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The Synthesis of 1-Methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene[1]

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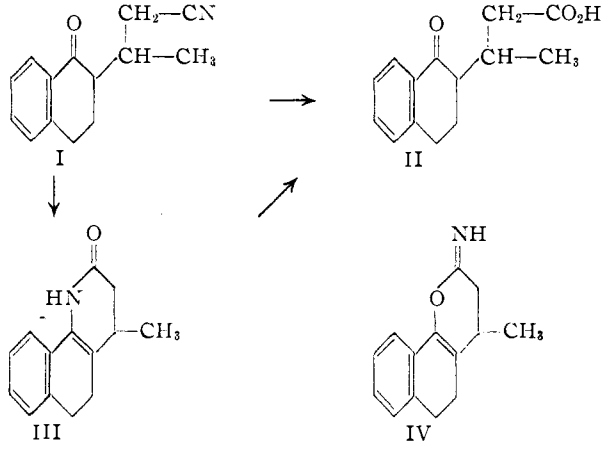
The synthesis of 1-methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XI) was accomplished through the cyanoalkylation of 3,4-dihydro-1,(2H)-naphthalenone with crotononitrile, followed by Reformatsky condensation with ethyl bromoacetate and Dieckmann ring closure as the principal steps. The end hexahydrophenanthroid ketone XI was condensed with dimethyl oxalate and the resulting glyoxalate (XII) converted into 1-methyl-2-carbomethoxy-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XIII) which includes some of the essential features of doisynolic acid. The cyanoalkylation step leading normally to β-(1-tetralone-2)-butyronitrile (I) was found to generate, under prolonged reaction time, an abnormal product shown to be β-(1-amino-3,4-dihydro-2-naphthalene)-butyrolactam (III). The cyanoalkylation reaction of ketones is therefore suggested as a one-step method for the preparation of piperidone derivatives.

In view of the current interest in the total synthesis of estrogenolic acids, a new route to useful intermediates in the preparation of compounds related to doisynolic acid was investigated. At the outset of this investigation in 1949, Bachmann and Johnson[3] reported the synthesis of 3-keto-1,2,3,-9,10,10a-hexahydrophenanthrene through the cyanoethylation of 2-carbomethoxy-1-tetralone followed by Reformatsky condensation and Dieckmann ring closure as the main steps. Independently, we followed a similar pattern of synthesis for the preparation of 1-methyl-3-keto-1,2,3,9,-10,10a-hexahydrophenanthrene (XI) which includes structural features necessary for its subsequent conversion into compounds related to doisynolic acid. Starting from the simpler 1-tetralone, the corresponding β-(1-tetralone-2)-butyronitrile (I) was readily obtained in good yield by allowing the former to react with allyl cyanide (generating crotononitrile in the basic medium) in the presence of potassium *t*-butoxide in *t*-butyl alcohol.[4] Alkaline hydrolysis of this reaction product led in good yield also to the corresponding crystalline ketoacid II.



However, when the amount of potassium *t*-butoxide was increased to molar proportions with the tetralone and the reaction carried at the boiling point of the solvent for a longer period of time, the amount of ketonitrile I was considerably diminished and the principal product was a crystalline substance melting at 178° which was formulated as III on the basis of the following evidence: (1) alkaline hydrolysis produced the ketoacid II; (2) the compound failed to react with semicarbazide or hydroxylamine, but decolorized instantaneously a bromine solution; therefore, a reactive double bond is present and that the latter is conjugated with the benzene ring was indicated by the strong absorption at 292 mμ (log *e* 3.80) (Fig. 1) that the compound exhibited; (3) the rejection of the isomeric imino-ether formulation IV follows from (a) the failure of the compound to yield a hydrochloride or to be altered by warm alcoholic hydrogen chloride,[5] (b) the stability of the abnormal product toward heat; this is in marked contrast with the known unstability of imino-ethers which regenerate the nitrile and alcoholic components when heated.[6] It is noteworthy that Kohler, Graustein and Merrill[7] showed that Δ-ketonitriles undergo rearrangement to piperidone derivatives in the presence of acid catalysts; however, no mention was made that basic reagents can effect the rearrangement as in the present example. The cyanoalkylation reaction of ketones can therefore be of use as a one-step method for the preparation of piperidone derivatives.

