purified material and the mixture was allowed to stand at room temperature. A dark color was produced immediately. After 21 hr. at room temperature, the mixture was distilled at 1 mm. and gave about 0.1 ml. of product having $n^{25}\text{D}$ 1.5465. The infrared spectrum of the distillate in carbon tetrachloride solution was identical with that of the starting dibromide.

Debromination of the Dibromide of I with Zinc.—To a stirred mixture of 5.0 g. (0.077 mole) of zinc powder and 5 ml. of 95% ethanol was added dropwise 3.2 g. (0.0136 mole) of the dibromide of I. The mixture was refluxed during the addition and each drop of dibromide caused a momentary increase in reflux rate. After 10 min., all of the dibromide had been added and the pressure on the system was reduced slightly and about 4 ml. of volatile product (and solvent) was collected in a Dry Ice trap. The trap was allowed to warm to room temperature and 5 ml. of distilled water was added. Two phases appeared and the upper layer was separated and washed with four 3-ml. portions of distilled water. The aqueous layer of the last wash was frozen and the organic layer was removed carefully. Distillation of the organic layer gave 0.6 g. (60%) of I, b.p. 67° and $n^{25}\text{D}$ 1.4470. The infrared spectrum of a carbon tetrachloride solution of the distillate was identical to that of an authentic sample of I. The identity of the product was also confirmed by its n.m.r. spectrum.

Isomerization of 1,3-Dimethylenecyclobutane.—Sodium amide was prepared from 0.035 g. (0.0016 mole) of sodium dissolved in about 5 ml. of liquid ammonia containing a trace of ferric chloride as catalyst and then the ammonia was allowed to evaporate until only about 1 ml. remained. Compound I (1.0 g., 0.0125 mole) (containing about 10% X) was added rapidly. The resulting dark mixture was allowed to reflux for 1.5 hr. and at the end of this time the ammonia was allowed to distil from the flask; 12 ml. of 1 *N* hydrochloric acid was added to the residue and the organic layer was removed after first freezing the aqueous layer. The slightly yellow organic phase amounted to 0.86 g. (86%) and had b.p. 68–69°. The infrared spectrum of the product was identical to that of an authentic sample of X.

In several experiments in which triethylamine and sodium hydroxide were used as the base, no isomerization occurred at room temperature.

Reaction between 1,3-Dimethylenecyclobutane (I) and Maleic Anhydride.—A mixture of 1.2 g. (0.0125 mole) of I, 1.0 g. (0.0125 mole) of maleic anhydride and 15 ml. of *m*-xylene was heated for 10 hr. at 100° in a sealed tube. Solid and liquid phases were obtained. Fractionation of the liquid phase yielded no starting materials except the solvent. The solid amounted to 0.6 g. of a white powder, m.p. >360°, which could not be dissolved in any common organic solvent or 1 *N* acid or base. The analysis corresponds to a polymeric substance made up of molecules of maleic anhydride and I in the ratio of 2 to 1, respectively.

Anal. Found: C, 60.94; H, 5.25.

Attempted Preparation of Iron and Nickel Complexes from 1,3-Dimethylenecyclobutane (I).—An olive-drab colored mixture of 0.013 mole of sodium amide, 1.0 g. (0.013 mole) of I and 15 ml. of tetrahydrofuran was added to a mixture of 0.013 mole of ferrous chloride in 40 ml. of tetrahydrofuran prepared according to the directions of Wilkinson.[15] The resulting brown mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the resultant residue was extracted with four 20-ml. portions of boiling *n*-hexane. Removal of the solvent from the combined extracts by distillation yielded about 0.1 ml. of a dark yellow liquid which contained no iron.

Another attempt to prepare an iron compound in which I was mixed directly with a solution of ferrous chloride containing diethylamine resulted only in the isolation of diethylamine hydrochloride.

Attempts to prepare nickel compounds of I and X by reaction with nickel carbonyl in both the gas and liquid phases at various temperatures resulted in the isolation of nickel, nickel oxide and polymeric substances containing no nickel.

