purple color of the solution. The mixture was refluxed one hour, filtered, and the solvent removed from the filtrate, leaving a yellow liquid that rapidly solidified into long needles. The solid was dissolved in 50 cc. of 80% ethanol containing 2 g. of potassium hydroxide and then heated for two hours. This solution was poured into a large volume of water, extracted with ether, dried, and the solvent removed. Treatment of the residue with petroleum ether gave 0.53 g. of the iodomonoglycol, m.p. 91.5–92° (from ethanol) (lit.[8] 92°).

Hydroxylation of II with Silver Iodobenzoate.—A 0.5-g. sample of II on treatment with silver iodobenzoate, as just described, gave 0.3 g. of an iodomonoglycol, m.p. 111.5–112°. A 1:1 mixture of this iodoglycol with that obtained from the natural monoölefin (m.p. 91.5–92°), melted 82–101°.

Anal. Calcd. for $C_{22}H_{37}O_3I$: C, 55.34; H, 7.74. Found: C, 55.05; H, 7.65.

Hydroxylation of I Using Osmium Tetraoxide.—A 0.1-g. sample of I was oxidized with osmium tetraoxide using the procedure previously described[12] giving the glycol, m.p. 98.4–99.2° (from ligroin), in 64% yield.

Anal. Calcd. for $C_{22}H_{38}O_3$: C, 75.38; H, 10.93. Found: C, 75.60; H, 10.80.

Periodic acid cleavage[21] of this glycol using the procedure previously described[10] gave *n*-heptaldehyde which was identified as the 2,4-dinitrophenylhydrazone.

Hydroxylation of II with Performic Acid.—A 0.1-g. sample of II was oxidized with performic acid using the procedure previously described[12] giving 0.1 g. of a glycol, m.p. 98.5–99° (from ligroin). A mixed melting point of this material with the glycol obtained by osmium tetroxide oxidation of I showed no depression.

Separation of a Mixture of 4-Iodo-3-pentadecylanisole and the Iodoglycol Prepared from I.—A 1:1 mixture of 4-iodo-3-pentadecylanisole[6] and the iodoglycol prepared from I started to melt at 45° and was completely melted at 75–80°. A 0.16-g. sample of this mixture was dissolved in 7 cc. of warm ethanol. On cooling, a voluminous precipitate formed which was filtered giving 0.04 g. of the 4-iodo-3-pentadecylanisole, m.p. 41–44°. The solvent was removed from the filtrate, and the residual oil was dissolved in 5 cc. of hot methanol. On cooling, a white precipitate formed which was recrystallized from a small volume of ligroin, giving 0.05 g. of the iodoglycol of I, m.p. 91.5–92°. The mixture was thus shown to be separated readily by the recrystallization procedure employed in an earlier investigation.[5]

Acknowledgment.—The authors are indebted to the Lederle Laboratories Division of the American Cyanamid Co. for a grant to Columbia University for support of this investigation.

NEW YORK, NEW YORK

[21] M. L. Malaprade, *Bull. soc. chim. France*, **1**, 833 (1934).

[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY OF NATURAL PRODUCTS, NATIONAL HEART INSTITUTE, NATIONAL INSTITUTES OF HEALTH]

Reduction of Phenols. New Synthesis of Oxyhexahydro-3-ketophenanthrenes by Cyclodehydration of 4-(β-Arylethyl)-1,3-cyclohexandiones

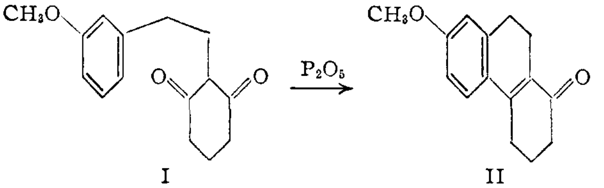
BY GORDON N. WALKER*

RECEIVED JULY 16, 1957

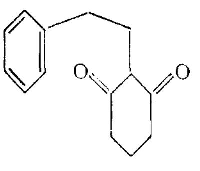
3-Aryl-7-acetoxycoumarins (III), prepared by condensation of methoxyphenylacetic acids with 2,4-dihydroxybenzaldehyde in the presence of acetic anhydride and three moles of potassium acetate, are hydrolyzed and reduced to α-aryl-β-(2,4-diketocyclohexyl)-propionic acids (V) by hydrogenation at 80° in the presence of 10% palladium–charcoal and dilute alkali. Polyphosphoric acid cyclization of methoxyphenyl compounds (V) gives methoxy-substituted 1,2,3,9,10,10a-hexahydro-3-keto-9-carboxyphenanthrenes (VI). The related *m*-hydroxyphenyl compound X, obtained in the same way as V, is cyclized by warm, dilute hydrochloric acid to 1,2,3,9,10,10a-hexahydro-3-keto-7-hydroxy-9-carboxyphenanthrene (XI). Proof for the structures of these compounds is given, notably decarboxylation to corresponding ketones and aromatization to 3-phenanthrols. A possible mechanistic interpretation of the cyclization is offered.

Introduction

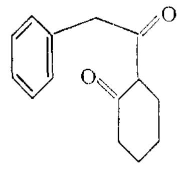
Robinson and Schlittler,[1] in 1935, found that 2-(β-*m*-methoxyphenylethyl)-1,3-cyclohexandione (I) is cyclized to a hydrophenanthrene ketone II by phosphoric anhydride in benzene. Subsequently, phosphoric anhydride–phosphoric acid reagent was also used to effect this reaction.[2] This cyclodehydration may now be considered as a prototype representing one (A) of three possible general categories (A, B and C) of synthesis of hydrophenanthrenes and related compounds by cyclodehydration *via* attack of a cyclic 1,3-dicarbonyl structural moiety upon an appropriately situated aromatic ring.



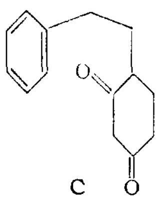
I II



A



B



C

An extension of the approach A to synthesis of a seven-membered B-ring compound has been described[3] as well as examples of cyclodehydrations in category B.[4] This paper presents a novel method of synthesis of compounds in category C and demonstrates that these also are amenable to cyclodehydration, giving 1,2,3,9,10,10a-hexahydro-3-ketophenanthrenes.[5]

Discussion

A plausible approach to the problem of getting required compounds of type C by a direct process

---

* CIBA Pharmaceutical Products, Inc., Summit, N. J

[1] R. Robinson and E. Schlittler, *J. Chem. Soc.*, 1288 (1935).

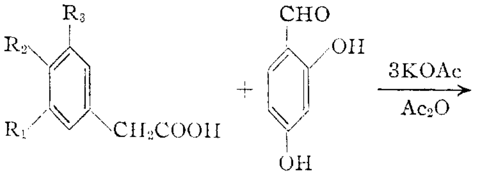
[2] A. J. Birch and H. Smith, *ibid.*, 1882 (1951).

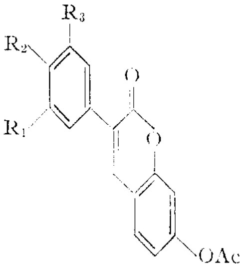
[3] G. N. Walker, THIS JOURNAL, **78**, 3201 (1956).

