Anal. Calcd. for $C_{22}H_{30}O_3$: C, 77.15; H, 8.83. Found: C, 77.4; H, 9.04.

Oppenauer Oxidation of the *cis-anti-trans*-8α-Hydroxy Compound XV.—The following is an adaptation of the procedure of Wettstein and Meystre.[44] A solution of 0.30 g. of aluminum isopropoxide in 10 ml. of dry toluene was added slowly over a period of 30 minutes to a slowly distilling mixture of 0.300 g. of the 8α-hydroxy compound, m.p. 150–152°, and 3 ml. of cyclohexanone in 20 ml. of toluene (nitrogen atmosphere). The mixture was cooled, 4 ml. of a saturated solution of Rochelle salt was added and steam was passed through the mixture for 1 hr. The residue was taken up in benzene, washed with water, then with saturated brine and finally dried over anhydrous sodium sulfate. The residue, m.p. 115–120°, obtained on evaporation of the solvent was crystallized from methanol to yield 0.200 g. of colorless needles, m.p. 131–133° with previous softening. Recrystallization from acetone–petroleum ether (60–68°) gave 0.162 g. (55% yield) of material, m.p. 131–135°, undepressed on admixture with ketone D described above.

MADISON, WISCONSIN

[44] A. Wettstein and Ch. Meystre, *Helv. Chim. Acta*, **30**, 1262 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Steroid Total Synthesis—Hydrochrysene Approach. IV.[1] 1-Methoxy-6a-hydroxy-8-keto-10a-methyl-5,6,6a,7,8,9,10,10a,11,12-decahydrochrysene and Reduction Products

BY WILLIAM S. JOHNSON, JAMES ACKERMAN,[2] JEROME F. EASTHAM[3] AND H. A. DEWALT, JR.[4]

RECEIVED MAY 31, 1956

The crystalline intermediate produced in the preparation of the tetracyclic ketone IV (from methyl vinyl ketone and the tricyclic ketone I) has been shown to be a mixture of epimeric ketols II and III. Acetylation of the ketols II and III followed by catalytic hydrogenation of the styrene double bond yielded a pair of dihydro compounds V and VI which on treatment with sodium methoxide yielded the same α,β-unsaturated ketone, namely, VII. Reduction of VII gave the *cis-syn-cis* (ketone-C) and the *trans-syn-cis* (ketone-F) isomers. The configuration of the latter has been proved unequivocally (in paper V) by epimerization of the hydrogen at C_{10b} through the agency of an 11-keto group to give the *trans-anti-trans* compound of established (by conversion to a natural product) configuration. The backbone configuration of ketone-C and consequently of the unsaturated ketone and its precursors was thus also established. The structures of some by-products produced in the above reactions have been elucidated and some evidence adduced for the configuration of the hydroxyl group in the ketols. Methods for producing the C- and the F-series stereoselectively from VII have been developed. An air-oxidation product of the enol ether XIV has been shown to have the structure XV or XVI which on treatment with acid or base was isomerized to the diketone XVII. Reduction of the ketol II or of the diol XVIII (obtained from II by the action of lithium aluminum hydride) with lithium and alcohol in ammonia gave the *syn-cis*-diol XIX as the preponderant product The configuration was established by oxidation with chromium trioxide–pyridine to the dihydroketol (V, H in place of Ac) and by lithium aluminum hydride reduction of the dihydroketol acetate V to XIX. When potassium was employed instead of lithium for the reduction of XVIII, in addition to XIX, a small amount of a stereoisomer, possibly the *anti-trans* compound, was isolated.

The base-catalyzed condensation of methyl vinyl ketone with the tricyclic ketone I to give the tetracyclic compound IV has been described.[5] When the condensation was carried out under mild conditions, a crystalline intermediate was formed corresponding in composition to a simple adduct without loss of water. This compound, therefore, could be formulated either as the diketone arising from a Michael addition of I to methyl vinyl ketone or as the ketol structure (formulas II or III). In the present paper evidence is provided in favor of the latter formulation, and in addition results are recorded of a study of the reduction of the 4b,10b-(styrene) double bond of the ketol and of its reactions involving β-elimination of the 6a hydroxyl and reduction of the resulting α,β-unsaturated carbonyl system.

The crystalline intermediate, in fact, proved to be a mixture of the epimeric (at 6a) ketols II and III which could be separated by fractional crystallization into an isomer-a, m.p. 215°, and an isomer-b, m.p. 188°. The proportion of these isomers varied somewhat with the concentration of the base employed in the condensation. When the reaction mixture was about 0.14 *N* with respect to sodium methoxide, 77% of isomer-a and 1.3% of isomer-b could be isolated. With a methoxide concentration of approximately 0.03 *N* the yields were 43 and 18%, respectively. An attempt to effect an acid-catalyzed interconversion[6] of the ketols failed.

The ultraviolet spectra of isomer-a and isomer-b were essentially identical and characteristic of the methoxydihydronaphthalene chromophore (see Fig. 1 in ref. 5). Besides the carbonyl absorption at 5.90 μ in the infrared, strong hydroxyl absorption was observed (mull) at 3.01 μ for isomer-a and at 2.82 μ for isomer-b, thus precluding the open diketone structure for either isomer. Isomer-a consumed two mole equivalents of lithium aluminum hydride as determined by the method of Higuchi and Zuck.[7] In addition, one mole equivalent of hydrogen was liberated in the presence of excess lithium aluminum hydride. These results confirm the presence of one carbonyl and one hydroxyl group.

In the presence of sodium methoxide both the a-

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[1] Paper III, W. S. Johnson, E. R. Rogier, J. Szmuszkovicz, H. I. Hadler, J. Ackerman, B. K. Bhattacharyya, B. M. Bloom, L. Stalmann, R. A. Clement, B. Bannister and H. Wynberg, THIS JOURNAL, **78**, 6289 (1956).

[2] Wisconsin Alumni Research Foundation and Sterling-Winthrop Research Institute Research Assistant, 1952–1954.

[3] Atomic Energy Commission Postdoctoral Fellow, 1952–1953.

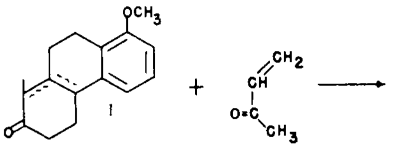
[4] National Research Council Postdoctoral Fellow, 1950–1951.

[5] Paper II, W. S. Johnson, J. Szmuszkovicz, E. R. Rogier, H. I. Hadler and H. Wynberg, THIS JOURNAL, **78**, 6285 (1956).

[6] By an unpublished procedure of A. L. Wilds, *et al.*, for the interconversion of a similar epimeric pair of tricyclic ketols (private communication from Professor Wilds).

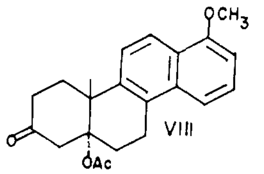
[7] T. Higuchi and D. A. Zuck, THIS JOURNAL, **73**, 2676 (1951). We are indebted to Drs. Higuchi and R. Kuramoto for performing this experiment.

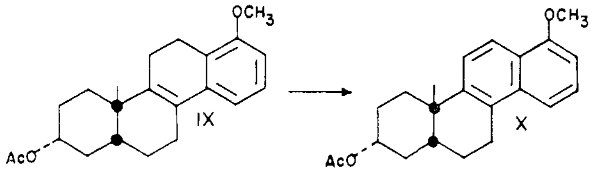
and b-ketol underwent dehydration to the α,β-unsaturated tetracyclic ketone IV. Approximate rates for these reactions were determined spectrophotometrically at 25° in about 0.1 N alcoholic sodium methoxide. The rates were roughly first order with respect to ketol and were about the same (half-life approximately 7.5 hr.) for both epimers.



Obviously these data shed no light on the problem of the configuration of the epimers which is considered below.

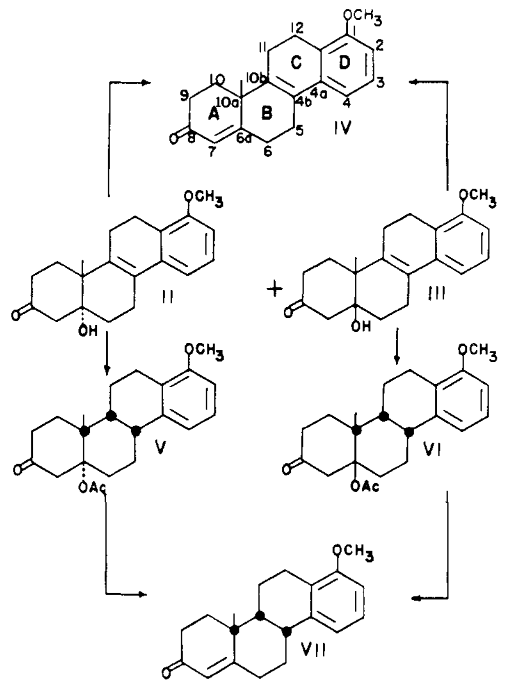
Acetylation of the ketols with either isopropenyl acetate or acetyl chloride gave in good yield an a-acetate, m.p. 154°, and a b-acetate, m.p. 115°, both showing expected double (ester and ketone) carbonyl absorption in the infrared. These acetates were readily converted by catalytic hydrogenation over 30% palladium hydroxide-on-strontium carbonate to an a-dihydroacetate, m.p. 181°, and a b-dihydroacetate, m.p. 147°, represented by formulas V and VI. The ultraviolet spectra of the dihydro compounds were characteristic of the anisole chromophore showing that the styrene (4b, 10b) bond had been reduced.