Attempts to Interconvert Methylenecyclobutane (XV) and 1-Methylcyclobutene (XVI).—A mixture of 0.8 g. of XV, 0.1 g. of 96% sulfuric acid and 1.6 g. of glacial acetic acid was shaken mechanically in a sealed tube for 1 hr. at room temperature. The brown one-phase solution then was flash distilled at room temperature (1 mm.) and the distillate was mixed with 5 ml. of water which caused two phases to form. The upper phase was isolated, washed with 5% sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Distillation from sodium yielded about 0.5 ml. of colorless sweet-smelling liquid, b.p. 100–130°, $n^{25}\text{D}$ 1.4180, which did not react with bromine in carbon tetrachloride solution. The infrared spectrum of the product was almost identical with that of 1-methylcyclobutyl acetate, b.p. 54.7–54.8° (40 mm.), $n^{25}\text{D}$ 1.4162, prepared previously.[11] A vapor-phase chromatogram showed the product to be 90% pure. The above procedure was repeated using absolute ethanol in place of glacial acetic acid with subsequent isolation of a compound, b.p. 107°, $n^{25}\text{D}$ 1.4100, which appears to be ethyl 1-methylcyclobutyl ether.

Solutions of XV and XVI in carbon tetrachloride and chloroform saturated with dry hydrogen chloride were allowed to stand at room temperature about 24 hr. No change in the infrared spectra of the solutions occurred during the stated reaction time. The solutions then were heated 3 hr. at 100° in sealed tubes after which the infrared spectra of the solutions were different but could not be interpreted.

In an attempt to interconvert XV to XVI under basic conditions, a mixture of 0.004 mole of sodium amide in 1 ml. of liquid ammonia and 1.7 g. (0.025 mole) of XV was allowed to reflux for 2 hr. The mixture then was treated with dilute hydrochloric acid and the organic layer was distilled to yield 0.9 g. of the starting material XV.

PASADENA, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Condensation Product of 9,10-Phenanthrenequinone and Ethyl Acetoacetate

BY ARTHUR C. COPE AND D. W. H. MACDOWELL[1]

RECEIVED MAY 15, 1958

The condensation product of 9,10-phenanthrenequinone and ethyl acetoacetate and the isomer into which it is converted by acids have been shown to be III and IV, respectively, rather than I and II as originally proposed by Japp, Klingemann and Streatfeild. Ultraviolet and infrared spectra provided the information essential for the new structural assignments. A number of compounds derived from III and IV that were prepared by earlier workers but for which no structures were proposed have been re-synthesized and assigned structures (V-XIII) that are in accord with all of the chemical and spectral data obtained for them.

The preparation of several derivatives of 1H-cyclopenta(*l*)phenanthrene from the condensation product of 9,10-phenanthrenequinone and ethyl acetoacetate has been described recently.[2] This condensation product was first prepared by Japp and Streatfeild,[3] who used aqueous ethanolic potassium hydroxide as the condensing agent, and later by Lachowicz,[4] who effected the condensation with piperidine in ethanol. Japp and Streatfeild as-

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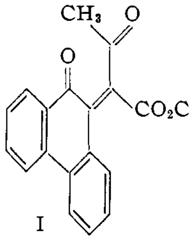
[1] Visking Corporation Fellow, 1953–1954.

[2] A. C. Cope, L. Field, D. W. H. MacDowell and M. E. Wright, THIS JOURNAL, **78**, 2547 (1956).

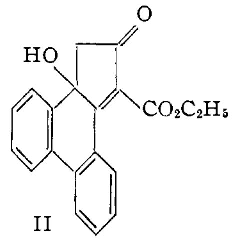
[3] F. R. Japp and F. W. Streatfeild, *J. Chem. Soc.*, **43**, 27 (1883).

[4] B. Lachowicz, *Monatsh.*, **17**, 344 (1896).

signed structure I to the compound on the basis of its molecular formula and degradation to 9,10-phenanthrenequinone by oxidation with chromic acid. Japp and Klingemann[5] assigned structure II to an isomer of I which they obtained by treatment of I with hot dilute sulfuric acid or hot concentrated formic acid; II forms a monoacetate. Although these workers studied several reactions of I and II, they did not formulate structures for the products.