[4] G. N. Walker, *ibid.*, **78**, 2340 (1956). A more complete description of this work is in print: *ibid.*, **79**, 3508 (1957).

[5] A preliminary report of this work has appeared, *ibid.*, **79**, 1772 (1957).

consists of condensation of 2,4-dihydroxybenzaldehyde and its relatives with methoxyphenylacetic acids and subsequent reduction. The literature provides but meager data on successful means for carrying out Perkin condensations of this sort with phenolic carbonyl compounds, but after some exploratory work it was found that good yields of 3-aryl-7-acetoxycoumarins (III) were obtained when three moles of potassium acetate were added to a boiling solution of arylacetic acid and β-resorcylaldehyde in acetic anhydride.



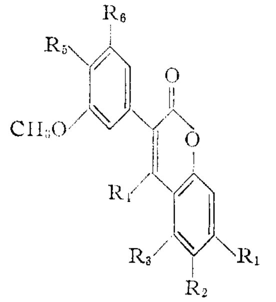


IIIa, $R_1 = R_2 = R_3 = H$
b, $R_1 = OCH_3$; $R_2 = R_3 = H$
c, $R_1 = R_2 = OCH_3$; $R_3 = H$
d, $R_1 = R_2 = R_3 = OCH_3$

Using this simple procedure, compounds IIIa-d were prepared from β-resorcylaldehyde and phenylacetic, *m*-methoxyphenylacetic, homoveratric and 3,4,5-trimethoxyphenylacetic acids, respectively. While as yet there are no comprehensive data on yields *versus* conditions in this reaction, it appears that excess potassium acetate must be present in order to ensure the salt exchange with carboxyl and/or methylene groups of the phenylacetic acids required to efficiently drive the condensation (initial stages of which are probably reversible) to completion.

Evidence indicating the coumarin structure for compounds IIIa-d was obtained from infrared spectra of these products, which in each case showed bands in the 5.65 and 5.80 μ regions, representing, respectively, the phenol acetate and conjugated phenol lactone groups. In compounds IIIb and IIIc, additional evidence for the presence of these groups was provided as follows. First, hydrogenation (palladium) under neutral conditions (ethyl acetate as solvent) gave corresponding 3-aryl-3,4-dihydro-7-acetoxycoumarins, the infrared spectra of which showed an expected shift of phenol lactone absorption to the vicinity of 5.75 μ and no appreciable change in phenol acetate band. Second, brief treatment of the acetoxycoumarins with warm 5% sodium hydroxide solution resulted in selective hydrolysis to corresponding hydroxycoumarins, as shown by disappearance of the 5.65 μ band and by other data.

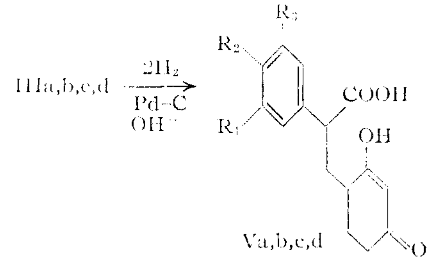
Some other compounds related to III were prepared by the same procedure involving use of appropriate amounts of potassium acetate and acetic anhydride. Thus reaction of *m*-methoxyphenylacetic acid with phloroglucinaldehyde, with phloroacetophenone and with 2,5-dihydroxybenzaldehyde in turn gave coumarins IVa, IVb and IVc, respectively, and condensation of 3,4,5-trimethoxyphenylacetic with phloroglucinaldehyde gave IVd.



IVa, $R_1 = R_3 = OAc$; $R_2 = R_4 = R_5 = R_6 = H$
b, $R_1 = R_3 = OAc$; $R_2 = R_5 = R_6 = H$; $R_4 = CH_3$
c, $R_2 = OAc$; $R_1 = R_3 = R_4 = R_5 = R_6 = H$
d, $R_1 = R_3 = OAc$; $R_2 = R_4 = H$; $R_5 = R_6 = OCH_3$

Evidently the reaction is quite general, and the present list of compounds no doubt can be amplified in further studies.

A method then was sought for simultaneous hydrogenation of the cinnamic double bond of III and conversion of the resorcinol unit to the corresponding 1,3-diketone, in order to get materials suitable for cyclization. Whilst Raney nickel is now customarily used in hydrogenation of resorcinol to dihydroresorcinol in alkaline solution,[6] it was recognized that other catalysts might serve equally well in this connection. Furthermore, the problem here is different in several respects from that of reduction of resorcinol itself, inasmuch as hydrolysis of both phenol acetate and phenol lactone groups must accompany the process, and these reactions, it was thought probable, would require elevation of temperature. At the same time it was necessary to avoid the possibility of hydrogenation of the methoxyphenyl part of the molecule, in which regard nickel and platinum catalysts are frequently unsuitable, whereas palladium has proved repeatedly to be very efficacious. Using palladium-charcoal (preferably 10%) as catalyst and conducting the hydrogenation in 1% sodium hydroxide solution containing 3.1 equivalents of the base, it was found that compounds III simultaneously underwent hydrolysis and smoothly absorbed two moles of hydrogen, once the temperature of the mixture had been raised above 70°. After subsequent acidification of the filtered solutions, 4-substituted dihydroresorcinols (V) were obtained in good yield and a gratifying state of purity. These compounds are much more stable than dihydroresorcinol itself. Two of the diketo-acids (Va and Vb) were obtained in crystalline form, but the other two (c and d) have remained glasses. As yet there is no evidence to show whether compounds V consist in each case of a single isomer or, as appears more probable, of a mixture of two isomers. In any event there is no doubt con-

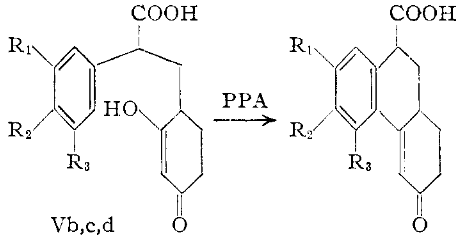


---

(6) R. B. Thompson, *Org. Syntheses*, **27**, 21 (1947).

cerning structure V for these reduction products, in view of their properties. Like dihydroresorcinol and dimedon, the compounds gave weak positive tests with ferric chloride and positive tests, but not derivatives, with 2,4-dinitrophenylhydrazine. The infrared spectra of compounds V, having ketone and acid bands in the 5.80 and 5.85 μ regions, respectively, in each case, also provided strong confirmation of the structures. Although it was possible to obtain correct analytical figures for only two of the compounds, the similarity of the aforementioned properties in all four, together with their consistent behavior in cyclization, as described below, shows that they all belong as a group to structure V.