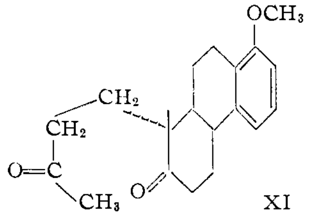




A by-product, m.p. 182°, was isolated from the hydrogenation of the a-acetate. The analysis and ultraviolet spectrum showed it to be the naphthalenic compound VIII presumably resulting from a disproportionation of the dihydronaphthalene ring system. The spectrum was very similar to that of the substance X, m.p. 195°, obtained in our laboratories by H. I. Hadler on dehydrogenation of the acetate IX with selenium dioxide in pyridine and toluene. The naphthalenic compound in the b-series was not isolated, but its presence in the crude hydrogenation product could be demonstrated by ultraviolet spectroscopy.

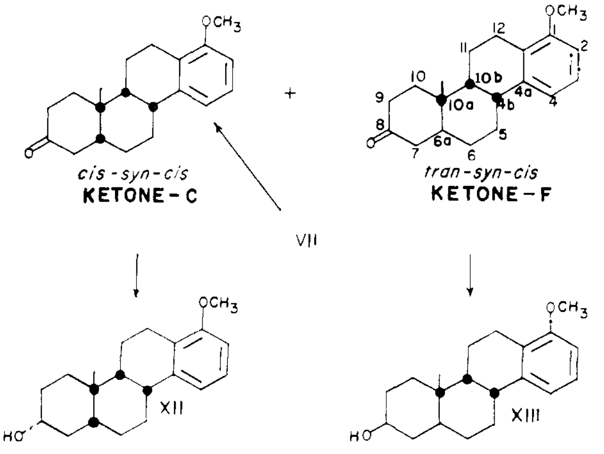
On treatment with sodium methoxide, both the a- and b-dihydroacetates (V and VI) lost the elements of acetic acid to give the same α,β-unsaturated ketone, m.p. 151°, which as shown below has the *syn-cis* configuration (formula VII). The two dihydroacetates (like their precursors), therefore differ in configuration only at C_{6a}. That the steric course of the hydrogenation of the 4b,10b-double bond is the same irrespective of the mode of fusion (*cis* or *trans*) of rings A and B is surprising in view of the fact that the hydrogenation of the corresponding pair of A/B *cis* and *trans* compounds in the 6a-desoxy series (formulas III and II with H in place of OH at 6a) proceeds stereoselectively to give, respectively, the *cis-syn-cis* and the *trans-anti-cis* arrangement.[1] In the 6a-desoxy series the hydrogens thus become attached preferentially on the same (front) side of the molecule bearing the angular methyl group when A/B is *cis*, but on the opposite (back) side when A/B is *trans* which is compatible with the expected mode of adsorption of these molecules on the surface of the catalyst.[1] The striking effect of an acetoxyl group at C_{6a} on the steric course of the hydrogenation may be rationalized by examination of molecular models. With the A/B *cis* form the approach of the catalyst to the back side is hindered by the bending of ring A toward the back just as in the case of the C_{6a}-desoxy derivative. With the *trans* isomer, the backside approach is relatively hindered by the bulky acetoxy group. Catalyst adsorption, and hence hydrogenation, is consequently preferred on the front face in both epimers.





Chromatography of the product of methoxide-catalyzed dehydroacetoxylation of the a-dihydroacetate V gave, in addition to the unsaturated ketone VII, a 2% yield of a compound, m.p. 202°, which proved to be the a-dihydroketol (formula V with H in place of Ac) as shown by acetylation to re-form the a-dihydroacetate in good yield. While this is an expected product of alcoholysis, we were surprised to find that the same a-dihydroketol was produced as a by-product in the dehydroacetoxylation of the b-dihydroacetate. This latter transformation is likely to occur only *via* a reverse aldol reaction, and indeed the intermediary diketone XI, m.p. 146°, could be isolated in yields as high as 28% when either the a- or the b-dihydroacetate was treated with methanolic methoxide for 1 instead of 4 hr. The structure of XI was established by the infrared spectrum which exhibited strong twin carbonyl absorption at 5.83 and 5.87 μ but none in the hydroxyl region. The diketone XI could be cyclized by sodium methoxide to VII, but only in 15% yield, which indicates that the major reaction in the methoxide-catalyzed dehydroacetoxylation of V (giving VII in over 80% yield) is a direct β-elimination and does not proceed *via* XI. The dehydroacetoxylation of VI, which gives VII in 56% yield, may, however, proceed *via* the diketone and the ketol corresponding to V. Such behavior is consistent with the A/B configurational assignments given. The axial (β) hydrogen atom at C_7, removal of which is required for direct β-elimination in the ketol acetate VI, is so crowded (see below) by the convex shape of the *cis-syn-cis* molecule that the base might be expected to attack preferentially the hydrogen of the C_{6a}-hydroxyl (formed first by alcoholysis of the acetate), thus initiating reverse aldolization.

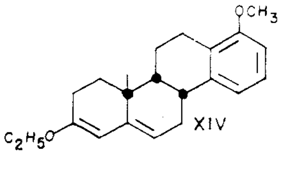
If the a-dihydroketol is the stereoisomer of thermodynamic control—a reasonable assumption in view of the probable reversibility of the reactions involved—this suggests also that the a-series is A/B *trans* and the b- *cis*, because the C_{6a}-α-axial (to ring B) hydroxyl of the A/B *trans* form would probably interfere less with the axial (to ring B) 11α-methylene group, than would the C_7-α-axial methylene group of the A/B *cis* form.[8] Further evidence for these configurational assignments is presented below.



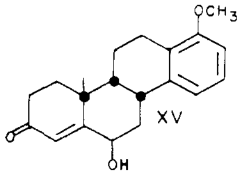
Catalytic hydrogenation of the unsaturated ketone VII in the presence of 5% palladium-on-carbon and a trace of potassium hydroxide proceeded readily to saturate the double bond α,β to the carbonyl group giving a mixture of C_{6a}-epimers, namely, ketones-C and -F. The latter, m.p. 163°, could be separated in poor yield by fractional crystallization. The configuration has been proved unequivocally as *trans-syn-cis* by conversion to the *trans-anti-trans* series (of established configuration by conversion to a natural product) by epimerization of the C_{10b}-hydrogen through the agency of a carbonyl group at C_{11}.[9] On reduction with lithium aluminum hydride, ketone-F was converted stereoselectively to an alcohol, m.p. 107 or 144°, undoubtedly having the hydroxyl group oriented in the β-configuration[10] (formula XIII). This material gave a precipitate with digitonin and formed an acetate, m.p. 135°.

Lithium aluminum hydride reduction of the mixture of ketones-C and -F described above, followed by acetylation yielded a mixture which could be separated readily by chromatography into a crystalline acetate, identical with that (described above) derived from ketone-F, and an oily acetate. The latter on saponification gave an alcohol, m.p. 127°, the identity of which with the C-alcohol XII was confirmed by Oppenauer oxidation. The oxidation product, m.p. 105°, was identical with the substance already described as ketone-C arising from catalytic hydrogenation of the tetracyclic ketone IV.[1] By the manner in which it was produced in the present work, ketone-C must be the C_{6a}-epimer of the 163° ketone (F) of known configuration (see above). Ketone-C, therefore, is established as the *cis-syn-cis* isomer.

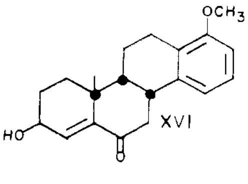
When the hydrogenation of the α,β-unsaturated ketone VII was conducted in the presence of hydrobromic acid instead of alkali, the steric course of the reaction was altered, and the product was almost entirely ketone-C. The F series could also be obtained stereoselectively by reducing the α,β-un-



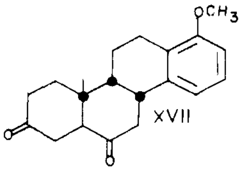
XIV



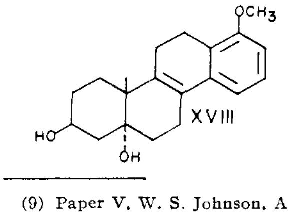
XV



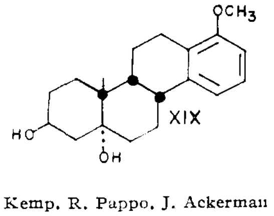
XVI



XVII



XVIII



XIX

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[8] The energy difference due alone to the *cis* and *trans* arrangements of rings A and B (exclusive of any interactions of ring C) would probably be very small: *cf.* the effect of angular substituents on the energy differences of *cis-* and *trans*-decalin, R. B. Turner, This Journal, **74**, 2118 (1952). The fact that the a-ketol (A/B *trans*) is favored over the b-form at higher concentrations of base (equilibration conditions?) is suggestive that even with these ketols, having two angular substituents and little if any interaction by ring C, the *trans* may be detectably more stable than the *cis* form.

[9] Paper V, W. S. Johnson, A. D. Kemp, R. Pappo, J. Ackerman and W. F. Johns, This Journal, **78**, 6312 (1956).

[10] *Cf.* footnotes 20 and 21 cited in paper III (ref. 1).

saturated ketone with lithium and alcohol in ammonia.[11,1] The F-alcohol XIII was thus produced directly in good yield. Selective hydrogenation of the enol ether XIV, m.p. 123°, was not stereoselective as in other cases[12,1] but gave after hydrolysis a mixture of ketones-C and -F.