I

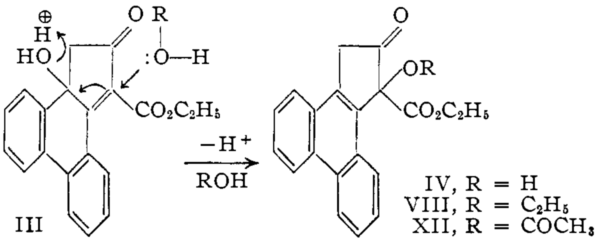


II

Treatment of I with hydriodic acid gave a compound $C_{20}H_{16}O_3$ (V), which on sublimation produced a compound $C_{17}H_{12}O$ (VI). Alkaline hydrolysis of V formed a dibasic acid $C_{18}H_{14}O_4$ (VII). Treatment of I with ethanol in the presence of a few drops of concentrated sulfuric acid yielded a compound $C_{22}H_{20}O_4$ (VIII) which was saponified to a dibasic acid $C_{20}H_{18}O_5$ (IX) that formed a dimethyl ester $C_{22}H_{22}O_5$ (X). Treatment of I with glacial acetic acid at 150° yielded a very insoluble compound, $C_{20}H_{14}O_3$ (XI), and a ketoester $C_{22}H_{18}O_5$ (XII). The latter compound also was obtained from II by treatment with acetic anhydride. Alkaline hydrolysis of either XII or II produced a monobasic acid $C_{18}H_{12}O_4$ (XIII).

In our studies, an examination of the infrared spectrum of I (Nujol mull) revealed the presence of a strong hydroxyl band (3350 cm.$^{-1}$), a band at 1680 cm.$^{-1}$ compatible with a cyclopentenone structure that is substituted in the β-position with an aromatic nucleus [*cf.* 4-hydroxy-3,4-diphenyl-2-cyclopenten-1-one, 1684 cm.$^{-1}$ (potassium bromide pellet)[6]], and a band at 1715 cm.$^{-1}$ expected for the carbonyl group of an α,β-unsaturated ester. The ultraviolet absorption spectrum of I in 95% ethanol contained two principal maxima, at 264 mμ (log ε 4.58) and 300 mμ (log ε 4.06), in contrast to the spectra of 1H-cyclopenta(*l*)phenanthrene derivatives which contain principal maxima at 257 mμ. The ultraviolet absorption spectrum of II in 95% ethanol has principal maxima at 257 mμ (log ε 4.78), at 290 mμ (log ε 4.03) and at 302 mμ (log ε 4.02). The infrared spectrum of II contains a hydroxyl band (3270 cm.$^{-1}$) and two carbonyl bands (1750 and 1720 cm.$^{-1}$). This information has led us to propose the tetracyclic structure III for the compound assigned structure I by Japp and Streatfeild. The compound obtained by acid-catalyzed isomerization of III, to which Japp and Klingemann assigned structure II, has been reformulated as IV. This acid-catalyzed isomerization may be regarded as an oxotropic rearrangement[7] in which the driving force presumably is the formation of a phenanthrene nucleus.

Several of the experiments of Japp, Streatfeild and Klingemann have been repeated and structures have been assigned to compounds V to XIII mentioned above on the basis of the newly assigned structures III and IV.



III

IV, R = H
VIII, R = C_2H_5
XII, R = $COCH_3$

Both chemical and spectral evidence were noted in the formulation of these structures. The ultraviolet spectra of IV, V, VI, VIII, X, XII, XIII, XIV and XVI contain maxima indicating the presence of a phenanthrene nucleus in each compound. The absence of a hydroxyl band in the infrared spectrum of XII together with its phenanthrene-like ultraviolet spectrum shows that it is neither the acetate of III nor the enol acetate of IV.

The compound V obtained from III by mild treatment with hydriodic acid gave a coloration with ferric chloride characteristic of a β-ketoester. Acid hydrolysis of V resulted in decarboxylation to yield the known ketone VI.[8] Alkaline cleavage of V gave 9,10-phenanthrenediacetic acid (VII),[8] which was converted to the diethyl ester XVI. Dieckmann cyclization of XVI gave V, identical with the sample prepared from III. The product XI, obtained from III upon treatment with glacial acetic acid, is very insoluble, and is believed to be a polymer of the unit shown.

The assignment of structure XIII to the compound obtained from the alkaline hydrolysis of IV is based upon a neutralization equivalent (which shows that it is monobasic), a phenanthrene-like ultraviolet spectrum and the fact that its ethyl ester XIV which is isomeric with IV contains no hydroxyl group according to its infrared spectrum. On the basis of the alkaline cleavages of V to VII and VIII to IX, it would be anticipated that the cyclopentenone ring of IV would be cleaved and the ester group saponified to form 10-carboxymethyl-9-phenanthreneglycolic acid, which would readily lactonize to yield XIII. This acid was first reported by Beschke[8] who formulated it as XVII and the corresponding ethyl ester as XVIII. These structures are no longer tenable in light of the phenanthrene-like ultraviolet spectra of the compounds.