Condensation of the ketonitrile I with ethyl bromoacetate led to a reaction mixture from which no pure product could be isolated. However, when the esterified ketoacid II was used, the half-ester VI was isolated in moderate yield. The structure of the latter as well as the intermediate formation of the unstable lactone V[8] follow from the work of Bachmann and Johnson[3] in an analogous case. Dieckmann cyclization of the diester VIII afforded in good yield a crystalline substance formulated as 1-methyl-3-keto-4-carbomethoxy-1,2,3,4,9,10-hexahydrophenanthrene (X) on the basis of the following evidence[9]: (a) the ultraviolet absorption

(1) Abstracted from the Ph.D. thesis of B. Belleau submitted to the Department of Biochemistry of McGill University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1950.

(2) The Sloan-Kettering Institute for Cancer Research, New York, N. Y.

(3) W. E. Bachmann and G. D. Johnson, THIS JOURNAL, **71**, 3463 (1949).

(4) For other examples of the use of allyl cyanide or crotononitrile in cyanoalkylation reactions, see H. A. Bruson, *ibid.*, **64**, 2457 (1942).

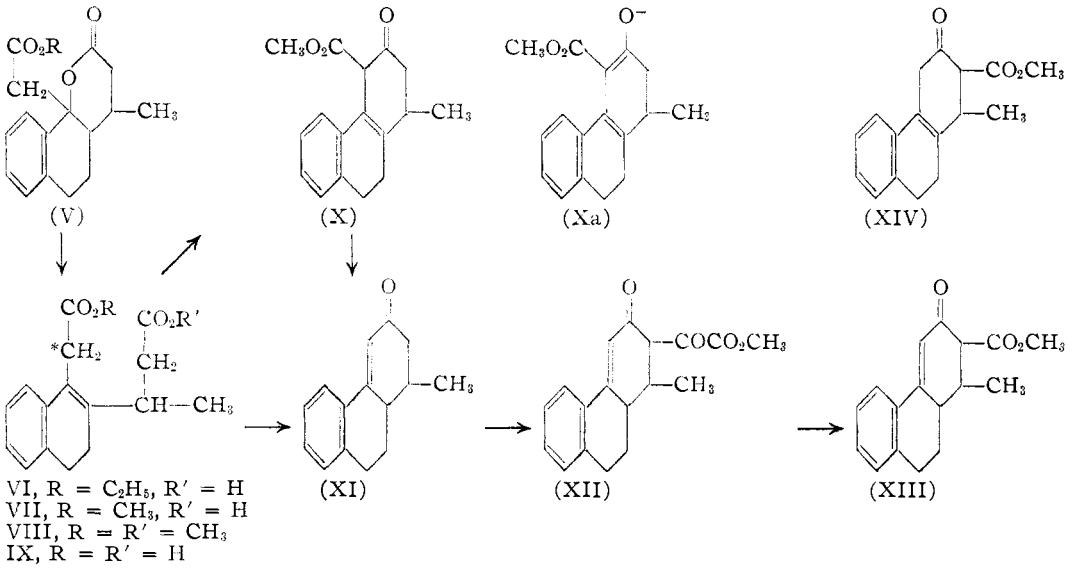
(5) J. Houben, "Die Methoden der Organischen Chemie," Vol. 4, edited by J. W. Edwards, Ann Arbor, Mich., 1941, p. 428.

(6) Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p. 85.

(7) E. P. Kohler, A. Graustein and D. R. Merrill, THIS JOURNAL, **44** 2536 (1922).

(8) The presence of the double bond in VI was indicated by the decolorization of bromine solutions and by the observation in the ultraviolet region of a peak of absorption at 266 mμ (log *e* 4.05) (Fig. 1) that the compound exhibited. Evidence for the endocyclic position of the double bond was shown by the failure of the acid IX to be reduced by sodium amalgam in alkaline solution.