A by-product, m.p. 206°, encountered in the preparation of the enol ether XIV proved to be an oxidation product which could be deliberately produced in 18% yield by aeration of a warm solution of pure XIV in benzene. The analysis and infrared spectrum (hydroxyl band at 2.93 μ and unsaturated carbonyl band at 5.96 μ) were compatible with a hydroxylated form of VII. The hydroxy ketone, on treatment with base or acid, was isomerized to a saturated diketone, m.p. 188°. This behavior suggests that the 206° compound is represented by formula XV or XVI, which is isomerized to the diketone XVII, a known type of reaction in the steroids.[13]

Reduction of ketol-a (II) with lithium aluminum hydride gave a mixture of diols, epimeric at C_8. The preponderant isomer melting at 153 or 166° was presumably[10] the 8β-hydroxy compound XVIII. The epimeric (presumably 8α-hydroxy) compound melting at 189° was isolated in 3% yield. An attempt to produce an acetonide from the preponderant diol failed, which is consistent with the assignment of the *trans* orientation of the hydroxyl groups.

Reduction of ketol-a (II) or of the diol-a (XVIII) with lithium and alcohol in ammonia[11,1] gave in over 50% yield a single product which was shown (see below) to be the *syn-cis* compound XIX. This product consisted of a mixture of polymorphic forms, and its homogeneity could be demonstrated by conversion to the diacetate, which was obtained in two separable and interconvertible dimorphic modifications. The structure was deduced by analogy[1] and confirmed by the ultraviolet spectrum which exhibited anisole rather than methoxydihydronaphthalene absorption proving that the styrene bond had, indeed, been reduced. The *syn-cis* configuration was demonstrated by oxidation with chromium trioxide–pyridine[14] to the a-dihydroketol (V, H in place of Ac) in 65% yield. Confirmation of this conclusion was afforded by lithium aluminum hydride reduction of the a-dihydroacetate V to a polymorphic diol XIX indistinguishable from that obtained directly from XVIII or II. The diol XIX was extremely resistant to Oppenauer oxidation. Chromatography of the product of one such attempt yielded mainly starting material along with a 5% yield of the diketone XI which arose, evidently, by the reverse aldol reaction of what little ketol was produced.

The formation of the same (*syn-cis*) configuration on reduction of the styrene bond either by the carbanion process or by catalytic hydrogenation was surprising, since we expected the former conditions to favor the thermodynamically more stable *anti-trans* arrangement.[1,15] This observation shows that the course of carbanion reductions may indeed be controlled by factors (probably steric) other than the thermodynamic stability of the product.

Sarett, *et al.*,[16] found that in the carbanion reduction of an α,β-unsaturated acid, involving the introduction of a new asymmetric center at the β-carbon, one stereoisomer was favored when lithium was employed, while the epimeric (probably the more stable) form was favored with potassium. This discovery, which incidentally constitutes another exception to the rule,[15] prompted us to try the latter metal in the reduction of the diol XVIII. The stereo course of the reaction thus appeared to be altered to a small extent. Acetylation and chromatography yielded as the major product (51% yield) the known diacetate of XIX. A new stereoisomeric diacetoxy compound, m.p. 151–157° (dimorphic mixture), perhaps the *trans-anti-trans* diol, was isolated in 7% yield. We also isolated a small amount of a monoacetoxy compound, either the 8-acetoxy-$\Delta^{6,6a}$ compound produced by acid-catalyzed elimination of the 6a-hydroxyl group during the acetylation process or the product of hydrogenolysis of the 6a-hydroxyl (see Experimental part). This acetate was not readily saponified under moderate conditions—suggestive of an axial C_8-acetoxy group—but was readily converted into the corresponding hydroxy compound, m.p. 148°, with lithium aluminum hydride.

The preferential production of the *syn-cis* configuration on carbanion reduction of the a-diol, provides further presumptive evidence for the *trans* A/B ring fusion. With these rings *cis* locked, the reduction would be expected to proceed as already established with the 8α-hydroxy A/B *cis* compound III (H in place of OH) to give the *anti-trans* arrangement,[1] because the hydroxyl group at C_{6a} would be equatorially oriented with respect to ring B and thus essentially out of the sphere of influence of the styrene bond. (We have yet to investigate the reduction of the b-diol and confirm this behavior.) With A/B *trans* locked, on the contrary, the 6-hydroxyl is axial to ring B and in the alkoxide form during reduction would be expected to inhibit assumption of anionic character by the 10b-carbon on the same (α) side of the molecule. The preferred β-orientation of the C_{10b}-anionic intermediate would accordingly result in β-protonation. The reductive protonation at C_{4b} might be similarly influenced by the C_{6a}-hydroxyl or may simply be a thermodynamic consequence of the (more strongly influenced) reduction at C_{10b}, the *trans-syn-cis*, being more stable than the *trans-syn-trans* arrangement.[17]

Acknowledgment.—We wish to thank the agencies mentioned in footnotes 2–4 for supporting this work.

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[11] *Cf.* A. L. Wilds and N. A. Nelson, This Journal, **75**, 5360 (1953).

[12] H. H. Inhoffen, G. Stoeck, G. Kölling and U. Stoeck, *Ann.*, **568**, 52 (1950).

[13] I. M. Heilbron, E. R. H. Jones and F. S. Spring, *J. Chem. Soc.*, 801 (1937); C. P. Balant and M. Ehrenstein, *J. Org. Chem.*, **17**, 1587 (1952).

[14] The method of G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, This Journal, **75**, 422 (1953).

[15] D. H. R. Barton and C. H. Robinson, *J. Chem. Soc.*, 3045 (1954).

[16] G. E. Arth, G. I. Poos, R. M. Lukes, F. M. Robinson, W. F. Johns, M. Feurer and L. H. Sarett, This Journal, **76**, 1715 (1954).

[17] W. S. Johnson, *Experientia*, **7**, 315 (1951); This Journal, **75**, 1498 (1953).

Experimental[18]

1-Methoxy-6a-hydroxy-8-keto-10a-methyl-5,6,6a,7,8,9,-10,10a,11,12-decahydrochrysene (II and III).—To a solution of 3.30 g. of crystalline tricyclic ketone I, m.p. 95–96°, in 50 ml. of anhydrous methanol was added (under nitrogen) 10 ml. of 0.4 *N* sodium methoxide in methanol. The mixture was chilled to 0°, and a cold solution of 2.10 g. of freshly distilled methyl vinyl ketone in 20 ml. of methanol was added rapidly with stirring. After standing for 2 hr. in the cold and for 58 hr. at room temperature, 2.58 g. (60% yield) of colorless crystals of isomer-a (A/B *trans*,[19] formula II), m.p. 204–206°, separated. Recrystallization from *n*-butyl acetate gave 2.22 g. (52% yield) of pure **isomer-a** as colorless prisms, m.p. 214–215.5° (in an evacuated capillary), λ_{max} 221 mμ (log ϵ 4.42), 269 (4.06); λ_{min} 243 (3.69); λ_{max}^{mull} 3.01 μ (OH), 5.90 (C=O).

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 77.0; H, 7.77.

Functional group analysis by the method of Higuchi and Zuck[7] gave the following results, cholesterol being employed as a control:

	Sample wt., g.	Equivalent × 10⁻⁴ Calcd.	Found
Cholesterol	1.707	44.2	44.5
	1.684	43.6	43.0
Ketol-a	0.925	59.2	54.5
	0.996	63.8	60.0

The active hydrogen determination was carried out in an apparatus essentially like that described for studying the decarboxylation of acids.[20] The reaction flask (250-ml. capacity) was charged with 200 ml. of a saturated solution of lithium aluminum hydride in tetrahydrofuran. After introduction of a sample, the hydrogen evolution was usually complete in about 15 minutes at room temperature. With cholesterol, which was used as a control, it was necessary to warm the reaction mixture to dissolve the compound. The following results were obtained:

	Sample wt., g.	Volume of hydrogen, corr. to S.T.P., ml. Calcd.	Found	Number of active hydrogens
Cholesterol	0.250	14.5	13.6	0.94
	.312	18.1	19.2	1.06
Ketol-a	.326	23.3	22.6	0.97
	.231	16.6	18.3	1.10

In another run with 12.1 g. of freshly recrystallized[21] tricyclic ketone, m.p. 85–103° (mixture of bond isomers),[5] 4 ml. of methyl vinyl ketone and 9 ml. of 4 *N* sodium methoxide in 250 ml. of methanol, there was obtained 12.5 g. (80% yield) of crude crystalline product. Fractional crystallization from methanol gave a total of 11.9 g. (77% yield) of crude isomer-a in fractions melting between 200–207° and 206–212°; 0.20 g. (1.3% yield) of crude isomer-b, m.p. 186–190°; and a trace of the unsaturated ketone IV. In a run carried out just like that described directly above, except that 12.0 g. of tricyclic ketone and only 2 ml. of 4 *N* sodium methoxide were employed, the total crude crystalline mixture of ketols amounted to 11.0 g. Fractional crystallization from methanol gave 6.70 g. (43%) of crude isomer-a in fractions melting between 201–207° and 205–211°; 2.86 g. (18%) of crude isomer-b (A/B *cis*,[19] formula III) in fractions melting from 183–186° and 185–188°; and 0.25 g. (1.7%) of the unsaturated ketone IV, m.p. 170–174°.

After repeated recrystallization from methanol, **isomer-b** was obtained as colorless hexagonal crystals, m.p. 185–188°, λ_{max} 222 mμ (log ϵ 4.44) 270 (4.10); λ_{min} 244 (3.7); λ_{max}^{mull} 2.82 μ (OH), 5.90 (C=O).

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.9; H, 7.71.

An attempt[6] to isomerize 0.25 g. of ketol-a by heating with 40 ml. of toluene and 2 ml. of concentrated hydrochloric acid for 5 hr. at reflux gave a total of 38% recovered isomer-a but no isomer-b. In a similar experiment with isomer-b, none of isomer-a was isolated.