Treatment of the sodium salt of XIII with sodium amalgam yielded 9,10-phenanthrenediacetic acid (VII) as reported by Beschke.[8] The formation of XIII from treatment of X with boiling hydrobromic acid occurs presumably by hydrolysis of the ester and cleavage of the ether linkage, followed by cyclization.

Experimental[9]

Ethyl 3,3a-dihydro-3a-hydroxy-2-oxo-2H-cyclopenta(*l*)-phenanthrene-1-carboxylate (III) was prepared as described

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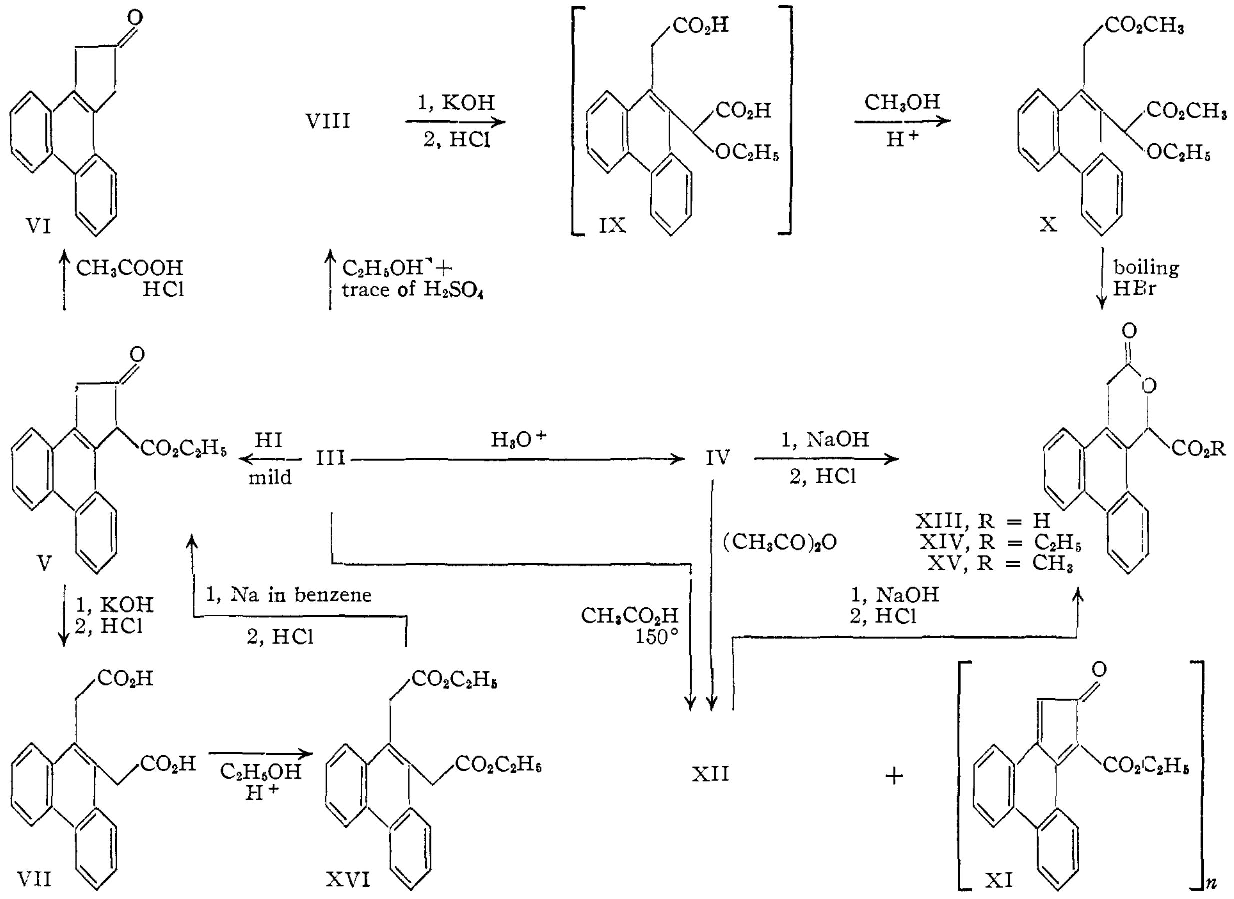
[5] F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **59**, 1 (1891).