(9) The results of the spectrophotometric measurements on X and XIII were added in proof.



spectrum (Fig. 1) revealed two bands at 263 mμ (log *e* 4.0) and 271 mμ (log *e* 4.0) indicating that the double bond had not shifted in conjugation with the carbomethoxyl and ketonic groups (compare with VI and XI) during the cyclization step; (b) that the ring-closed product could hardly be the position isomer XIV was shown by measuring the ultraviolet spectrum in the presence of sodium hydroxide. Conversion of X into its enolate ion Xa alters the chromophoric system in a predictable manner: the appearance of the enolate chromophore should cause a bathochromic shift of about 27 mμ whereas the dienic system should give rise to another band displaced by about 11 mμ toward shorter wave lengths because of the cross-conjugation.[10] On the other hand, assuming XIV as the reaction product, the corresponding enolate should exhibit a new band at longer wave lengths without any noticeable change in the dihydronaphthalene chromophore. Since the addition of base produced two new absorption bands at 247 mμ (log *e* 4.23) and 300 mμ (log *e* 4.03) (Fig. 1) in close agreement with the predicted values for Xa, the ring closed product was assigned structure X. On other theoretical grounds, the same conclusion can be drawn: because the diester VIII includes a methylene group (starred atom) subject to a carboxylic as well as an allylic activation, a unidirectional Dieckmann cyclization through preferential attack by the methoxide ion at the site of this methylene group and leading mostly to X, would be expected.[11]

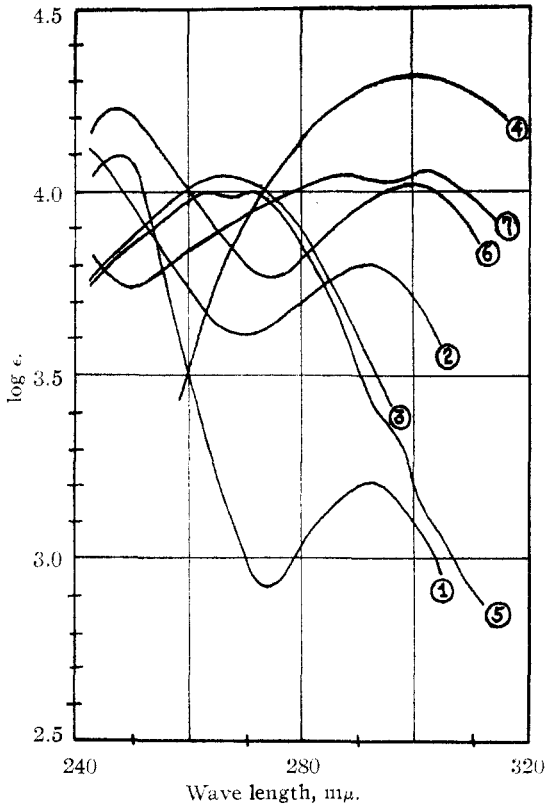


Fig. 1.—Ultraviolet absorption spectra of: (1) β-(1-tetralone-2)-butyric acid (II); (2) β-(1-amino-3,4-dihydro-2-naphthalene)-butyrolactam (III); (3) β-(1-carbethoxymethyl-3,4-dihydro-2-naphthyl)-butyric acid (VI); (4) 1-methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XI); (5) 1-methyl-3-keto-4-carbomethoxy-1,2,3,4,9,10-hexahydrophenanthrene (X); (6) enolate of X; (7) 1-methyl-2-carbomethoxy-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene.

Alkaline hydrolysis of X caused acid cleavage leading to the dibasic acid IX (also obtained by saponification of VI or VII). On the other hand, acid hydrolysis produced in low yield 1-methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XI) which exhibited a strong absorption band at 298 mμ (log *e* 4.32) (see Fig. 1) in agreement with the

(10) Enolic β-ketoesters are known to absorb around 267 mμ (log *e* 4.1) as reported by J. B. Brown, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 3634 (1950), and conversion to the corresponding enolate causes a bathochromic shift of about 27 mμ as we have observed in the case of acetoacetic ester. Also, as reported by Dannenberg, *Abhandl. preuss. Akad. Wiss.*, **21**, 3 (1939), the introduction of cross-conjugation in a dienic system causes a shift toward shorter wave lengths. In the case of $\Delta^{6\text{-}8(14),9(11)}$-cholestatriene-3-ol-acetate a shift of 11 mμ from the calculated value is reported.