Rates of Dehydration of a- and b-Ketols.—The ultraviolet spectra of these two isomers are essentially identical (see above). They show a λ_{min} in the 240 mμ region which was selected for observing conversion to the α,β-unsaturated ketone, since the latter has strong absorption at 242 mμ. A series of known mixtures of a-ketol II and α,β-unsaturated ketone was prepared, and it was found that the increase in % of the latter was accompanied by a linear increase in optical density at 242 mμ.

Stock solutions were prepared by dissolving 16.2 mg. of the ketols (a-, m.p. 216.5–218.5° and b-, m.p. 184.5–186.5°) in 100 ml. of optically-void, oxygen-free, 95% ethanol and diluting a 10-ml. aliquot of each solution to 100 ml. with the 95% ethanol, giving a molar concentration of 5.2×10^{-5}. For the determinations, 0.5 ml. of stock solution was admixed with 1 ml. each of distilled water and of a solution prepared by dissolving 2.5 g. of sodium in 100 ml. of the 95% ethanol. The solution was then diluted to 10 ml. with the 95% ethanol and maintained at 25 ± 0.5°. The optical density at 242 mμ was determined with a Cary spectrophotometer against a blank solution prepared as described above (but without the ketol) and similarly maintained at 25 ± 0.5°. The results of typical runs are shown in Table I, where

$$\%\text{ ketol} = c = 100 - \frac{(d_t - d_0)\,100}{0.37}$$

TABLE I

OPTICAL DENSITY MEASUREMENTS OF ALCOHOLIC ALKALINE SOLUTIONS OF a- AND b-KETOLS

t, time, hr.	*d*, optical density at 242 mμ	*c*, % a-ketol	*t*, time, hr.	*d*, optical density at 242 mμ	*c*, % b-keto
0	0.132	100	0	0.130	100
2.12	.215	78	0.25	.140	97
6.7	.30	55	2.28	.202	81
18.9	.42	22	7.1	.29	57
30.7	.51	0	19.1	.41	24
43.0	.51	0	43.7	.48	5

Acetylation of Ketol-a (II).—The preferred method of acetylation is with isopropenyl acetate: a mixture of 160 ml. of this reagent, 0.2 g. of *p*-toluenesulfonic acid monohydrate and 31.20 g. of crude ketol-a, m.p. 198–203°, was heated on the steam-bath for 4 hr., dissolution being complete after 1.5 hr. The acid was neutralized with a few drops of pyridine, the solvent evaporated in a current of air and the residue dissolved in hot 95% ethanol. The solution was filtered, concentrated to about 120 ml. and allowed to cool, whereupon 33.20 g. (94%) of a-acetate, m.p. 152–153°, crystallized. A lower-melting modification was also encountered (see below).

The alternative method of acetylation follows: a mixture of 2.00 g. of ketol-a, 2 ml. of acetyl chloride and 250 ml. of dry benzene was boiled under reflux for 12 hr., then washed thoroughly with 10% sodium carbonate followed by saturated salt solution.

Concentration and cooling gave 1.41 g. of the crude **a-acetate**, m.p. 137–142°. Two recrystallizations from 95% ethanol gave 1.33 g. of colorless plates, m.p. 144–145°. The higher-melting modification was finally obtained as colorless prisms, m.p. 153.5–154.5°, λ_{max} 5.78 μ (ester C=O), 5.83 (ketone C=O).

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.5; H, 7.21.

Like the free ketol, the acetate was converted to the unsaturated ketone by methanolic sodium methoxide.

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[18] The new substances described herein are racemic compounds, but the prefix "*dl*" has been omitted. Unless otherwise indicated melting points of analytical specimens are corrected for stem exposure. Ultraviolet absorption spectra were determined on either a Beckman model DU quartz spectrophotometer or a Cary recording spectrophotometer (model 11 MS), 95% alcohol being employed as the solvent. Infrared spectra were determined on a Baird double beam infrared recording spectrophotometer, model B. Unless otherwise specified, carbon disulfide was used as the solvent.

[19] Tentative configuration.

[20] W. S. Johnson and W. E. Heinz, THIS JOURNAL, **71**, 2913 (1949).

[21] If the ketone was not freshly crystallized, the yields were significantly lower.

The ketol was converted to the unsaturated ketone also by heating with *p*-toluenesulfonic acid in a 1:1 mixture of *n*-butyl acetate and toluene, although the yield was only 32%.

The oxime of the a-acetate was obtained from alcohol as colorless rods, m.p. 239–240° dec.

Anal. Calcd. for $C_{22}H_{27}O_4N$: C, 71.52; H, 7.37. Found: C, 71.5; H, 7.34.

The 2,4-Dinitrophenylhydrazone of the a-acetate was obtained as yellow crystals from ethanol, m.p. 183.8–184.5°.

Anal. Calcd. for $C_{28}H_{30}O_7N_4$: C, 62.91; H, 5.66. Found: C, 63.2; H, 5.90.

Acetylation of Ketol-b (III).—A mixture of 3.32 g. of ketol-b, m.p. 183–188°, 25 ml. of isopropenyl acetate and 0.02 g. of *p*-toluenesulfonic acid monohydrate was heated on the steam-bath for 1.5 hr. and worked up as described above for the a-isomer. The crystallized product amounted to 3.25 g. (first crop), m.p. 113–115.5°, and 0.12 g. (second crop), m.p. 112–116°, or a total yield of 89%. Recrystallization of the combined crops from 95% ethanol gave 2.84 g. (75%) of the b-acetate, m.p. 114–116°.

The alternative procedure of refluxing a solution of 0.92 g. of ketol-b, m.p. 184–194°, in 25 ml. of acetyl chloride for 10 hr. yielded after crystallization 0.77 g. (first crop), m.p. 111–114.5°, and 0.11 g. (second crop), m.p. 107–110°. Recrystallization of the combined crops gave 0.75 g. (72%) of the b-acetate, m.p. 113.5–116°. Repeated recrystallization from 95% ethanol gave the **b-acetate** as colorless prisms, m.p. 114–115.5°, λ_{max} 5.78 μ (ester C=O), 5.85 (ketone C=O).

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.35; H, 7.44.

1-Methoxy-6a-acetoxy-8-keto-10a-methyl-4b,5,6,6a,7,8,-9,10,10a,10b,11,12-dodecahydrochrysene. (a) **The** ***trans***[19]**-*syn-cis* Isomer V.**—A solution of 4.63 g. of the a-acetate (see above), m.p. 145.5–146.5°, in 200 ml. of 95% ethanol (pretreated with Raney nickel) was hydrogenated over 1.5 g. of 30% palladium hydroxide-on-strontium carbonate catalyst[22] at 30–40 p.s.i. and room temperature. After shaking for 20 hr. one mole equivalent of hydrogen had been absorbed and the reaction was interrupted. The mixture was filtered, the catalyst washed on the filter with hot benzene to dissolve product which had crystallized, and the combined filtrate and washings were evaporated. Crystallization of the residue from 95% ethanol gave 3.73 g. (80% yield) of colorless product, m.p. 177–181°.

In another similar run on 2.24 g. of the a-acetate, m.p. 144–145°, in which a 1:1 mixture of ethyl acetate and 95% ethanol was employed as the solvent, the crude product, m.p. 175–179°, was obtained in 85% yield. Recrystallization from 95% ethanol gave 1.86 g. (83% yield) of colorless rhombic plates, m.p. 180–181.5°, λ_{max} 272 mμ ($\log \epsilon$ 3.26), 279 (3.28); λ_{min} 245 (2.45), 276 (3.21); λ_{max} 5.78 μ (ester C=O), 5.85 (ketone C=O).

Anal. Calcd. for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.0; H, 8.10.

The combined mother liquors from several such hydrogenation experiments deposited on long standing a small amount of a by-product which, after repeated recrystallization from methanol, was obtained as colorless prisms, m.p. 177–182°. The ultraviolet spectrum—λ_{max} 224 mμ ($\log \epsilon$ 4.71), 287 (3.83), 298 (3.87), 312 (3.74), 325 (3.60); λ_{min} 257 (3.55), 290 (3.82), 309 (3.69), 322 (3.37)—resembled very closely that of X described below. This by-product is, therefore, assigned the structure **1-methoxy-6a-acetoxy-8-keto-10a-methyl-5,6,6a,7,8,9,10,10a-octahydrochrysene (VIII).**

Anal. Calcd. for $C_{22}H_{24}O_4$: C, 74.97; H, 6.86. Found: C, 74.8; H, 6.87.

The proportion of VIII present in the crude hydrogenation product was estimated to be about 4% from the extinction at 325 mμ.

(b) **The *cis*[19]-*syn-cis* Isomer (VI).**—A 2.84-g. sample of the b-acetate, m.p. 114–116°, was hydrogenated in 60 ml. of 95% ethanol over 1.5 g. of 30% palladium hydroxide-on-strontium carbonate[22] as described above for the a-acetate. The hydrogenation stopped after one mole equivalent of hydrogen was absorbed (23 hr.). Crystallization of the crude product from 95% ethanol gave 1.50 g. (first crop), m.p. 146–148°; 0.60 g. (second crop), m.p. 144–147°; and 0.15 g. (third crop), m.p. 144–145.5°. The total yield was thus 2.25 g. or 79%. Recrystallization of the combined crops gave 1.90 g. (67%) of colorless crystals, m.p. 146–147°. Repeated recrystallization gave material having the same m.p., λ_{max} 272 mμ ($\log \epsilon$ 3.22), 279 (3.28); λ_{min} 245 (2.40), 276 (3.17); λ_{max} 5.78 μ (ester C=O), 5.85 (ketone C=O).

