **8**, 26 (1949).

[2] Naves, *Perfumery Essent. Oil Record.*, **40**, 41 (1949).

[3] Doeuvre, *Bull. soc. chim.*, [5] **3**, 613 (1936).

[4] Naves, Brus and Allard, *Compt. rend.*, **200**, 1112 (1935).

[5] Carroll, *Perfumery Essent. Oil Record*, **38**, 226 (1947).

[6] Barnard, *et al.*, *J. Chem. Soc.*, 915 (1950).

[7] Doeuvre, *Bull. soc. chim.*, [4] **45**, 351 (1929).

[8] Naves, *Perfumery Essent. Oil Record*, **37**, 120 (1946).

[9] Davenport and Sutherland, *Univ. Queensland, Papers, Dept. Chem.*, **1**, No. 39 (1950).

[10] Bricker and Roberts, *Anal. Chem.*, **21**, 1331 (1949).

[11] Kuhn and Roth, *Ber.*, **65**, 1285 (1932).

CHEMISTRY DEPARTMENT
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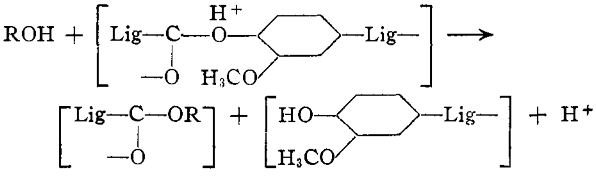
RECEIVED JANUARY 23, 1951

Solubility Effects in Lignin Alcoholysis Reactions

BY CONRAD SCHUERCH, JR.

Evidence gained from studies on isolated ethanol lignins indicates that in the isolation of lignin with ethanol and hydrogen chloride changes occur which include introduction of ethoxyl groups,[1] depolymerization[2] and the liberation of phenolic groups.[3] Making the as yet unproven but plausible assumptions, first that protolignin exists in a high polymeric form, and second that these three reactions are interrelated, one arrives at the conclusion that this isolation method may be an acid-catalyzed solvolytic cleavage of hydrophobic polymer or polymers in the presence of a suitable solvent.[4] In its simplest form such an interpretation can be pictured schematically as follows (ignoring reaction mechanism)



and appears not to conflict with our present qualitative knowledge of the reactions of lignin with mercaptans, alcohols, phenols and perhaps carboxylic acids.[5]

Fortunately this speculation invites experimental verification or disproof by a variety of methods. As a first step in a more rigorous analysis, we choose to adopt the idea as a working hypothesis and to

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[1] W. S. MacGregor, T. H. Evans and H. Hibbert, THIS JOURNAL, **66**, 41 (1944), and many earlier references.

[2] W. B. Hewson and H. Hibbert, *ibid.*, **65**, 1173 (1943), and earlier references.

[3] C. Schuerch, Jr., *ibid.*, **72**, 3838 (1950).

[4] This statement is not completely original, having been stated at least in part by previous workers and in part implied by the term alcoholysis. The author's debt can easily be traced in any of several published reviews and in references listed here.

[5] Similarly the sulfite process is now interpreted as the introduction of hydrophilic functional groups into the lignin complex and a subsequent acid-catalyzed hydrolytic cleavage of lignin–lignin or lignin–carbohydrate bonds. It is not surprising that variable percentages of phenolic groups and variable oxygen contents seem common in lignin sulfonic acid preparations. See H. Erdtman, B. O. Lindgren and T. Petterson, *Acta. Chem. Scand.*, **4**, 228 (1950).