(11) A similar ring closure of a diester analogous to VIII (minus the methyl group) described in ref. 3 was stated to yield a β-ketoester with an unplaced carbomethoxyl group. On the basis of our observations, it is likely that the ring closure led to 3-keto-4-carbomethoxy-1,2,3,4,9,10-hexahydrophenanthrene.

value predictable on the basis of data reported by Wilds and co-workers.[12]

The spectrum of the ketone XI coincides with that reported[3] for the analogous 3-keto-1,2,3,9,10,-10a-hexahydrophenanthrene. The position of the carbonyl group in XI and final proof of the ring structure were established by converting the ketone into its corresponding methylcarbinol followed by dehydration and dehydrogenation to 1,3-dimethylphenanthrene. The ketone XI could also be obtained by the slow distillation of an acetic anhydride solution of the dibasic acid IX. The yield by this method was superior to the Dieckmann cyclization. A condensation of the ketone with dimethyl oxalate afforded the crystalline glyoxalate XII which consisted most probably of a mixture of stereoisomers. Upon heating with powdered glass, it evolved gas to yield an amorphous mixture of stereoisomerides of 1-methyl-2-carbomethoxy-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XIII) which exhibited absorption maxima at 289 mμ (log *e* 4.04) and 303 mμ (log *e* 4.05) (Fig. 1) as expected (compare with ketone XI).

Acknowledgment.—I am greatly indebted to the Quebec Scientific Bureau for grants in aid and to Dr. R. D. H. Heard for his interest in this work.

Experimental[13]

β-(1-Tetralone-2)-butyronitrile (I).—To a solution of 1.60 g. of potassium in 90 ml. of *t*-butyl alcohol was added 24 g. of tetralone followed by the portionwise addition, while cooling, of 18 g. of allyl cyanide (strongly exothermic isomerization to crotononitrile). The mixture was heated under reflux for 6 hours and allowed to stand at room temperature for 16 hours. It was then acidified with hydrochloric acid and diluted with ether. This was washed with water, dried and evaporated *in vacuo*. The residual dark colored oil was distilled *in vacuo* to yield 3.5 g. of unreacted tetralone, b.p. 100° (0.1 mm.), and 21 g. of the yellow β-(1-tetralone-2)-butyronitrile (I), b.p. 165–180° (0.1 mm.). A considerable high boiling residue consisting most probably of biscyanoalkylated product was discarded. The yield of pure ketonitrile amounted to 72% based on unrecovered tetralone.

Anal. Calcd. for $C_{14}H_{15}ON$: N, 6.57. Found: N, 6.76.

β-(1-Tetralone-2)-butyric Acid (II).—A solution of 16.3 g. of β-(1-tetralone-2)-butyronitrile in 80 ml. of ethanol containing 10 g. of potassium hydroxide was heated under reflux for 5 hours, after which time half of the solvent was distilled off and the solution poured into water. After one ether-wash, the alkaline solution was acidified to liberate an oil which solidified on standing. It was collected and the crude acid (13 g. or 74% yield) after recrystallization from a large volume of heptane afforded colorless prisms of **β-(1-tetralone-2)-butyric acid** (II), m.p. 101–102°.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.41; H, 6.89; neut. equiv., 232. Found: C, 72.24; H, 6.85; neut. equiv., 232.

The ultraviolet absorption of the pure acid was determined in 95% ethanol; it shows maxima at 248 mμ (log *e* 4.1) and 292 mμ (log *e* 3.2).