Anal. Calcd. for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.2; H, 8.25.

The extinction at 325 mμ of the total crude hydrogenation product indicated the presence of 15–20% of the disproportionation product (C_{6a}-epimer of VIII), which, however, was not isolated.

***cis*-1-Methoxy-8α-acetoxy-10a-methyl-5,6,6a,7,8,9,10,10a-octahydrochrysene (X).**—The experiment described below was performed by H. I. Hadler. It is noteworthy that the conventional procedure utilizing alcohol as the solvent did not effect reaction even after refluxing for 24 hr.

A solution of 0.100 g. of the acetate of IX,[1] m.p. 131–134°, in 5 ml. of dry toluene was added to 0.065 g. of selenium dioxide dissolved in 5 ml. of dry pyridine. The mixture was boiled under reflux overnight, cooled, filtered to remove selenium and the filtrate evaporated on the steam-bath in a stream of nitrogen. The residue was dissolved in benzene, treated with Norit, filtered and evaporated. The residue, m.p. 178–192°, was crystallized from acetone–methanol (Norit) giving 0.079 g. (79% yield) of almost colorless needles, m.p. 195–198°. Repeated crystallization and sublimation at 170° (0.05 mm.) gave material melting at 195.2–195.6°, λ_{max} 227.5 mμ ($\log \epsilon$ 4.70), 285 (3.74), 295.5 (3.84), 310 (3.67), 323 (3.46); λ_{min} 254 (3.08), 288 (3.74), 308 (3.63), 321 (3.13).

Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 78.4; H, 7.99.

An 0.0785-g. sample of the above acetate, m.p. 195–198°, in 5 ml. of dioxane and 20 ml. of ether was cleaved to the free 8α-hydroxy compound by the action of excess lithium aluminum hydride (0.00077 mole) in 3 ml. of ether. The product was isolated as already described.[23] After crystallization from acetone–petroleum ether (60–68°), there was obtained 0.058 g. (84% yield) of colorless silky needles of ***cis*-1-methoxy-8α-hydroxy-10a-methyl-5,6,6a,7,8,9,10,-10a-octahydrochrysene**, m.p. 181.4–182.5°. Repeated recrystallization and sublimation at 160° (0.05 mm.) gave material melting at 183.4–184.4°.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.8; H, 8.22.

***syn-cis*-1-Methoxy-8-keto-10a-methyl-4b,5,6,8,9,10,10a,-10b,11,12-decahydrochrysene (VII).** (a) **From the a-Dihydroacetate V.**—A solution of 17.80 g. of V (see above), m.p. 173–180°, in 100 ml. of dry benzene was added to a solution of 7 g. of sodium in 750 ml. of absolute methanol, and the mixture was boiled under reflux for 5 hr. Acetic acid was added to the orange solution until it turned yellow, and most of the solvent was removed under reduced pressure. Water and benzene were added to the residue, the layers were separated and the aqueous layer extracted thoroughly with ether. The combined organic solutions were washed with saturated brine, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The yellow crystalline residue (14.48 g.), m.p. 132–144°, was crystallized from 95% ethanol to give 10.61 g. (first crop), m.p. 148–150°, and 1.85 g. (second crop), m.p. 146–149°. The total yield was thus 12.46 g. or 84%. Repeated recrystallization gave material, which usually crystallized as colorless prisms, m.p. 150–151°, although occasionally a lower-melting (140°) modification was encountered as colorless prisms. The purest material had λ_{max} 232 mμ ($\log \epsilon$ 4.27), 240 (4.26), 278 (3.30); λ_{min} 236 (4.25), 275 (3.27).

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.9; H, 8.31.

The 2,4-dinitrophenylhydrazone was obtained from ethyl acetate–95% ethanol as red needles, m.p. 211–212.5°.

Anal. Calcd. for $C_{26}H_{28}O_5N_4$: C, 65.53; H, 5.92. Found: C, 65.7; H, 6.04.

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[22] See footnote 39 in ref. 1.

[23] See ref. 1 under the preparation of "VII."

(b) **From the b-Dihydroacetate VI.**—A solution of 1.90 g. of VI (see above), m.p. 144–145.5°, in 5 ml. of benzene was treated with a solution of 2 g. of sodium in 250 ml. of methanol essentially as described above for the a-isomer. The crude product was partly oily and was therefore chromatographed on 40 g. of F-20 Alcoa Activated Alumina. The benzene eluate yielded 1.00 g. of crystalline material which on recrystallization from 95% ethanol gave 0.59 g. (first crop) of the α,β-unsaturated ketone VII, m.p. 150–151°, and 0.30 g. (second crop), m.p. 146–149°. The total yield was thus 0.89 g. or 56%. Admixture of the first crop material with the analytical specimen derived from the a-isomer gave no depression of the m.p. The infrared spectra of the two specimens were identical.

1-Methoxy-6a-hydroxy-8-keto-10a-methyl-4b,5,6,6a,7,8,9,10,10a,10b,11,12-dodecahydrochrysene was isolated as a by-product in the dehydroacetoxylation reactions as follows. The crude product from the dehydroacetoxylation of 2.91 g. of the a-isomer V, m.p. 177–179° (see above), was chromatographed on 30 g. of F-20 Alcoa activated alumina. Elution with benzene gave the crude α,β-unsaturated ketone in 89% yield. Further elution with isopropyl alcohol gave 0.053 g. (2% yield) of material, m.p. 201–203°. Repeated recrystallization from 95% ethanol gave small colorless cubical prisms, m.p. 199–202°, $\lambda_{\max}$ 272 mμ (log ϵ 3.27), 278 (3.30); $\lambda_{\min}$ 244 (2.40), 275 (3.22); $\lambda_{\max}^{\text{mull}}$ 2.92 μ (OH), 5.80 (C=O).

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.3; H, 8.52.

Acetylation of this ketol with isopropenyl acetate gave in 85% yield, the a-dihydroacetate V, m.p. 179–181.5°, undepressed on admixture with the authentic material described above.

Similarly the isopropyl alcohol eluate from the chromatography of the product from the b-isomer VI described above yielded 0.056 g. (3% yield) of the same ketol, m.p. 201–204°, undepressed on admixture with the material derived from the a-isomer. Acetylation gave in 87% yield the a-dihydroacetate V, m.p. 181–182°, undepressed on admixture with the authentic material.

1-(γ-Keto-*n*-butyl)-1-methyl-2-keto-8-methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (XI).—Treatment of 0.504 g. of the a-dihydroacetate V, in 15 ml. of benzene with a solution of 0.5 g. of sodium in 100 ml. of methanol exactly as described above except that the mixture was refluxed for only one hour, yielded 0.498 g. of a crude product as an oil. On dissolution in 95% alcohol and standing, 0.125 g. (28% yield) of the crude diketone, m.p. 141–145°, crystallized. Repeated recrystallization gave colorless needles, m.p. 145–146°, $\lambda_{\max}$ 271 mμ (log ϵ 3.18), 278 (3.20); $\lambda_{\min}$ 244 (2.30), 275 (3.13); $\lambda_{\max}$ 5.83 μ (C=O), 5.87 (C=O).

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.3; H, 8.57.

A similar experiment with 0.200 g. of the b-isomer VI, m.p. 146–147°, gave 0.050 g. (28% yield) of the diketone, m.p. 146–146.5°, undepressed on admixture with the analytical specimen derived from the a-isomer.

The cyclization of the diketone (0.420 g., m.p. 145–146°) was effected by heating under reflux for 4 hr. with a solution of 0.5 g. of sodium in 100 ml. of anhydrous methanol. The product was isolated by a combination of crystallization and chromatographic procedures described above, and the yield of α,β-unsaturated ketone was 0.200 g. (51%), m.p. 147–148.5°, undepressed on admixture with authentic material (see above).

Catalytic Hydrogenation of the α,β-Unsaturated Ketone VII in the Presence of Alkali.—In a typical experiment 0.46 g. of the α,β-unsaturated ketone, m.p. 150.5–151.5°, was hydrogenated in about 16 ml. of benzene and 4 ml. of 95% ethanol, containing 1 drop of 15% potassium hydroxide, over 0.25 g. of 5% palladium-on-carbon[24] at room temperature and atmospheric pressure. After agitation for 6.5 hr., 1 mole equivalent of hydrogen had been absorbed and uptake had ceased. The mixture was filtered and the solvent evaporated leaving 0.43 g. of colorless crystalline residue, m.p. 119–140°. Four recrystallizations from petroleum ether (60–68°) yielded 0.04 g. of ***trans-syn-cis*-1-methoxy-8-keto-10a-methyl-4b,5,6,6a,7,8,9,10,10a,10b,11,12-dodecahydrochrysene** (ketone-F) as colorless prisms, m.p. 162.5–163.5°. The m.p. was not altered by further recrystallizations, although occasionally a less stable form was encountered which melted at 149–151°, resolidified, then remelted at the higher temperature. The purest material showed $\lambda_{\max}$ 271 mμ (log ϵ 3.14), 278 (3.16); $\lambda_{\min}$ 244 (2.43), 275 (3.09); $\lambda_{\max}$ 5.90 μ (C=O).

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78. Found: C, 80.4; H, 8.91.

The 2,4-dinitrophenylhydrazone was obtained from chloroform–95% ethanol as orange leaflets, m.p. 242–243.5°.

Anal. Calcd. for $C_{26}H_{30}O_5N_4$: C, 65.26; H, 6.32. Found: C, 64.9; H, 6.49.