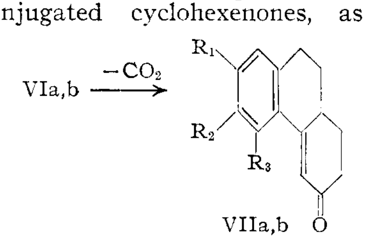
Once the problem of devising an efficient synthesis of compounds V had been solved, there remained only the question of cyclodehydration. This was done, as for other 1,3-dicarbonyl compounds in recent years, with polyphosphoric acid (PPA), and thus we now have another type of cyclodehydration to which this reagent is admirably adaptable. Diketo-acids Vb, Vc and Vd with polyphosphoric acid at 100° afforded respective hydrophenanthrene ketones VIa, b and c, in yields of 95, 52 and 28%, respectively. No more than in cyclodehydrations[3,4] of compounds of type A and B was it possible here to obtain a tricyclic product from the phenyl-unsubstituted diketo-acid Va, even through the prolonged action of concentrated sulfuric acid at 25°. It may now be concluded rather safely that all three syntheses of tricyclic compounds from A, B and C type diketones are inapplicable unless the aromatic ring is made reactive by suitably-placed electron-releasing groups.



Vb,c,d

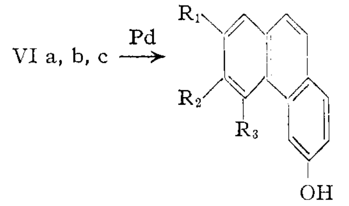
VIa, $R_1 = OCH_3$; $R_2 = R_3 = H$
b, $R_1 = R_2 = OCH_3$; $R_3 = H$
c, $R_1 = R_2 = R_3 = OCH_3$

Formula VI for the cyclized compounds was proved in several ways. Chloroform solutions of the keto-acids, when obtainable, showed infrared absorption in the 6.0–6.1 μ region, characteristic of phenyl-conjugated cyclohexenones, as well as peaks at 5.85 μ representing the carboxyl group. Conjugation of the double bond with the ketone group was also indicated plainly by the ultraviolet spectra (data in Experimental part), and by the deep red color of 2,4-dinitrophenylhydrazones of keto-esters prepared from compounds VI. Two of the keto-acids, VIa and VIb, were decarboxylated successfully to corresponding unsaturated ketones VII by boiling quinoline solutions of the acids for a few minutes. Ketone VIIa was the same in regard to melting point, ultraviolet spectrum and m.p. of the 2,4-dinitrophenylhydrazone, as that ketone obtained by Russian workers[7] through a longer sequence of reactions involving two cyclization steps.[8] In both VIIa and VIIb, the double bond and ketone carbonyl are conjugated, as shown again by means of their infrared and ultraviolet[9] spectra.



VIIa,b

Aromatization of keto-acids VI in the presence of palladium–charcoal at 180° was accompanied by decarboxylation, resulting in formation of methoxy 3-phenanthrols (VIII), identified as O-acetates in cases a and b. This reaction is probably a disproportionation, since compounds VIII were obtained consistently in approximately 50% yield; however, corresponding saturated compounds could not be isolated from the residues remaining after separation of the phenanthrols. Additional evidence for structure VIa was provided by the fact that sodium borohydride reduction of VIa to the corresponding hydroxy-acid, followed by dehydrogenation, dehydration and decarboxylation in the presence of palladium–charcoal at 180°, gave 2-methoxyphenanthrene.



VIII a, b, c

The question of isomerism arises in connection with VI, since two diastereoisomers are possible in each of these compounds. Two isomers of VIa, similar in ultraviolet spectra but quite dissimilar in their infrared patterns, actually were isolated upon fractional crystallization of the cyclized product in this case. The higher-melting isomer (m.p. 218–219°) was obtained in about 20% yield, and the second isomer (m.p. 183–186°) predominated in the mother liquors remaining after separation of the first. Diazomethane esterification of these keto-acids gave two isomeric keto-esters, m.p. 109–110° and m.p. 120–121°, respectively, again having similar ultraviolet spectra but different infrared spectra. However, from two additional facts it appears likely that the isomers of VIa are interconvertible. The isomer of VIa, m.p. 183–186°, after melting, resolidified and remelted at approximately the same temperature as the m.p. of the other isomer; and esterification of both isomeric acids with methanol in the presence of sulfuric acid resulted in formation of the same methyl ester, m.p. 120–121°, as was obtained by action of diazomethane upon the acid, m.p. 183–

---

(7) G. T. Tatevosyan, P. A. Zagorets and A. G Vardanyan, *J. Gen. Chem., U.S.S.R.*, **23**, 979 (1953); *Zhur. Obshchei Khim.*, **23**, 941 (1953); *cf. C. A.*, **48**, 7593 (1954); **49**, 4604 (1955).

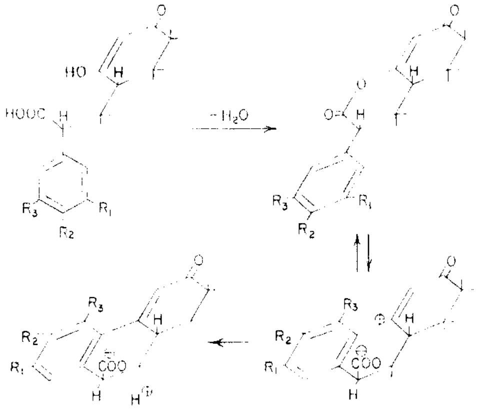
(8) For syntheses of ketones of this type from tetralones, see W. E. Bachmann and G. D. Johnson, THIS JOURNAL, **71**, 3463 (1949).

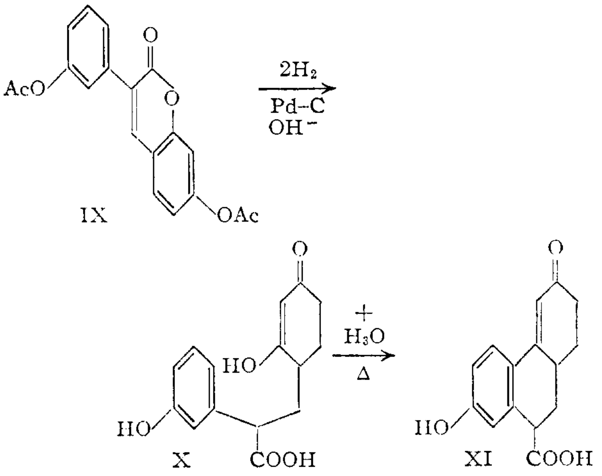
(9) *Cf.* A. L. Wilds, *et al.*, *ibid.*, **69**, 1985 (1947).

186°. Until more data are available, these isomeric changes cannot be linked specifically with either asymmetric center (positions 9 and 10a), and the respective structures of the isomers cannot be assigned with certainty.

Compound VIb, as obtained from cyclization of Vc, also seemed from its cryoscopic behavior to consist of a mixture of two isomers. However, in this case the higher-melting form was predominant; fractional crystallization of the cyclized material gave 80% of yellow crystals, m.p. above 210°, and the small remaining amount of lower-melting material could not be obtained in pure condition. Only one isomer was found in the case of keto-acid VIc. This compound was colorless, as might be expected in any stereochemical event, because of likely steric interaction between the 5-methoxyl group (R_3) and ring C resulting in a certain skewing of the C ring and thus some loss of conjugate coplanarity with ring A. Comparison of the principal ultraviolet maximum of VIc (323 mμ) with that of VIb (341 mμ) supports this conclusion.