β-(1-Amino-3,4-dihydro-2-naphthalene)-butyrolactam (III).—To a solution of 5.3 g. of potassium in 100 ml. of *t*-butyl alcohol was added 20 g. of 1-tetralone followed by the slow addition, while cooling, of 9.2 g. of allyl cyanide. One drop of water was added and the solution heated under reflux for 24 hours. It was cooled, acidified with hydrochloric acid and diluted with ether. After one water-wash, the solution was quickly shaken with anhydrous sodium sulfate, filtered and evaporated *in vacuo*. The semi-solid residue was triturated under 50 ml. of ether and chilled for several hours. A white crystalline mass weighing 8.1 g. separated and was saved. The mother liquor was evaporated and the residue distilled *in vacuo* to yield 2.5 g. of unreacted tetralone, b.p. 70° (0.1 mm.), 6 g. of β-(1-tetralone-2)-butyronitrile (I), b.p. 160–190° (0.1 mm.) and 4 g. of crystalline distillate, b.p. 200–230° (0.1 mm.). The crystalline fractions were combined (12.1 g. or 40% yield) and recrystallized from methanol to produce colorless needles of **β-(1-amino-3,4-dihydro-2-naphthalene)-butyrolactam** (III), m.p. 178°.

Anal. Calcd. for $C_{14}H_{15}ON$: C, 78.87; H, 7.04; N, 6.57; mol. wt., 213. Found: C, 78.55; H, 7.19; N, 6.55; mol. wt. (isothermic method), 220.

The ultraviolet absorption of the compound was determined in 95% ethanol; it exhibited a maximum at 292 mμ (log *e* 3.85). The compound decolorized instantaneously a bromine–acetic acid solution and produced a deep red coloration with alcoholic ferric chloride.

A solution of 1 g. of the compound in 10 ml. of 10% potassium hydroxide in methanol was heated under reflux for 5 hours. Most of the methanol was distilled off and the residue dissolved in water; the solution after one ether-wash was acidified to liberate an oil which solidified on standing. It was collected (0.90 g. or 82% yield) and recrystallized from heptane to yield colorless prisms melting at 101–102°; it caused no depression of the melting point of the ketoacid II described above.

When 1 g. of the compound was heated to boiling for 30 minutes in 15 ml. of 5% alcoholic hydrogen chloride and the solution diluted with water, the starting material was recovered quantitatively.

β-(1-Carboxymethyl-3,4-dihydro-2-naphthyl)-butyric Acid (IX).—Twelve grams of β-(1-tetralone-2)-butyric acid (II) was esterified by heating under reflux for 1 hour in 50 ml. of methanol containing 5 ml. of concentrated sulfuric acid. About one-half of the solvent was removed *in vacuo* and the solution poured into 100 ml. of water followed by extraction with ether. The ether extracts were combined, washed with water and saturated bicarbonate solution and finally dried and evaporated. Distillation of the residue *in vacuo* yielded a yellowish distillate, b.p. 155–160° (0.1 mm.), weighing 11 g. (86%).

The Reformatsky condensation with this ester and ethyl or methyl bromoacetate was carried out according to a previously described technique.[3] In this manner, ethyl bromoacetate yielded 7 g. (52%) of **β-(1-carbethoxymethyl-3,4-dihydro-2-naphthyl)-butyric acid** (VI), m.p. 64–68°. Three additional recrystallizations from hexane afforded colorless prisms, m.p. 68.5–69.5°.

Anal. Calcd. for $C_{18}H_{22}O$: C, 71.52; H, 7.28. Found: C, 71.38; H, 7.24.

When methyl bromoacetate was used, the corresponding methyl half-ester VII was obtained in an equal yield. The compound formed colorless prisms from hexane, m.p. 96–97°. Both half-esters (VI and VII) decolorized instantaneously a bromine–carbon tetrachloride solution or a solution of permanganate in acetone.

The ultraviolet absorption of the ethyl half-ester VI was determined in methanol; it showed a maximum at 266 mμ (log *e* 4.05) (Fig. 1).