***trans-syn-cis*-1-Methoxy-8β-hydroxy-10a-methyl-4b,5,6,6a,7,8,9,10,10a,10b,11,12-dodecahydrochrysene (XIII).**—To a stirred solution of 0.425 g. of ketone-F, m.p. 161–163°, in 10 ml. of dry benzene, 80 ml. of dry ether and 25 ml. of purified dry dioxane, was added 15 ml. of 1 *M* lithium aluminum hydride in ether over a 5-minute period. The solution was boiled under reflux for 2.5 hr., ethyl acetate added to decompose the excess lithium aluminum hydride, and the mixture was acidified (to litmus) with dilute sulfuric acid. The aqueous layer was separated, extracted thoroughly with ether, and the combined organic layers were washed with saturated brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave 0.481 g. of oily residue which was chromatographed on 15 g. of F-20 Alcoa activated alumina. Elution with 2:3 chloroform–benzene gave 0.427 g. of colorless oil which on crystallization from benzene–petroleum ether (90–100°) afforded 0.286 g. (first crop), m.p. 89.5–92°, and 0.067 g. (second crop), m.p. 103–107°. The m.p. of a mixture of the two crops was 90–105° (polymorphism?). The total yield was thus 0.353 g. or 82%. Repeated recrystallization gave colorless crystals, m.p. 105–107°, $\lambda_{\max}$ 2.74 μ (OH). A polymorphic modification, m.p. 143–144°, has since been obtained. The pure material gave a precipitate with digitonin.[25]

Anal. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.8; H, 9.27.

The acetate was prepared directly from the crude product of reduction (see above) of 0.355 g. of ketone-F, m.p. 162.5–164°, by heating with 15 ml. of isopropenyl acetate and 0.01 g. of *p*-toluenesulfonic acid monohydrate on the steam-bath for 2 hr. Pyridine (2 drops) was added and the solvent evaporated leaving 0.405 g. of brown oily residue which was chromatographed on 12 g. of F-20 Alcoa activated alumina. Elution with 1:1 benzene–petroleum ether (60–68°) and further with benzene alone, gave a total of 0.319 g. (78% yield, from ketone-F) of crystalline acetate, m.p. 126–129°. Repeated recrystallization from petroleum ether (60–68°) gave colorless clusters of leaflets, m.p. 134.5–135.5°, $\lambda_{\max}$ 5.80 μ (C=O).

Anal. Calcd. for $C_{22}H_{30}O_3$: C, 77.15; H, 8.83. Found: C, 76.9; H, 8.85.

Separation of the Mixture Obtained on Catalytic Hydrogenation of VII *via* the 8-Acetoxy Derivatives.—An 0.78-g. sample consisting of the total crude mixtures obtained from hydrogenations of VII carried out essentially as described above was reduced with 40 ml. of 1 *M* lithium aluminum hydride according to the procedure described above. The crude oily product (0.731 g.) was acetylated with 40 ml. of isopropenyl acetate and 0.02 g. of *p*-toluenesulfonic acid monohydrate as described above to give 0.875 g. of a crude mixture of acetates which was chromatographed on 40 g. of alumina (see above). The fractions eluted with petroleum ether (60–68°) through 1:3 benzene–petroleum ether yielded a total of 28 mg. of oil which was discarded. Elution with 1:2 through 2:5 benzene–petroleum ether gave a total of 0.313 g. of oily acetate. The last of the 2:3 benzene–petroleum eluates contained 0.049 g. of oily and 7 mg. of crystalline acetate. The latter was combined with subsequent 1:1 benzene–petroleum ether through pure benzene eluates to give a total of 0.115 g. of crude acetate of XIII which on recrystallization afforded 0.070 g., m.p. 130–132°, undepressed on admixture with the authentic acetate described above.

The 0.313-g. fraction was rechromatographed on 25 g. of Florisil and elution with 7:3 benzene–petroleum ether

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[24] *Org. Syntheses*, **26**, 77 (1946).

[25] The procedure of C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 687 (1950), was employed.

60–68°) yielded 0.297 g of a colorless, but still oily, acetate. A portion was evaporatively distilled at 180° (0.015 mm.), λ_{max} 5.78 μ (ester C=O).

Anal. Calcd. for $C_{22}H_{30}O_3$: C, 77.15; H, 8.83. Found: C, 76.2; H, 8.96.

The remainder (0.179 g.) of the rechromatographed oily acetate was saponified by heating with 30 ml. of methanol and 5 ml. of 15% potassium hydroxide solution. After refluxing 5 hr., the mixture was acidified with acetic acid and evaporated in a current of air. Water and ether were added to the residue, the aqueous layer was extracted thoroughly with ether and combined ether layers were washed with saturated brine. Evaporation of the ether gave 0.232 g. of oily residue which was chromatographed on 6 g. of F-20 Alcoa activated alumina. Elution with 2:3 chloroform–benzene gave 0.144 g. (18% over-all yield from ketone VII) of crystalline *cis-syn-cis*-**1-methoxy-8α-hydroxy-10a-methyl-4b,5,6,6a,7,8,9,10,10a,10b,11,12-dodecahydrochrysene (XII)**, m.p. 121–124.5°. Repeated recrystallization from petroleum ether (90–100°) gave colorless hexagonal crystals, m.p. 125–127°, undepressed on admixture with the material prepared by lithium aluminum hydride reduction of the 105° ketone (C).[1]

Anal. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 80.0; H, 9.25.

Oxidation of the *cis-syn-cis*-Tetrahydro Alcohol XII.—The following is a slight modification of an established procedure.[26] A mixture of 0.065 g. of the tetrahydro alcohol XII, m.p. 125–127°, 80 ml. of dry toluene, 20 ml. of freshly distilled cyclohexanone and 0.4 g. of aluminum isopropoxide was boiled under reflux for 20 hr. Excess dilute sulfuric acid was added, and the toluene and excess cyclohexanone were removed by steam distillation. The aqueous residue was extracted thoroughly with ether and the combined ether solutions washed with saturated brine and dried over anhydrous magnesium sulfate. The oily residue (0.080 g.) left upon evaporation of the ether was chromatographed on 3 g. of F-20 Alcoa activated alumina. The fraction eluted with 1:1 benzene–petroleum ether (60–68°) amounted to 0.026 g. (40% yield) of the *cis-syn-cis*-tetrahydro-8-keto compound (ketone-C), m.p. 99–102°. Recrystallization from methanol gave colorless prisms, m.p. 104–106.5°, undepressed on admixture with the analytical specimen of ketone-C, m.p. 103–105°, described in paper III.[1] The infrared spectra of the two specimens, moreover, were identical.

Catalytic Hydrogenation of the α,β-Unsaturated Ketone VII in the Presence of Hydrobromic Acid.—A mixture of 0.800 g. of the α,β-unsaturated ketone, m.p. 148–150°, 25 ml. of 4:1 benzene–95% ethanol, one drop of 48% hydrobromic acid and 0.100 g. of 10% palladium-on-carbon[27] was agitated with hydrogen at room temperature and atmospheric pressure. After 3 hr. one mole equivalent of hydrogen had been absorbed and the uptake ceased. The mixture was filtered and the filtrate evaporated leaving 0.774 g. (96%) of crude ketone-C, m.p. 97–101°. Recrystallization from 95% ethanol gave in 74% recovery, colorless material, m.p. 98.5–101°.

A specimen (0.191 g.) of the crude ketone, m.p. 97–101°, was reduced with lithium aluminum hydride as described in paper III.[1] The yield of recrystallized alcohol XII, m.p. 123–125°, was 0.127 g. or 66% which is comparable to that obtained from ketone-C produced in another way.[1] The m.p. was undepressed on admixture with the analytical specimen described above.

Lithium Reduction[11] of the α,β-Unsaturated Ketone VII.—A mixture of 4.00 g. of the α,β-unsaturated ketone, m.p. 149–151°, 100 ml. of absolute ethanol and 1200 ml. of liquid ammonia was stirred while 2.5 g. of lithium wire was added over a 2–3 minute period during which the solution became deep blue in color. An additional 5 g. of lithium wire was then added over a 20-minute period and stirring was continued for an additional 10 minutes, the blue color gradually fading. Ether was added slowly and the ammonia evaporated by warming the flask first in a water-bath then on the steam-bath. Water (500 ml.) was added, the aqueous layer was separated and washed thoroughly with ether. The combined ether solutions were washed with saturated brine, dried over anhydrous sodium sulfate and evaporated. The red oily residue (4.27 g.) was heated for 3 hr. on the steam-bath with 50 ml. of isopropenyl acetate and 0.1 g. of *p*-toluenesulfonic acid monohydrate. The crude product was isolated as described above and crystallized from 95% ethanol to give 3.24 g. (first crop), m.p. 130–132°, and 0.41 g. (second crop), m.p. 128–130°. The total yield of the acetate of XIII from the α,β-unsaturated ketone was thus 3.65 g. or 79%

In a similar experiment 0.500 g. of the α,β-unsaturated ketone, m.p. 148–149°, was reduced with 1.7 g. of lithium in 200 ml. of ammonia and 20 ml. of ethanol. The crude oily hydroxy compound was chromatographed directly on 12 g. of F-20 Alcoa activated alumina. Elution with benzene gave 0.025 g. of oily material. Elution with 1:24 chloroform–benzene afforded 0.015 g. (3% yield) of crude ketone-F, m.p. 156–163°. Finally, elution with 1:1 chloroform–benzene gave 0.443 g. (88% yield) of the *trans-syn-cis*-hydroxy compound XIII, m.p. 140–143°, undepressed on admixture with authentic material (see above). In other runs the yields of ketone-F were 1–10% and of hydroxy compound XIII 87–94%.