The remaining question in this work concerns the mechanism of the cyclodehydration reaction V → VI. Unlike cyclodehydrations of type A and B compounds so far studied,[3,4,10] the present reaction is applicable to the trimethoxyphenyl compound Vd. While this fact may be due merely to a lower susceptibility of C-type diketone reactions to steric influences, it seems likely that other factors also determine the difference of C from A and B in this respect. In view of the excellent yield of product obtained in favorable circumstances, *i.e.*, VIa, it is reasonable to assume that the carboxyl group does not interfere in any way with the cyclization reaction. On the contrary, the carboxyl group may even aid the process. A way in which this could happen involves initial formation of an enol-lactone from V. Such an enol-lactone is, electronically speaking (vinylogously, in classical terms) more or less the same as a dicarboxylic acid anhydride. It seems acceptable to picture, as follows, direct attack of a vinylogous carbonylium ion upon the benzene ring with elimination of a proton, or at least to say that this particular cyclization may, electronically speaking, follow a path very similar to that which is considered most probable in classical acylations of aromatic rings with cyclic anhydrides. This suggested picture is different from the usual interpretation of cyclodehydration,[11] which involves in effect addition of benzene C–H to the double bond of the keto or enol form of a carbonyl compound, followed by elimination of water from an intermediate hydroxy compound. It seems very unlikely that this classical mechanism could be involved in the present cyclizations, in view of the evident highly crowded nature of the hypothetical hydroxyketone intermediate preceding compound VIc. Although direct evidence implicating the classical mechanism was found in studying cyclization of B-type diketones,[4] there is no direct evidence presently available which bears upon the new mechanism presented above. However, some additional observations are significant in further indicating the ease with which compounds such as V are cyclized. Compound IX was synthesized by condensation of 2,4-dihydroxybenzaldehyde with *m*-hydroxyphenylacetic acid, using four moles of potassium acetate and acetic anhydride. Hydrolytic hydrogenation of IX in alkaline solution under the same conditions used in reaction III → V afforded no product immediately, upon subsequent acidification with hydrochloric acid. Evidently the hydroxy-diketo-acid X is soluble in water. When the dilute acidic solution of X was warmed, however, crystalline hydroxy-keto-acid XI separated in 71% yield. Structure XI for this compound follows from its spectra, which are very closely allied with those of VIa, from preparation of the 2,4-dinitrophenylhydrazone of the corresponding methyl ester, and from its reaction with diazomethane to give a methoxy methyl ester identical with one obtained by esterification of VIa. The importance of reaction X → XI, aside from the fact that it shows the applicability of the process to hydroxy- as well as to methoxy-phenyl compounds, lies in the observation that the cyclodehydration occurs readily in the presence of hydronium ions when heat is applied, although it is *not* observed at 10° or lower, even over a long period of time. This indicates that the first step here, as in other cases,[12] may be interaction of the carboxyl





IX

X

XI

---

[10] Attempts to extend the syntheses of references 3 and 4 to trimethoxyphenyl compounds have not been successful; unpublished observations.

[11] C. K. Bradsher, *Chem. Revs.*, **38**, 487 (1946).

[12] E. C. Horning and G. N. Walker, This Journal, **74**, 5147 (1952), presented the dilute hydrochloric acid-promoted cyclization of

TABLE I

Compound	Yield, %	Recrystd. from	M.p. °C.	Color	Infrared λmax, μ	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
IIIa	72	EtOAc	185–187	Colorless	5.67 5.79–5.83[a]	$C_{17}H_{12}O_4$	72.85	4.32	73.08	4.31
IIIb	66	EtOAc	145–146	Very pale yellow	5.67 5.80 (5.78)[a]	$C_{18}H_{14}O_5$	69.67	4.55	69.50	4.54
IIIc	68	EtOAc	173–175	Pale yellow (blue fluor.)	5.68 5.84[a]	$C_{19}H_{16}O_6$	67.05	4.74	66.82	4.76
IIId	50	MeOH	158–160	Colorless (blue fluor.)	5.63 5.75–5.77	$C_{20}H_{18}O_7$	64.86	4.90	64.56	4.91
IVa	36	MeOH	154–155	Pale yellow	5.60–5.62 5.75	$C_{20}H_{16}O_7$	65.21	4.38	64.92	4.38
IVb	31	MeOH	144–145	Pale yellow	5.63–5.65 5.79–5.84	$C_{21}H_{18}O_7$	65.96	4.74	65.98	4.47
IVc	35	EtOAc	122–124	Pale yellow	5.64–5.66 5.75–5.78	$C_{18}H_{14}O_5$	69.67	4.55	69.39	4.60
IVd	77	EtOAc	186–187	Yellow	5.61 5.72–5.76	$C_{22}H_{20}O_9$	61.68	4.71	61.58	4.85

[a] Infrared spectrum determined in Nujol mull. The remaining spectra were determined in chf. solution.

group with the enol, before attack upon the aromatic ring ensues.

Cyclodehydrations of keto-acids other than those included in this report, where presumably five- or six-membered enol-lactones may intervene and promote reaction of an aromatic ring with a carbonyl group, are conceivable and should be worthy of future investigation.

Acknowledgments.—I am indebted to Dr. William C. Alford and his staff for microanalytical data, and to Miss Catherine Monaghan, Miss Patricia Wagner and Mrs. Katherine S. Warren for infrared and ultraviolet spectra.

Experimental[13]

3-Arylcoumarins (III). General Procedure.—A mixture of 0.100 mole of arylacetic acid, 0.105 mole of dihydroxybenzaldehyde (or other phenolic aldehyde or ketone), 0.310 mole of anhydrous potassium acetate and 80 ml. of acetic anhydride was warmed to boiling. Usually a voluminous solid appeared during this initial period of heating, and redissolved when the temperature approached the boiling point; at the same time, a transient deep red or purple color often was observed. The solution was refluxed for two hours and then, while still boiling-hot, was poured with stirring into 500 ml. of warm water. After hydrolysis of excess acetic anhydride was complete and the mixture had cooled to 30–40°, the product was collected, washed with 200 ml. of water, and air-dried. The crude material was triturated with methanol or ethyl acetate, as dictated by solubility, washed with a small portion of the same solvent, and dried again. Yields were determined at this stage, when the melting point was within ten degrees or less of that of completely purified material. Pure samples of the coumarins were prepared by recrystallization from the same solvents; several of these compounds displayed fairly strong blue or violet fluorescence in solution.

Compounds IV were prepared by the same procedure except that the reactions were run on a smaller scale (approximately 0.030 mole of each compound) and an additional equivalent of potassium acetate was added in the reactions of phloroglucinol derivatives.

Data for compounds III and IV are given in Table I.

Hydrogenation of IIIb and IIIc in Ethyl Acetate.—In each case, a solution of 1.0 g. of coumarin in 250 ml. of ethyl acetate containing 2 g. of 10% palladium–charcoal was shaken under hydrogen (40 lb.) at 70° for 3 hours. Filtration of the catalyst and evaporation of the solvent gave nearly pure products in virtually quantitative yield.

3-(*m*-Methoxyphenyl)-3,4-dihydro-7-acetoxycoumarin, from IIIb, was triturated with ether and recrystallized from cyclohexane; colorless needles, m.p. 108–110°. The infrared spectrum (chf. or Nujol) had a very intense peak at 5.65–5.67 μ and a shoulder at 5.74 μ.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.22; H, 5.17. Found: C, 69.51; H, 5.19.