Upon treatment for 1 hour of 4 g. of the ethyl half-ester VI in 50 ml. of boiling methanol containing 2 g. of potassium hydroxide, the corresponding diacid was obtained by pouring the alcoholic solution into 100 ml. of 10% hydrochloric acid. The solid mass which separated was recrystallized from toluene to yield 3.1 g. (91%) of material, m.p. 188–192°. Several recrystallizations from the same solvent afforded colorless needles of **β-(1-carboxymethyl-3,4-dihydro-2-naphthyl)-butyric acid** (IX), m.p. 191–193°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.07; H, 6.57. Found: C, 69.80; H, 6.48.

1-Methyl-3-keto-4-carbomethoxy-1,2,3,4,9,10-hexahydrophenanthrene (X).—Five grams of β-(1-carbethoxymethyl-3,4-dihydro-2-naphthyl)-butyric acid was esterified in methanol as described above in the case of the ketoacid II. In this manner 4.7 g. (94%) of the yellowish liquid ester VIII, b.p. 175–180° (0.1 mm.), was obtained.

A solution of 1 g. of sodium in 10 ml. of methanol was evaporated to dryness *in vacuo* at 100° and the solid cake of sodium methoxide pulverized. A solution of 2 g. of the diester in 20 ml. of benzene was added and the mixture heated

(12) A. L. Wilds and co-workers, THIS JOURNAL, **69**, 1985 (1947).

(13) All boiling points and melting points are uncorrected and Mr. Y. Perron of University of Montreal kindly performed the microanalyses. Ultraviolet spectra were all measured with a standard Beckman quartz spectrophotometer.

under reflux for 90 min. It was cooled, diluted with ether and hydrolyzed with excess dilute hydrochloric acid. The organic phase after one water-wash was dried and evaporated to yield a viscous oil which solidified when triturated with 80% aqueous methanol. Crystallization from this solvent afforded material, m.p. 94–99°, and weighing 1.30 g. (72% yield). Three additional recrystallizations produced colorless needles of **1-methyl-3-keto-4-carbomethoxy-1,2,3,4,9,-10-hexahydrophenanthrene (X)**, m.p. 98–100°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.64; H, 6.81. Found: C, 75.83; H, 6.66.

The compound decolorized a bromine–carbon tetrachloride solution instantaneously and imparted a light green coloration to alcoholic ferric chloride. The ultraviolet absorption spectrum (Fig. 1) of the compound was measured in 95% ethanol; it showed maxima at 263 mμ (log *e* 4.0) and 271 mμ (log *e* 4.0). In the presence of excess sodium hydroxide, the maxima were at 247 mμ (log *e* 4.23) and 300 mμ (log *e* 4.03).

When heated for 3 hours in alcoholic potassium hydroxide, it underwent cleavage to the dibasic acid IX as shown by means of a mixed melting point determination.

1-Methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XI) (a) From 1-Methyl-3-keto-4-carbomethoxy-1.2,3,4,9,-10-hexahydrophenanthrene (X).—Of the above 1-methyl-3-keto-4-carbomethoxy-1,2,3,4,9,10-hexahydrophenanthrene, 400 mg. was added to a mixture of 40 ml. of glacial acetic acid, 20 ml. of concentrated hydrochloric acid and 2 ml. of water. Upon heating under reflux, a persistent red coloration appeared; after 4 hours, the solution was cooled, poured into 200 ml. of water and the insoluble oil extracted with ether. The ether extracts were combined, washed with dilute sodium hydroxide and water and finally dried and evaporated. The solid residue upon crystallization from methanol afforded 95 mg. (30% yield) of material, m.p. 118–123°. Three additional recrystallizations from methanol produced slightly yellowish rectangular plates of **1-methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XI)**, m.p. 124–125°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.68. Found: C, 84.90; H, 7.54.

The ketone decolorized instantaneously a bromine–carbon tetrachloride solution. Its ultraviolet absorption was measured in methanol; it exhibited a strong absorption maximum at 298 mμ (log *e* 4.32).

The oxime was obtained under the usual conditions. It crystallized from 75% methanol in the form of needles, m.p. 179.5–180.5°.

Anal. Calcd. for $C_{15}H_{17}ON$: N, 6.16. Found: N, 6.10.