1-Methoxy-8-ethoxy-10a-methyl-4b,5,9,10,10a,10b,11,12-octahydrochrysene (XIV).—The procedure was essentially the same as that described for the preparation of the 4b,10b-dehydro compound.[1] Thus from 2.48 g. of the α,β-unsaturated ketone VII, m.p. 148–149.5°, 12.5 ml. of benzene, 2.5 ml. of absolute ethanol, 3.0 ml. of ethyl orthoformate and a total of 0.45 ml. of 15% hydrogen chloride in absolute ethanol (added in 0.25-, 0.10- and 0.10-ml. portions), there was obtained, on crystallization of the crude oily product from 30 ml. of 95% ethanol, 2.12 g. (78% yield) of the enol ether, m.p. 110–117°. Repeated recrystallization from 95% ethanol containing a trace of pyridine gave material, m.p. 117–120° (evacuated capillary). After sublimation at 115° (0.02 mm.), the m.p. was 121–123° (evacuated capillary), λ_{max} 241 mμ (log ε 4.37), 278 (3.23); λ_{min} 275 (3.17).

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.7; H, 8.81.

Hydrogenation and Hydrolysis of the Enol Ether XIV.—A 1.00-g. sample of the enol ether, m.p. 117–121° (evacuated capillary), was hydrogenated in a total of 16 ml. of benzene and 8 ml. of 95% ethanol over 0.5 g. of 6% palladium-on-strontium carbonate[28] at room temperature and atmospheric pressure. After agitation for 47 minutes, one mole equivalent of hydrogen had been absorbed and the reaction was interrupted. One milliliter of pyridine was added, the mixture was filtered and the filtrate evaporated in a current of air. The oily residue, which could not be induced to crystallize, was dissolved in 2 ml. of benzene and 14 ml. of 95% ethanol. Water (2 ml.) was added, the mixture was warmed and a solution of 0.4 ml. of concentrated sulfuric acid in 4 ml. of water was added. Since no crystalline material was obtained on cooling, pyridine was added to neutralize the acid, the solvents evaporated and the benzene-soluble portion of the residue chromatographed on 20 g. of F-20 Alcoa activated alumina. The fractions eluted with 1:1 benzene–petroleum ether (60–68°) through pure benzene were crystalline and amounted to 0.372 g. These fractions all melted over wide ranges, as low as 100° and as high as 130°, reminiscent of the mixtures of ketones-C and -F obtained on catalytic hydrogenation of VII in the presence of alkali (see above). As in this case also, crystallization of the combined crystalline fractions from 95% ethanol gave a small amount (0.17 g.) of crude ketone-F, m.p. 134–140°. There was no indication of the presence of α,β-unsaturated ketone in these fractions as shown by the ultraviolet absorption spectra.

By-product of Air Oxidation of the Enol Ether XIV. (a) Isolation from Mother Liquors.—After standing at room temperature in contact with air, the combined crystallization mother liquors from several preparations of the enol ether deposited some colorless crystals, m.p. 200–203°. Repeated recrystallization from 95% ethanol gave the hydroxy α,β-unsaturated ketone XV or XVI as colorless prisms, m.p. 205.5–206°, λ_{max} 230 mμ (log ε 4.30), 278 (3.27); λ_{min} 275 (3.17); λ_{max}^{mull} 2.93 μ (OH), 5.96 (C=C—C=O).

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.6; H. 7.88.

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(26) C. Djerassi in R. Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 235.

(27) Supplied by the American Platinum Works.

(28) See footnote 33, ref. 1.

(b) **Formation by Aeration at Reflux Temperature.**—A slow stream of air was passed through a refluxing solution of 0.110 g. of the enol ether, m.p. 117–120° (evacuated capillary), in 30 ml. of benzene for 6 hr. The solvent was then evaporated in a current of air and the residue crystallized from a small volume of 95% ethanol to give 0.035 g. of starting material, m.p. 118.5–120° (evacuated capillary). The residue obtained upon evaporation of the mother liquor was chromatographed on 3 g. of F-20 Alcoa activated alumina. Elution with 3:2 chloroform–benzene gave 0.026 g. of oily material followed by 0.019 g. of crude hydroxy α,β-unsaturated ketone, m.p. 188–199°. Recrystallization gave material melting at 201–204° alone or on admixture with the analytical specimen described above.

trans-syn-cis-**1-Methoxy-6,8-diketo-10a-methyl-4b,5,6,6a,7,8,9,10,10a,10b,11,12-dodecahydrochrysene (XVII).** (a) **By Base-catalyzed Isomerization.**—A solution of 0.2 g. of sodium in 10 ml. of methanol was admixed with a solution of 0.100 g. of the hydroxy ketone XV or XVI, m.p. 200–203°, in 10 ml. of methanol, and the solution was boiled under reflux for 2.5 hr. The mixture was cooled, acidified with acetic acid and concentrated. Ether and water were added, the aqueous layer extracted with ether, and the combined ether solutions were dried over anhydrous magnesium sulfate. Evaporation of the ether gave 0.085 g. of yellow oil which was chromatographed on 4 g. of F-20 Alcoa activated alumina. The fraction eluted with 2:3 chloroform–benzene amounted to 0.063 g. (63% yield) of colorless crystals, m.p. 181–185°. Repeated recrystallization from 95% ethanol gave colorless, elongated prisms, m.p. 186–188°, λ_{max} 272 mμ (log ϵ 3.23), 279 (3.24): λ_{min} 275 (3.19); λ^{mull}_{max} 5.86 μ (C=O).

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.7; H, 8.09.

(b) **By Acid-catalyzed Isomerization.**—A solution of 0.100 g. of the hydroxy ketone, m.p. 200–203°, and 5 ml. of concentrated hydrochloric acid in 15 ml. of 95% ethanol was boiled under reflux for 2 hr. Most of the alcohol was evaporated in a current of air, and the remaining pink solution was neutralized with saturated sodium bicarbonate solution. The resulting pale yellow solution was extracted thoroughly with ether, and the combined ether solutions were washed with saturated brine. Evaporation of the ether gave 0.075 g. of partially crystalline residue. Crystallization from 95% ethanol gave 0.045 g. (45% yield) of diketone, m.p. 184–187°, undepressed on admixture with the analytical specimen described above under part a.

Reduction of a-Ketol (II) with Lithium Aluminum Hydride.—Five grams of the a-ketol, m.p. 213–218°, was dissolved by refluxing in 100 ml. of tetrahydrofuran (purified by boiling with, then distilling from in succession potassium hydroxide, sodium and finally lithium aluminum hydride). The solution was cooled to about 40°, and 20 ml. of 0.5 *M* lithium aluminum hydride in ether was added dropwise at such a rate that the mixture boiled gently without external heating. After the addition was complete (about 10 minutes), the mixture was heated under reflux for 2.5 hr., then 3 ml. of dry ethyl acetate was added dropwise to the warm solution. After the addition (10 minutes), the mixture was allowed to stand for 10 minutes. It was acidified with dilute hydrochloric acid, more ether was added; then the organic layer was separated, washed with dilute hydrochloric acid, then with saturated brine and filtered through anhydrous sodium sulfate. The solution was concentrated to a volume of about 25 ml., 75 ml. of hot petroleum ether (95–100°) was added, and the concentration continued until the volume was about 35 ml. The crystals obtained on cooling and scatching were separated and washed with petroleum ether (62–66°); yield 4.0 g., m.p. 145–155°. This mixture was boiled under reflux with 95 ml. of ether until solution was complete. On concentration to a volume of 45 ml. and cooling, the solution deposited 0.54 g. of crystals, m.p. 160–175°. Recrystallization from ether as above gave 0.17 g. (3.4% yield) of **1-methoxy-$6a\alpha,^{19}8\alpha^{19}$-dihydroxy-10a-methyl-5,6,6a,7,8,9,10,10a,11,12-decahydrochrysene** (C_8-epimer of XVIII), m.p. 187–189°. One additional recrystallization gave colorless rods, m.p. 188.2–188.8° (evacuated capillary).

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.1; H, 8.33.

The mother liquor material from the first recrystallizations of the 4.0 g. mixture of diols (see above) was fractionally recrystallized from ether–petroleum ether (62–66°) to give a total of 3.58 g. (71% yield) of the **$6a\alpha,^{19}8\beta^{19}$-dihydroxy compound (XVIII)** as a mixture of polymorphs, m.p. 153–163°, consisting of two forms which could be separated mechanically. The preponderant form consisted of long colorless rods, m.p. 163–166°.

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.4; H, 8.46.

The second modification was obtained as large colorless prisms, m.p. 151–153°.

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.3; H, 8.39.

Recrystallization of either of the pure forms regenerated the mixture of crystals melting between 153 and 166°. Admixture of either of the pure polymorphic forms with the 188° diol described above gave a marked depression of the m.p.

An attempt to produce an acetonide from 0.400 g. of the diol, m.p. 153–166°, by stirring with 40 ml. of acetone and 5 g. of anhydrous copper sulfate for 72 hr. at room temperature failed. The product isolated (0.38 g.) consisted of starting material, m.p. 153–166°.