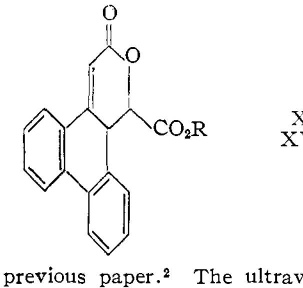
[6] P. Yates, N. Yoda, W. Brown and B. Mann, THIS JOURNAL, **80**, 202 (1958).

[7] E. A. Braude, *Quart. Revs.*, **4**, 404 (1950).

[8] E. Beschke, *Ann.*, **398**, 265 (1913).

[9] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.





XVII, R = H
XVIII, R = C_2H_5

in a previous paper.[2] The ultraviolet spectrum in 95% ethanol showed λ_{max} 264 mμ (log ε 4.58), λ_{max} 300 mμ (log ε 4.06), and the infrared spectrum of a Nujol mull had a strong hydroxyl band at 3350 cm.$^{-1}$ and two carbonyl bands at 1680 and 1715 cm.$^{-1}$

Ethyl 2,3-Dihydro-2-oxo-1H-cyclopenta(*l*)phenanthrene-1-carboxylate (V).—To the condensation product III (20 g.) was added 50 ml. of hydriodic acid (sp. gr. 1.7, 55–58% HI). The mixture was warmed with swirling in a bath at 70° for 1 minute. Water (500 ml.) was added and the solid product was removed by filtration. The product was washed with water and then digested twice with hot 5% aqueous sodium bisulfite solution. One crystallization of the product from ethyl acetate followed by recrystallization from 95% ethanol gave 10.1 g. (53%) of V, m.p. 122–124° (lit.[3] 124°). The ultraviolet spectrum in 95% ethanol showed λ_{max} 257 mμ (log ε 4.82), λ_{max} 289 mμ (log ε 4.06) and λ_{max} 302 mμ (log ε 4.12).

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 79.14; H, 5.37.

A solution of V in isopropyl alcohol or ethanol gave a green coloration with an ethanolic solution of ferric chloride.

Acid Hydrolysis of V.—A mixture of V (0.30 g.), glacial acetic acid (15 ml.) and concentrated hydrochloric acid (10 ml.) was heated under reflux for 1.8 hours. The mixture was cooled and the solid which had separated from the solution was removed by filtration and recrystallized from dioxane and gave 0.20 g. (88%) of the ketone VI, m.p. 222.5–223.0°, undepressed on admixture with an authentic sample of VI[8].

Alkaline Hydrolysis of V.—A mixture of V (1.0 g.) and 60 ml. of 5% aqueous potassium hydroxide solution was boiled for 10 minutes. The reaction mixture was treated with Norit, filtered, and the filtrate cooled in ice. Acidification of the filtrate with hydrochloric acid gave 9,10-phenanthrenediacetic acid (VII, 0.87 g., 90%), m.p. 298.5–300.0° (lit.[8] 305°), which was converted to its diethyl ester XVI in 73% yield by heating under reflux with ethanol containing hydrogen chloride, m.p. 97.4–98.2° (lit.[8] 94°). The ultraviolet spectrum of XVI had λ_{max} 214 mμ (log ε 4.47), λ_{max} 225 mμ (log ε 4.41) and λ_{max} 257 mμ (log ε 4.79).

The dimethyl ester of 9,10-phenanthrenediacetic acid (XVII) was prepared from 1.8 g. of the acid by heating under reflux with methanol containing hydrogen chloride in a yield of 1.78 g. (90%), m.p. 146–148°. An analytical sample that was recrystallized from methanol melted at 146.0–146.8°.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 74.52; H, 5.63. Found: C, 74.62; H, 5.64.