3-(3′,4′-Dimethoxyphenyl)-3,4-dihydro-7-acetoxycoumarin, from IIIc, was recrystallized from ethyl acetate; colorless crystals, m.p. 148–149°. The infrared spectrum (Nujol) showed an intense doublet at 5.65 and 5.73 μ.

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.51; H, 5.30.

Hydrolysis of IIIb and IIIc.—In each case a suspension of 1.4 g. of coumarin in 45 ml. of 5% sodium hydroxide solution was boiled briskly for 4–6 minutes. The solution was cooled quickly, clarified by filtration, and acidified with hydrochloric acid at room temperature. The crude product was collected, washed with 20 ml. of cold water, and dried.

3-(*m*-Methoxyphenyl)-7-hydroxycoumarin, from IIIb, was triturated with methanol, which afforded 1.1 g. of crystals, m.p. 180–184°. Recrystallization from ethyl acetate gave very pale yellow crystals, m.p. 186–188°. The infrared spectrum had peaks at 2.92 and 5.88 μ.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.55; H, 4.53.

3-(3′,4′-Dimethoxyphenyl)-7-hydroxycoumarin, from IIIc, was triturated with ethyl acetate, which gave 0.9 g. of crystals, m.p. 216–220°. Recrystallization from the same solvent gave pale yellow crystals, m.p. 221–223°. The infrared spectrum (Nujol) had sharp peaks at 3.00 and 5.90 μ (shoulders at 5.85 and 5.94 μ).

Anal. Calcd. for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.62; H, 4.76.

Both hydroxycoumarins gave weak greenish tests with ferric chloride solution.

General Procedure. Preparation of Compounds V by Hydrolytic Hydrogenation of Compounds III.—A suspension of 0.0275 mole of coumarin (III) and 8 g. of 10% palladium–charcoal in a solution of 0.850 mole of sodium hydroxide in 300 ml. of water was shaken under hydrogen (45 lb.), while the temperature was raised gradually, during a period of 0.75 hour, to 80°. No appreciable consumption of hydrogen, other than that due to adsorption on the palladium (blank), was observed until the temperature reached about 75°. Then, as the compound dissolved gradually, two moles of hydrogen were absorbed, over a period of 1.5 hours, after which time the absorption rate became very slow. The mixture was allowed to cool while the shaking was continued (half-hour), and was filtered. The catalyst was washed with 100 ml. of warm water. The weakly alkaline solution in each case was colorless at first, but became somewhat pink or orange upon exposure to the atmosphere. The solution was acidified immediately with hydrochloric acid and was chilled in ice. The pre-

---

α-(3,4-dimethoxybenzylidene)-β-acetylsuccinic anhydride to 1-methyl-6,7-dimethoxy-3-naphthoic acid, which may take place through a similar group interaction.

(13) Melting points are corrected.

cipitated product was collected, if crystalline, or extracted with ethyl acetate–ether, if oily.

α-**Phenyl**-β-(**2,4-diketocyclohexyl**)-**propionic acid** (**Va**) was obtained in 86% yield as colorless crystals, m.p. 173–174°. Recrystallization from ethyl acetate raised the m.p. to 180–181°. The infrared spectrum (Nujol) had a broad peak at 3.1–3.2 μ and an intense, sharp doublet at 5.80 and 5.95 μ. The compound was insoluble in chloroform.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 68.86; H, 6.31.

α-(**3-Methoxyphenyl**)-β-(**2,4-diketocyclohexyl**)-**propionic acid** (**Vb**) also was obtained in crystalline form immediately; 92% yield of colorless crystals, m.p. 147–148°. Recrystallization from cyclohexane–ethyl acetate did not raise this m.p. The infrared spectrum (Nujol) showed a shoulder at about 3.2–3.25 μ and an intense peak at 5.85 μ with shoulders at 5.88 and 5.94 μ. The infrared spectrum in chf. had an intense doublet at 5.77 and 5.85 μ.

Anal. Calcd. for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.03; H, 6.31.

α-(**3,4-Dimethoxyphenyl**)-β-(**2,4-diketocyclohexyl**)-**propionic acid** (**Vc**) was obtained (quantitative crude yield) in the form of a slightly discolored, very viscous glass, which did not crystallize in the presence of various solvents. The infrared spectrum (Nujol) of a dried, degassed sample showed absorption at 3.15–3.25 and 5.79–5.87 μ (doublet). The infrared spectrum in chf. had the intense doublet at 5.78 and 5.84 μ.

α-(**3,4,5-Trimethoxyphenyl**)-β-(**2,4-diketocyclohexyl**)-**propionic acid** (**Vd**) was also a pale-yellow glass, obtained in 77% yield. In this case it was necessary to keep the acidified, aqueous solution at ice temperature for several weeks in order to obtain the maximum amount of product, which is somewhat water soluble. A well-dried sample showed infrared absorption (chf.) at 5.73–5.76 and 5.82 μ (doublet).

All four of these diketo-acids gave weak greenish coloration with ferric chloride solution. Attempts to prepare 2,4-dinitrophenylhydrazones in each case resulted first in formation of bright-red solutions, and later separation of red, oily material which could not be made to crystallize and evidently consisted of a mixture of several compounds.

Cyclization of Compounds V to VI.—A mixture of diketo-acid V and 10 parts by weight of polyphosphoric acid was heated on a steam-cone and stirred well for an hour. The resulting solution, which was deep-red or deep-green in color, was cooled to 5° and treated with 30–40 parts (by weight) of cold water with stirring. When hydrolysis was complete, the crude product was collected, washed with water, air-dried, and triturated with ethyl acetate in which the products were very sparingly soluble, while any unchanged starting material was soluble. The yield of triturated and air-dried compounds was then determined.

3-Keto-7-methoxy-9-carboxy-1,2,3,9,10,10a-hexahydrophenanthrene (**VIa**) was obtained in 95% yield from Vb, as pale yellow crystals, m.p. 180–200° dec.; 1.5 g. of this product was recrystallized from 120 ml. of methanol. The first crop (0.3 g.) consisted of nearly pure, higher-melting isomer, m.p. 215–218° dec. Further recrystallization from methanol raised the m.p. to 218–219° dec. This isomer was insoluble in chloroform and carbon tetrachloride. The infrared spectrum (Nujol) had an intense peak at 5.78–5.81 μ; no band representing the conjugated ketone was observed in this solid-state spectrum, apparently because of association. The ultraviolet spectrum (ethanol) had λ_{max} 209, 241, and 326 mμ (log ε 3.88, 4.04 and 4.41, respectively).

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.39; H, 5.89.

The filtrate from the first crop was evaporated to two-thirds its original volume and was kept at 0–10° for several days. A second crop of crystals, m.p. 179–184° (resolidified; remelted 201–207° dec.), amounting to 1.1 g. was then collected. Further recrystallization of this isomer from methanol gave colorless crystals, m.p. 183–186° (resolidified; remelted 207–211° dec.). The infrared spectrum (chf.) had intense peaks at 5.86 μ (shoulders at 5.74 and 5.80 μ) and 6.02–6.07 μ. As in the case of the first isomer, the infrared spectrum in Nujol mull lacked the conjugated ketone band and showed the carboxyl group band at 5.80 μ. The ultraviolet spectrum (ethanol) had λ_{max} 209, 243 and 328 mμ (log ε 3.97, 4.03 and 4.41, respectively).