Reduction of the a-Ketol (II) with Lithium in Ammonia.—A solution of 20.0 g. of the a-ketol, m.p. 213–218°, in 1 l. of purified (see above) tetrahydrofuran was added slowly to a vigorously stirred solution of about 7 g. of lithium wire in 3 l. of dry ammonia. When about one-third of this tetrahydrofuran solution was added, an additional 7 g. of lithium was introduced; and at the two-thirds point, a final 6 g. of lithium was added making the total amount of metal 20 g. After the final third of the solution was added, the mixture was stirred for 45 minutes, then a mixture of 250 ml. each of ether and absolute ethanol was introduced whereupon the solution, originally blue, turned colorless. Most of the ammonia was evaporated (finally at the steam-bath) and gradually replaced by ether. Water (1.5 l.) was added, the ether layer washed with two 1-l. portions of water, once with dilute hydrochloric acid and finally with saturated brine. After filtration through anhydrous sodium sulfate, the ether solution (about 1500 ml.) was diluted with 200 ml. of benzene and concentrated to a volume of about 200 ml. Crystallization occurred on cooling and swirling. Thus a total of 13.5 g. (in two crops) of crude **1-methoxy-$6a\alpha,^{19}8\beta^{19}$-dihydroxy-10a-methyl-4b,5,6,6a,7,8,9,10,10a,10b,11,12-dodecahydrochrysene (XIX)** was isolated. Recrystallization from chloroform gave 12.1 g. (60% yield) of colorless prisms, m.p. 210–217°. Repeated recrystallizations from a variety of solvents failed to improve the m.p. significantly. Once material, m.p. 220–223°, was obtained, but on recrystallization this specimen melted at 212–222°. The acetylation experiment described below indicates the polymorphic nature of this mixture. The analytical specimen melted at 210–217°, λ_{max} 272 mμ (log ϵ 3.23), 278 (3.30). The infrared spectrum showed no carbonyl absorption.

Anal. Calcd. for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.78; H, 8.96.

A similar reduction of 1.0 g. of the a-ketol using sodium in place of lithium afforded 0.46 g. of the diol, m.p. 214–220°, undepressed on admixture with authentic material.

Acetylation of the Diol XIX.—A solution of 0.50 g. of the diol, m.p. 212–217°, prepared as described above (part a) in 10 ml. of isopropenyl acetate containing one drop of concentrated sulfuric acid was heated on the steam-bath for 40 minutes. The solution was neutralized with 0.1 ml. of pyridine, concentrated and the oily residue crystallized from methanol to give 0.39 g. (62% yield) of the **diacetate**, m.p. 149.5–153.5°. The infrared spectrum showed no absorption in the hydroxyl region.

Anal. Calcd. for $C_{24}H_{32}O_5$: C, 71.97; H, 8.05. Found: C, 72.0; H, 8.12.

On recrystallization a higher melting modification was obtained admixed with the lower melting form, so that such products usually melted between 150 and 170°. A sample, m.p. 173–178°, was obtained after chromatography on acid-washed alumina and elution with benzene. The infrared spectra of this specimen and of the 149.5–153.5° sample described above were identical.

Reduction of the Diol XVIII with Metals in Ammonia.—When 0.5 g. of the diol, m.p. 150–153°, was reduced by lithium (0.5 g.) as described above, there were obtained

0.24 g. of the diol, m.p. 212–220°, and, after acetylation of the residues, 0.15 g. of diacetate, m.p. 150–160° (low-melting form).

In another experiment a solution of 2.00 g. of the diol, m.p. 156–166°, in 50 ml. of purified (see above) tetrahydrofuran was added over a 15-minute period to a solution of 4 g. of potassium in 400 ml. of ammonia. An additional 4 g. of potassium was added, the mixture stirred for 30 minutes, then 15 ml. of absolute ethanol in 100 ml. of dry ether was added. The ammonia was removed (see above) and replaced by ether, water was added and the ether layer washed with water, dilute hydrochloric acid, again with water and dried over anhydrous potassium carbonate. One-tenth of this solution was concentrated to a volume of about 5 ml. and on cooling 0.062 g. (31% yield) of colorless crystals, separated, m.p. 193–207°. Recrystallization gave 0.051 g., m.p. 202–214°, which had an infrared spectrum essentially identical with the diol XIX. This product was evidently contaminated with another (isomeric) material since several recrystallizations were required to raise the m.p. above 210°. Attempts to isolate other materials by fractional crystallization failed.

The remaining nine-tenths of the ether solution of the crude product (see above) was evaporated, and the pale yellow crystalline residue (1.81 g.) was heated on the steam-bath with 30 ml. of isopropenyl acetate and 0.08 ml. of sulfuric acid for 40 minutes. Pyridine (0.3 ml.) was added, the solution concentrated at reduced pressure and ether was added. The ether solution was washed with water, dilute hydrochloric acid, dried over anhydrous potassium carbonate and evaporated. The residue (crystalline) was dissolved in 25 ml. of benzene, 25 ml. of petroleum ether (60–68°) was added and the solution placed on a chromatographic column of 150 g. of F-20 Alcoa activated alumina.

The major fraction eluted with 1:1 benzene–petroleum ether (60–68°) amounted to 0.029 g., m.p. 150–159°. Recrystallization from ether–petroleum ether gave 0.023 g. of a crude monoacetoxy compound, m.p. 148–153°, which was probably contaminated with some diacetoxy compound.

Anal. Calcd. for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29. Calcd. for $C_{22}H_{30}O_3$: C, 77.15; H, 8.83. Found: C, 76.8; H, 8.36.

A 0.05-g. sample of this crude acetate in 1 ml. of tetrahydrofuran was treated with 1 ml. of 1 *M* lithium aluminum hydride, and the mixture was heated under reflux for 1 hr. The product was isolated as described above, and crystallization from petroleum ether (60–68°) gave 0.038 g. (86% yield) of crude hydroxy compound, possibly 1-methoxy-8-hydroxy-10a-methyl-4b,5,7,8,9,10,10a,10b,11,12-decahydrochrysene, m.p. 140–148°. Recrystallization raised the m.p. to 145–148°, λ_{max} 272 mμ (log ϵ 3.26), 278 (3.34); λ_{min} 244 (2.34), 276 (3.19).

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78. Found: C, 80.2; H, 8.90.

This substance might alternatively be formulated as **1-methoxy-8-hydroxy-10a-methyl-4b,5,6,6a,7,8,9,10,-10a,10b,11,12-dodecahydrochrysene**,[29] (Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39).

Further elution of the chromatographic column with pure benzene gave two products. From the earlier fractions a new diacetoxy compound, stereoisomeric with the diacetate of XIX, was isolated. The yield after two recrystallizations from 60–68° petroleum ether was 0.0145 g., m.p. 151–157°. The ultraviolet spectrum was identical with that of the diacetate of XIX. Partial resolidification was observed during melting, indicative of polymorphism.

Anal. Calcd. for $C_{24}H_{32}O_5$: C, 71.97; H, 8.05. Found: C, 71.8; H, 8.28.

From the later fractions of the benzene elution a total of 1.17 g. (51% yield) of the known diacetate of XIX was isolated after crystallization from ether–petroleum ether (60–68°). This material, m.p. 172–178°, was largely in the higher-melting form, and its infrared spectrum was identical with that of the lower-melting analytical specimen described above. Treatment of a specimen with lithium aluminum hydride gave the diol XIX as the usual polymorphic mixture, m.p. 210–218°.

Oxidation of the Diol XIX. (a) **By Chromium Trioxide in Pyridine.**[14]—Chromium trioxide (0.030 g.) was added to 0.3 ml. of dry pyridine, the mixture was swirled until it turned to an orange paste, then 0.100 g. of the diol, m.p. 212–220°, was added and the mixture kept in the refrigerator for 48 hr. with occasional swirling. Water and ether were added, the mixture shaken vigorously and the ether layer was decanted, washed with dilute hydrochloric acid, water, dilute sodium hydroxide and finally dried over anhydrous potassium carbonate. The ether was concentrated, cooled, and the material which crystallized was twice recrystallized from ether to give 0.065 g. of the a-dihydroketol (formula V with H in place of Ac), m.p. 196–203°, undepressed on admixture with the analytical specimen, m.p. 199–202°, described above.

(b) **By the Oppenauer Method.**—A slight modification of a general procedure[26] was used. A mixture of 0.300 g. of the diol, m.p. 212–220°, 11 ml. of toluene, 3 ml. of cyclohexane and 0.26 g. of aluminum isopropoxide was boiled under reflux for 3 hr. and then allowed to stand at room temperature overnight. Ether was added and the mixture washed with dilute hydrochloric acid, followed by saturated brine and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue crystallized from 95% ethanol to give 0.115 g. of needles, m.p. 214–219°, undepressed on admixture with starting material. Evaporation of the mother liquor and crystallization of the residue from benzene gave an additional 0.045 g. of crude diol, m.p. 207–216°. The mother liquor was chromatographed on 5 g. of F-20 Alcoa activated alumina. The benzene eluate was recrystallized from ether–petroleum ether (60–68°) to give 0.015 g. (5% yield) of material, m.p. 140–142°, undepressed on admixture with diketone XI. The infrared spectra of the two specimens were identical.

Lithium Aluminum Hydride Reduction of the a-Dihydroacetate V.—A 0.050-g. sample of the a-dihydroacetate (see above), m.p. 180.5–182°, was dissolved in 4 ml. of purified (see above) tetrahydrofuran, 0.7 ml. of 1 *M* ethereal lithium aluminum hydride was added and the resulting clear solution was boiled under reflux for 1.5 hr. Excess ethyl acetate in ether was added, followed by dilute hydrochloric acid. The organic layer was washed with dilute hydrochloric acid, then with water and dried over anhydrous sodium sulfate. Evaporation and crystallization from benzene–ether gave 0.030 g. of a mixture of needles and prisms, which could be separated mechanically. The latter melted at 210–222°, and the m.p. was not depressed on admixture with the analytical specimen of the diol XIX described above: the infrared spectra of the two were identical. The needles melted at 197–202°, but the m.p. was not depressed on admixture with the prisms, the mixture melting at 197–222°.

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[29] *Cf.* the comparable hydrogenolysis product described by P. Bladon, H. B. Henbest, E. R. H. Jones, B. J. Lovell and G. F. Woods, *J. Chem. Soc.*, 125 (1954).