Dieckmann Cyclization of XVI.—A mixture of the ester XVI (1.0 g.), dry benzene (35 ml.) and powdered sodium (0.1 g.) was heated under reflux for 2 hours and then poured into a mixture of hydrochloric acid and ice. The product was extracted with ether and the extract washed with sodium carbonate solution and with water. Removal of the ether afforded an oil which upon trituration with cold ether yielded white crystals that were purified by repeated recrystallization from ethyl acetate. The yield of pure ethyl 2,3-dihydro-2-oxo-1H-cyclopenta(*l*)phenanthrene-1-carboxylate (V) was 0.17 g. (23%), m.p. 124.5–125.5°, undepressed on admixture with the sample of V prepared from III as de-

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Ultraviolet spectra were determined with a Cary ultraviolet spectrophotometer, model 11 MS. Infrared spectra were determined with a Baird double beam recording spectrometer, model B, fitted with a sodium chloride prism.

scribed above. Samples of V from both sources had identical infrared spectra.

Ethyl 2,3-dihydro-1-hydroxy-2-oxo-1H-cyclopenta(*l*)phenanthrene-1-carboxylate (IV) was prepared by a method similar to that of Japp and Klingemann.[5] A mixture of III (2.0 g.), concentrated sulfuric acid (25 ml.) and water (100 ml.) was heated under reflux for 17 hours. The solid material was collected by filtration and washed with water. Recrystallization from ethyl acetate afforded 0.7 g. (35%) of IV as white prisms, m.p. 175–176° (lit.[5] 177°). The ultraviolet absorption spectrum of IV in 95% ethanol had $\lambda_{\max}$ 257 mμ (log ε 4.78), $\lambda_{\max}$ 290 mμ (log ε 4.03) and $\lambda_{\max}$ 302 mμ (log ε 4.02). The infrared spectrum of IV (potassium bromide pellet) contained a hydroxyl band (3270 cm.$^{-1}$) and two carbonyl bands (1750 and 1720 cm.$^{-1}$).

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 75.01; H, 5.03. Found: C, 74.98; H, 5.03.

Action of Ethanol Containing a Trace of Sulfuric Acid on III.—The procedure described by Japp and Klingemann[5] was used. The product obtained from 5.0 g. of III was recrystallized from ethyl acetate and afforded 3.42 g. (63%, of VIII as white crystals containing a small amount of a red colored impurity, m.p. 144.1–145.0° (lit.[5] 143–144°). The ultraviolet absorption spectrum of VIII in 95% ethanol showed $\lambda_{\max}$ 257 mμ (log ε 4.76), $\lambda_{\max}$ 291 mμ (log ε 4.04) and $\lambda_{\max}$ 303 mμ (log ε 4.02). The infrared spectrum (potassium bromide pellet) possessed two carbonyl bands (1750 and 1730 cm.$^{-1}$).

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.83; H, 5.78.

Saponification of VIII and Esterification of the Product.—A mixture of 2.0 g. of VIII and 50 ml. of 5% aqueous potassium hydroxide solution was boiled for 10 minutes. The solid material which remained was removed by filtration. Acidification of the cold filtrate with hydrochloric acid gave 1.90 g. (98%) of the impure acid IX, which was heated under reflux for 24 hours with 150 ml. of methanol containing hydrogen chloride. The yield of methyl ester X was 1.71 g. (91%), m.p. 124.1–125.1° (lit.[5] 125°). The ultraviolet absorption spectrum of X in 95% ethanol had $\lambda_{\max}$ 214 mμ (log ε 4.45), $\lambda_{\max}$ 226 mμ (log ε 4.39) and $\lambda_{\max}$ 257 mμ (log ε 4.78).

Anal. Calcd. for $C_{22}H_{22}O_5$: C, 72.11; H, 6.05. Found: C, 71.93; H, 5.92.

Action of Acetic Acid on III.—The condensation product III (5.0 g.) was heated under reflux with glacial acetic acid (45 ml.) for 1.5 hours. The solid which had separated from solution was removed by filtration, washed with glacial acetic acid and dried. The yield of white needles of XI was 1.54 g. (33%), m.p. 288.0–289.4° (lit.[5] 285°). The infrared spectrum (potassium bromide pellet) of XI showed two carbonyl bands (1765 and 1720 cm.$^{-1}$).

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found: C, 79.45; H, 4.54.