(b) From β-(1-Carboxymethyl-3,4-dihydro-2-naphthyl)-butyric Acid (IX).—A solution of 1.50 g. of the dibasic acid IX in 10 ml. of acetic anhydride was slowly distilled first at atmospheric pressure and then, after about one hour, under a vacuum of 0.1 mm. The bath temperature was slowly raised to 250° at which temperature a yellowish oil distilled over. The distillate was digested with dilute aqueous potassium hydroxide and extracted with ether. The ethereal phase was dried and evaporated to yield an oil which solidified when triturated with a little methanol. In this manner, 473 mg. (41% yield) of material, m.p. 117–122°, was obtained. Three additional recrystallizations from methanol raised the m.p. to 124–125° which was not depressed when the compound was admixed with the ketone XI obtained in the preceding experiment.

1,3-Dimethylphenanthrene.—The preceding ketone XI (420 mg.) was converted into its corresponding methylcarbinol by reaction with excess methylmagnesium iodide in ether. The oily reaction product was heated for 1 hour at 160–170° with 1.5 g. of potassium acid sulfate and the dehydration product obtained in this way was then heated in a nitrogen atmosphere at 300–320° during 45 min. in the presence of 100 mg. of 10% palladium-on-charcoal.[3] Crystallization of the reaction product from methanol afforded colorless needles of 1,3-dimethylphenanthrene, m.p. 74.5–75.5°, which yielded an orange-colored picrate separating from methanol as long needles, m.p. 155–156° (reported[14] for 1,3-dimethylphenanthrene, 75–76°; picrate, 154–155°).

Methyl 1-Methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene-2-glyoxalate (XII).—A solution of 132 mg. of sodium in a little methanol was evaporated *in vacuo* at 100°. To the solid sodium methoxide was added 680 mg. of dimethyl oxalate in 4 ml. of benzene. The mixture was heated under reflux for 10 min., then cooled and treated with a solution of 640 mg. of 1-methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XI) in 5 ml. of benzene. The flask was filled with nitrogen, stoppered and allowed to stand at room temperature for 4 hours. The resulting dark green solution was diluted with ether and hydrolyzed with dilute hydrochloric acid followed by extraction with 2% aqueous sodium hydroxide. The combined alkaline extracts were acidified and extracted with ether. The ether extracts after one water-wash were dried and evaporated to yield 600 mg. (66% yield) of orange-colored crystals, m.p. 130–135°. Three additional recrystallizations from methanol afforded yellow plates of **methyl 1-methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene-2-glyoxalate (XII)**, m.p. 132–137° (evolution of gas). Further recrystallizations failed to sharpen the melting point.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04. Found: C, 72.32; H, 6.03.

The compound produced a deep red-brown coloration with alcoholic ferric chloride.

1-Methyl-2-carbomethoxy-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XIII).—Of the preceding glyoxalate XII, 220 mg. was heated to 150° under a nitrogen atmosphere and into the melt, 150 mg. of powdered soft glass[15] was introduced. The tube was then heated to 185–190° at which temperature a vigorous evolution of gas ensued. After 15 min., the tube was cooled under nitrogen and the reddish oil dissolved in ether. The ethereal solution was extracted twice with 2% aqueous sodium hydroxide and the alkaline extracts acidified and extracted with ether. The latter extracts were dried and evaporated to yield an orange-colored oil which failed to crystallize in the presence of the usual solvents. However, the oil imparted a dark-brown coloration to alcoholic ferric chloride and underwent cleavage to the diacid IX when submitted to alkaline hydrolysis as described above in the case of the β-keto-ester X. Because of the impossibility of purifying this oil, poor analytical figures were obtained.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.64; H, 6.81. Found: C, 74.87; H, 6.20.

The ultraviolet absorption spectrum of the oil was measured in 95% ethanol; it exhibited absorption bands at 289 mμ (log *e* 4.04) and 303 mμ (log *e* 4.05).

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(14) R. D. Haworth, C. R. Mavin and G. Sheldrick, *J. Chem. Soc.*, 454 (1934).

(15) W. E. Bachmann, W. Cole and A. L. Wilds, THIS JOURNAL, **62**, 824 (1940).