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.86; H, 5.99.

The infrared spectra (Nujol) of these two isomers were similar below 6.0 μ, but were quite different in the fingerprint region (6.2–12.5 μ). Although the isomer, m.p. 218–219°, had a yellowish appearance, even after recrystallization in the presence of Norit, the spectra in the visible region (ethanol) showed no appreciable absorption beyond 395 mμ in either case.

3-Keto-6,7-dimethoxy-9-carboxy-1,2,3,9,10,10a-hexahydrophenanthrene (**VIb**) was obtained in 52% yield from Vc, as yellow crystals, m.p. 199–213° dec. This material (4.3 g.) was triturated with 100 ml. of boiling methanol, and the suspension was allowed to cool to 30°; filtration then gave 3.0 g. of pale yellow crystals, m.p. 218–223° dec. Further recrystallization from methanol afforded a pure sample; pale yellow needles, m.p. 229–231° dec. The infrared spectrum (Nujol) had a sharp, intense peak at 5.84 μ; as in the Nujol spectrum of VIa, no conjugated carbonyl band was evident. The acid was insoluble in chloroform. The ultraviolet spectrum (ethanol) had λ_{max} 226, 242 and 341 mμ (log ε 4.02, 4.06 and 4.31, respectively), and an inflection point at 314 mμ (log ε 4.15).

Anal. Calcd. for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.43; H, 5.97.

The filtrate remaining after separation of the major portion of the product was allowed to evaporate to a volume of 40 ml., whereupon two more crops of crystals (0.5 g. each) were obtained; the m.p. of each was in the range 190–215°. Further recrystallization of these fractions did not give samples having sharp melting points.

Esterification of triturated keto-acid VIb with ethanol in the presence of sulfuric acid, as for VIa, and subsequent treatment with 2,4-dinitrophenylhydrazine reagent gave the **2,4-dinitrophenylhydrazone of the ethyl ester**; tiny, deep red crystals from ethyl acetate–benzene, m.p. 245–246° dec.

Anal. Calcd. for $C_{25}H_{26}O_8N_4$: C, 58.82; H, 5.13. Found: C, 58.93; H, 5.28.

3-Keto-5,6,7-trimethoxy-9-carboxy-1,2,3,9,10,10a-hexahydrophenanthrene (**VIc**) was obtained from Vd, initially as a mixture of purplish gum and crystals; additional crystalline material was obtained when the original aqueous, acidic solution was kept at ice temperature for a week. Trituration with ethyl acetate gave a 28% yield of VIc as discolored crystals, m.p. 172–178°. Recrystallization from the same solvent (Norit) afforded colorless crystals, m.p. 178–180°. The infrared spectrum (chloroform) had intense peaks at 5.82–5.85 and 6.00–6.06 μ. The ultraviolet spectrum (ethanol) showed λ_{max} 230, 246 and 323 mμ (log ε 4.05, 4.04 and 4.37, respectively).

Anal. Calcd. for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 65.05; H, 5.86.

The 2,4-dinitrophenylhydrazone of the corresponding methyl ester was prepared as in preceding cases; tiny, deep purple-red crystals, m.p. 204–206° dec.

Anal. Calcd. for $C_{25}H_{26}O_9N_4$: C, 57.03; H, 4.98. Found: C, 56.92; H, 4.98.

Attempted Cyclization of Va.—This diketo-acid was recovered (about 50%) after treatment with PPA at 100° for an hour, or with concentrated sulfuric acid at room temperature for 4 days. The infrared spectra of recrystallized, recovered material and starting material were identical, and no evidence (spectra, 2,4-dinitrophenylhydrazine tests) was found for the presence of tricyclic keto-acid in the residual materials.

Methyl Esters of VIa.—(A) The two isomers of VIa were esterified in turn as follows: 0.3 g. of keto-acid was treated with a solution of 1 ml. of concentrated sulfuric acid in 100 ml. of reagent methanol, and the solution was boiled on a steam-cone for a half-hour, allowing excess methanol to escape, until the volume was reduced to about 25 ml. The cooled solution was diluted with 100 ml. of cold water, and the neutral product was extracted with ether, washed with dilute base and water, dried, and recovered by evaporation of the ether. The same product, identical in respect to m.p., mixed m.p. and infrared spectrum, was obtained in each case, after recrystallization from cyclohexane–ether; colorless or very pale yellow crystals, m.p. 120–121°. The infrared spectrum (chf.) showed peaks at 5.79–5.81 and 6.03–6.07 μ; when the infrared spectrum was measured in

KBr pellet, these peaks occurred at 5.74 and 5.98 μ. The ultraviolet spectrum (ethanol) had λ_{max} 242 and 326 mμ (log ε 4.05 and 4.39, respectively).

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.43. Found: C, 71.32; H, 6.33.

The 2,4-dinitrophenylhydrazone was recrystallized from ethanol–ethyl acetate, then from ethyl acetate–benzene; deep purplish-red crystals, m.p. 246–247° dec. The infrared spectrum (chf.), like that of the parent compound, had an ester peak at 5.78 μ, in addition to the usual features.

Anal. Calcd. for $C_{23}H_{22}O_7N_4$: C, 59.22; H, 4.76. Found: C, 59.33; H, 4.82.

(B) A sample of VIa isomer, m.p. 183–186°, was treated with a large excess (*ca.* 10 equivalents) of ethereal diazomethane (prepared from Diazald, obtained from Aldrich Chemical Co.). Slow nitrogen evolution and slow solution of the material were observed. The solution was allowed to stand overnight, and the ether was evaporated. The residue was recrystallized from cyclohexane–ether; colorless crystals, m.p. 121–122°. The mixed m.p. with the ester obtained in A was not depressed, and the infrared spectra of the samples were identical, both in chf. and in KBr.

(C) A sample of VIa isomer, m.p. 218–219°, was treated with excess diazomethane as described in B; the product was triturated with ether and recrystallized from cyclohexane until the m.p. was constant. There were obtained colorless, tiny needles, m.p. 109–110°. The infrared spectrum (KBr) showed peaks at 5.73 and 5.98–6.02 μ, and was quite different from the spectrum of ester from A and B in the fingerprint region; in particular, the spectrum of this ester showed a somewhat weaker peak at 6.17 μ and more fine structure between 7.5 and 8.7 μ than was seen in the spectrum of the other methyl ester. The ultraviolet spectrum (ethanol) had λ_{max} 241 and 324 mμ (log ε 4.11 and 4.45, respectively).

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.08; H, 6.38.

Decarboxylation of Ketoacids VI to Ketones VII.—A mixture of 1.0 g. of keto-acid and 7 ml. of quinoline was boiled for 3–6 minutes; during the first minute or two effervescence was noted. The cooled solution was poured into 300 ml. of water, 20 ml. of hydrochloric acid was added, and the mixture was allowed to stand at 0–10° for several days. The product was extracted with ether–ethyl acetate, and the organic solution was washed with 4 portions of 1:1 hydrochloric acid, followed by portions of 5% sodium hydroxide solution and water. The dried solution was then evaporated, and the crystalline ketone was triturated with ether or methanol.