The acetate XII was obtained from the filtrate of XI as described by Japp and Klingemann.[5] The red filtrate from XI was poured into 300 ml. of water and the solid which separated was collected by filtration and recrystallized once from ethanol and twice from ethyl acetate. The yield of white prisms of XII was 2.51 g. (44%), m.p. 165.0–166.4° (lit.[5] 165–171°). The ultraviolet spectrum of XII in 95% ethanol exhibited $\lambda_{\max}$ 257 mμ (log ε 4.76), $\lambda_{\max}$ 293 mμ (log ε 4.03), $\lambda_{\max}$ 305 mμ (log ε 4.03), and the infrared spectrum in chloroform showed carbonyl bands at 1750 and 1725 cm.$^{-1}$ but no hydroxyl band. An analytical sample had m.p. 166.0–167.5°.

Anal. Calcd. for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 72.90; H, 4.96.

3,4-Dihydro-3-oxo-1H-phenanthro(9,10-*c*)pyran-1-carboxylic Acid (XIII). (a) **From XII.**—A mixture of 2.6 g. of XII and 25 ml. of 10% aqueous sodium hydroxide was heated for 5 minutes. Water (10 ml.) was added and the mixture was filtered. Acidification of the cold filtrate with hydrochloric acid gave 1.85 g. (88%) of the acid XIII, m.p. 273–275°. One recrystallization from 95% ethanol raised the melting point to 274.0–275.2° dec., lit.[5] 267–269°. Beschke[8] reports m.p. 280° dec. for XIII, which he formulated as XVII. The ultraviolet absorption spectrum of XIII in 95% ethanol showed $\lambda_{\max}$ 257 mμ (log ε 4.66), $\lambda_{\max}$ 293 mμ (log ε 3.93) and $\lambda_{\max}$ 322 mμ (log ε 3.93). The infrared spectrum of XIII (potassium bromide pellet) contained a hydroxyl band at 3230 cm.$^{-1}$ and a broad carbonyl band at 1725 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{12}O_4$: C, 73.96; H, 4.14; neut. equiv., 292. Found: C, 73.76; H, 4.17; neut. equiv., 298.

(b) *From IV.*—The ester IV (1.0 g.) was heated with 2.0 g. of sodium hydroxide and 40 ml. of water for 15 minutes. The solution was cooled, acidified with hydrochloric acid and extracted with ether. Concentration of the extract and crystallization of the residue from 95% ethanol yielded 0.62 g. (68%) of pure XIII, m.p. 274.0–275.2°, undepressed on admixture with the sample of XIII prepared from XII described above.

Ethyl Ester of XIII.—The acid XIII (0.5 g.) was heated under reflux with 50 ml. of ethanolic hydrogen chloride for 1 hour. The solid product which separated from the clear solution upon cooling was collected and air-dried. The yield of the ester XIV was 0.48 g. (87%), m.p. 237.7–238.9°. Recrystallization from dioxane did not change the melting point. The ultraviolet absorption spectrum of XIV in 95% ethanol exhibited $\lambda_{\max}$ 249 mμ (log ε 4.67), $\lambda_{\max}$ 257 mμ (log ε 4.80), $\lambda_{\max}$ 291 mμ (log ε 4.01), $\lambda_{\max}$ 303 mμ (log ε 4.04), and the infrared spectrum of XIV in a Nujol mull showed a carbonyl band at 1730 cm.$^{-1}$ and a shoulder at 1710 cm.$^{-1}$ but no hydroxyl band. Beschke[8] reports m.p. 234° for this ester which he formulated as XVIII.

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 75.01; H, 5.03. Found: C, 74.82; H, 5.32.

The methyl ester XV of the acid XIII was prepared both by the action of ethereal diazomethane and methanolic hydrogen chloride on XIII in 71 and 78% yield, respectively, m.p. 254.9–255.5°.

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.41; H, 4.52.

Conversion of X to XIII.—A mixture of 0.15 g. of X, 5 ml. of glacial acetic acid and 20 ml. of 44% hydrobromic acid was heated under reflux for 6 hours. The reaction mixture was cooled and the brown solid removed by filtration. The solid was heated under reflux for 14 hours with 2 g. of potassium hydroxide in a mixture of 5 ml. of methanol and 25 ml. of water. The mixture was filtered and the filtrate was acidified with hydrochloric acid. The acid XIII which separated was collected and recrystallized once from 95% ethanol (Norit). The yield of the pure acid XIII was 0.057 g. (48%), m.p. 273.5–274.2°, undepressed on admixture with a sample of XIII prepared from XII or IV described above.

CAMBRIDGE, MASS.