3-Keto-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (VIIa), m.p. 103–108°, was obtained (0.3 g.) from VIa. Recrystallization from cyclohexane–ether gave pale-yellow crystals, m.p. 114–115.5° (reported[7] m.p. 114–115°). The infrared spectrum (chf.) had an intense peak at 6.02–6.07 μ. The ultraviolet spectrum (ethanol) had λ_{max} 242 and 328 mμ (log ε 4.02 and 4.40, respectively) (reported[7] λ_{max} *ca.* 330 mμ; log ε 4.4).

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07. Found: C, 78.95; H, 6.94.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate; tiny, deep purplish-red crystals, m.p. 219–220° dec., with marked shrinking at 212–214° (reported[7] m.p. 219–220°).

Anal. Calcd. for $C_{21}H_{20}O_5N_4$: C, 61.76; H, 4.94. Found: C, 61.60; H, 5.13.

3-Keto-6,7-dimethoxy-1,2,3,9,10,10a-hexahydrophenanthrene (VIIb) was obtained (0.35 g.) from VIb as bright yellow crystals, m.p. 210–212°. Recrystallization from ethyl acetate gave yellow crystals, m.p. 213–215°. The infrared spectrum (chf.) had an intense peak at 6.04–6.07 μ. The ultraviolet spectrum (ethanol) had λ_{max} 225, 243, 310 and 345 mμ (log ε 3.99, 4.01, 4.11 and 4.31, respectively).

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.19; H, 7.19.

An attempt to decarboxylate VIc by the same procedure gave only 10% of neutral product, from which a pure ketone could not be isolated. This compound appears to have been destroyed almost entirely in boiling quinoline. When more material is available, it is probable that decarboxylation can be conducted successfully by merely heating the keto-acid to about 200°, as effervescence was observed in the melt of VIc at this temperature.

Dehydrogenation and Decarboxylation of Ketoacids VI to Phenanthrols VIII.—In each case, a mixture of 0.70 g. of VI, 1.0 g. of 10% palladium–charcoal and 40 ml. of redistilled *p*-cymene was refluxed vigorously for 1.5 hours. The boiling-hot solution was filtered quickly, and the catalyst was washed with about 50 ml. of ethyl acetate. Evaporation of the solvents on a steam-cone gave crude products which were treated as described below.

2-Methoxy-6-acetoxyphenanthrene (VIIIa).—The crude material obtained from VIa was dissolved in 5 ml. of cyclohexane and the minimum required quantity of ether, and the solution was chilled for several days. The brownish precipitate was collected and was washed with the same solvent mixture; yield 0.24 g. This phenanthrol became oily again when attempts were made to recrystallize it from various solvents, and acquired a darker color gradually in the presence of air. The material was acetylated by refluxing it in 20 ml. of acetic anhydride for 2 hours. Evaporation of the excess reagent gave well-crystallized material; colorless crystals from methanol, m.p. 114–115°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.57; H, 5.53.

The infrared spectrum (chf.) showed the expected peak at 5.68 μ, and the ultraviolet spectrum (ethanol) had λ_{max} 221, 255, 278, 291, 319, 334 and 350 mμ (log ε 4.38, 4.84, 4.27, 4.17, 2.76, 2.91 and 2.83, respectively).[14]

2,3-Dimethoxy-6-acetoxyphenanthrene (VIIIb).—The crude product from dehydrogenation of VIb began to crystallize during evaporation of the solvents; the crystals were collected after the volume had been reduced to 15 ml. (cymene), and were washed with cyclohexane–ethyl acetate. The phenanthrol (0.28 g.) was somewhat gummy and lacking in good crystalline properties, in the presence of solvents, and became somewhat discolored upon standing in the air. The compound was acetylated by refluxing with 25 ml. of acetic anhydride for an hour, and the excess reagent was evaporated. Trituration of the residue with methanol gave 0.28 g. of crystals, m.p. 125–131°. Recrystallization from methanol afforded very pale yellow flakes, m.p. 139.5–140.5°. The infrared spectrum (chf.) had an intense peak at 5.65–5.67 μ; the ultraviolet spectrum (ethanol) had λ_{max} 257, 278, 335 and 351 mμ (log ε 4.73, 4.51, 3.23 and 3.08, respectively), and a point of inflection at 319 mμ (log ε 3.29).

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.90; H, 5.49.

2,3,4-Trimethoxy-6-hydroxyphenanthrene (VIIIc).—Evaporation of the cymene in this case gave a viscous, yellow oil. The solution of this material in 20 ml. of cyclohexane and minimum ether, upon standing at ice temperature overnight deposited first a small amount of gum, from which the remaining solution was decanted, and then colorless crystals. The crystals were collected and were washed with ether–cyclohexane; 0.3 g., m.p. 173–177°. Recrystallization from cyclohexane–ethyl acetate gave colorless needles, m.p. 180.5–181.5°. The infrared spectrum (chf.) showed hydroxyl bands as expected at 2.73 and 2.95–3.05 μ. The ultraviolet spectrum (ethanol) had λ_{max} 259, 283, 310, 341 and 357 mμ (log ε 4.79, 4.25, 4.01, 3.23 and 3.22, respectively), and an inflection point at 297 mμ (log ε 3.99).

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.81; H, 5.67. Found: C, 71.83; H, 5.73.

Acetylation of this phenanthrol gave a non-crystalline O-acetate, the infrared spectrum of which, after decolorizing and drying, had an intense peak at 5.65–5.67 μ. The ultraviolet spectrum (ethanol) was similar to that of the phenanthrol, having λ_{max} 221, 259, 303, 336 and 352 mμ (intensities *ca.* the same as those of corresponding peaks in the phenanthrol spectrum).

2-Methoxyphenanthrene. (A) Sodium Borohydride Reaction.—A suspension of 1.4 g. of ketoacid VIa in 60 ml. of methanol was treated with excess sodium borohydride (*ca.* 5 g.) in small portions over a period of 15 minutes, which resulted in solution of the crystals and exothermic action. The solution was boiled on a steam-cone for 15 minutes, allowing excess methanol to escape, until a concentrated

---

[14] See R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y. 1951, curve #373.

mixture was obtained. The cooled, semi-solid residue was dissolved in 30 ml. of water and the solution was acidified with hydrochloric acid. The precipitated product was collected, washed with 3 small portions of water, and air-dried; there was obtained 1.2 g. of nearly colorless, rather gummy crystals, which evidently consisted of a mixture of isomers, since recrystallization from several solvents proved to be impossible. The infrared spectrum of the crude hydroxy-acid (chf.) showed bands at 2.9–3.0 and 5.85 μ.

(B) **Aromatization.**—A mixture of 1.0 g. of crude (A), 2.5 g. of 10% palladium–charcoal and 60 ml. of *p*-cymene was refluxed vigorously for 1.5 hours. Filtration of the hot solution and evaporation of the cymene at 100° gave an oil which gradually crystallized. A preliminary recrystallization from cyclohexane–benzene, in which some insoluble brown gum was left behind, was followed by repetition with the same solvents using Norit as well, and then by recrystallization from ether at −78° until the m.p. was constant at 93–95° (reported[15] m.p. 99°). The ultraviolet spectrum (ethanol) of the colorless crystals showed typical phenanthrene characteristics: λ_{max} 229, 254, 277, 289, 319, 334 and 350 mμ (log ϵ 4.24, 4.89, 4.27, 4.19, 2.85, 3.02 and 3.00, respectively).

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.50; H, 5.81. Found: C, 86.33; H, 5.69.

The picrate, prepared from purified material and recrystallized from methanol, had m.p. 122–123° (reported[15] m.p. 124°).

3-(3′-Acetoxyphenyl)-7-acetoxycoumarin (IX).—A mixture of 12.9 g. (0.0849 mole) of *m*-hydroxyphenylacetic acid, 11.8 g. (0.0854 mole) of 2,4-dihydroxybenzaldehyde, 35.2 g. (0.359 mole) of anhydrous potassium acetate and 108 ml. of acetic anhydride was refluxed for 2 hours. The hot solution was poured into 900 ml. of hot water, and the mixture was stirred until hydrolysis of excess acetic anhydride was complete. After the suspension had cooled to 30°, the product was collected, washed with two 100-ml. portions of water, and dried. Recrystallization from ethyl acetate gave two crops of the material, m.p. 157–159°, totaling 19.6 g. (68%). Further recrystallization from the same solvent gave colorless crystals, m.p. 160.5–161°. The infrared spectrum (chf.) had an intense doublet, 5.64 and 5.77 μ.

Anal. Calcd. for $C_{19}H_{14}O_6$: C, 67.45; H, 4.17. Found: C, 67.2; H, 4.09.

3-Keto-7-hydroxy-9-carboxy-1,2,3,9,10,10a-hexahydrophenanthrene (XI).—A suspension of 5.9 g. (0.0175 mole) of IX and 5 g. of 10% palladium–charcoal in a solution of 3.2 g. (0.0800 mole) of sodium hydroxide in 300 ml. of water was shaken under hydrogen (45 lb.) and warmed to 80°. Absorption of hydrogen and dissolution of the crystals began when the temperature reached about 70°, and two moles of hydrogen were absorbed during the next hour; after this time the consumption of hydrogen became much slower. The cooled mixture was filtered, the catalyst was washed with 100 ml. of warm water, and the colorless filtrate was acidified with hydrochloric acid (*ca.* 20 ml.). No precipitation or turbidity was noticed either immediately or after the solution had been allowed to stand in an ice-box for 4 days. The solution was warmed on a steam-cone and evaporated slowly in a current of air or nitrogen. The solution was colorless in the beginning, but upon heating soon acquired a greenish color. After 1.5 hours, when the volume of the solution had been reduced by about a third, crystals began to separate, and the quantity of these increased as heating and evaporation were continued. Finally, after 3 hours, when the volume of the suspension was about a third that of the original solution, the product was collected from the cooled mixture, was washed with water and dried; 1.9 g. of slightly discolored crystals, m.p. 209–219° dec. A second crop, 1.3 g., m.p. 206–213° dec., was obtained upon further evaporation of the filtrate on the steam-cone, bringing the yield to 3.2 g. (71% from IX). Recrystallization of either fraction from methanol afforded colorless crystals, m.p. 226–228.5° dec. The infrared spectrum (Nujol) had peaks at 2.97–3.01, 5.87 and 6.08 μ. The ultraviolet spectrum (ethanol) had λ_{max} 244 and 332 mμ (log ϵ 4.03 and 4.40, respectively), and was very similar to the spectrum of compound VIa. The compound gave a weak greenish color with ferric chloride.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46. Found: C, 69.92; H, 5.61.

Esterification of a sample (0.4 g.) of this acid with a solution of 1 ml. of concentrated sulfuric acid in 100 ml. of methanol, as with VIa, and subsequent treatment with 2,4-dinitrophenylhydrazine reagent gave the **2,4-dinitrophenylhydrazone of the methyl ester**; dark red crystals from ethyl acetate, having no sharp m.p. but decomposing gradually above 250°.

Anal. Calcd. for $C_{22}H_{20}O_7N_4$: C, 58.40; H, 4.46. Found: C, 58.15; H, 4.66.

Another sample of this hydroxy-keto-acid was suspended in a small amount of methanol and was treated with a large excess of ethereal diazomethane. Slow nitrogen evolution and gradual solution of the material (2 hours) took place, after which the solution was allowed to stand overnight. The solvent was evaporated, and the gummy residue was fractionally crystallized from cyclohexane–ethyl acetate. The first two (small) crops of crystals, melting over the range 188–205°, were discarded. The filtrate, upon evaporation, gave a mixture of viscous oil and a few crystals. A solution of this material in ether was filtered and allowed to evaporate slowly, whereupon the residual oil slowly crystallized. Recrystallization from cyclohexane–ether gave very pale yellow crystals, m.p. 109–111°. The mixed m.p. with the methyl ester, m.p. 109–110°, from VIa was undepressed, while the mixed m.p. with the methyl ester, m.p. 120–121°, from VIa was 92–106° (depressed). The ultraviolet spectrum (ethanol) had λ_{max} 241 and 324 mμ (log ϵ 4.07 and 4.40, respectively); both this spectrum and the infrared spectrum (KBr) were identical within experimental error with the corresponding spectra of the methyl ester, m.p. 109–110°, obtained by esterification of the higher-melting form of VIa with diazomethane.

A sample (0.7 g.) of hydroxy-keto-acid XI was hydrogenated in the presence of 1 g. of 10% palladium–charcoal catalyst in 300 ml. of ethyl acetate at 80° and 45 lb. for 3 hours. Filtration of the catalyst and evaporation of the solvent gave colorless glass which crystallized slowly in the presence of ethyl acetate at ice temperature (3 days). The crystalline material (0.15 g.) obtained in this way evidently was one of several possible isomers of **3,7-dihydroxy-9-carboxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrene**. Recrystallization from ethyl acetate gave colorless crystals, m.p. 244–246° dec. The infrared spectrum (Nujol) had peaks at 2.85–2.92, 3.10 and 5.87 μ, in agreement with this formula. Additional crystalline material having the same composition separated slowly from an ethyl acetate solution of the original hydrogenation product at ice temperature, until a total of 0.3 g. of crystals was obtained. The remainder of the crude product (0.4 g.) was a glass.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.38; H, 7.11.

Somewhat similar results were obtained in hydrogenation of ketone VIIa under the same conditions. The product was a mixture of hydroxylic and ketonic material (infrared absorption at 2.9–3.0 and 5.86 μ). A 2,4-dinitrophenylhydrazone prepared from the crude material did not correspond in elementary composition to that derivative of dihydro-VIIa. The results in hydrogenation of XI and VIIa point out the difficultly-accessible nature of the double bond in compounds of this type, which apparently permits at least partial reduction of the carbonyl group before hydrogenation of the double bond.

BETHESDA 14, MARYLAND

---

[15] R. Pschorr and C. Seidel, *Ber.*, **34**, 3998 (1902).