of cellulose triacetate is not increased by irradiation in nitrogen, and its acetyl content remains unchanged. However, on irradiation in oxygen, far-reaching deacetylation occurs and copper number and uronic acidity increase considerably. The increase of the latter shows that hydroxyl groups in the 6 positions are oxidized.

4. That cellulose triacetate irradiated in nitrogen suffers a pronounced post-irradiation effect seems to show that, in cellulose itself, the hydroxyl groups are not essentially involved in that part of the irradiation reaction which leaves the glycosidic linkages in a condition unstable to oxygen.

5. Oxygen allowed to act upon cellulose triacetate with ultraviolet light excluded produces no changes in D. P., copper number and uronic acid.

6. The behavior of cellulose triacetate which has been irradiated in an oxygen atmosphere toward storage in nitrogen and in oxygen is much the same as previously observed with cellulose itself under the same conditions.

APPLETON, WIS. RECEIVED AUGUST 20, 1945

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

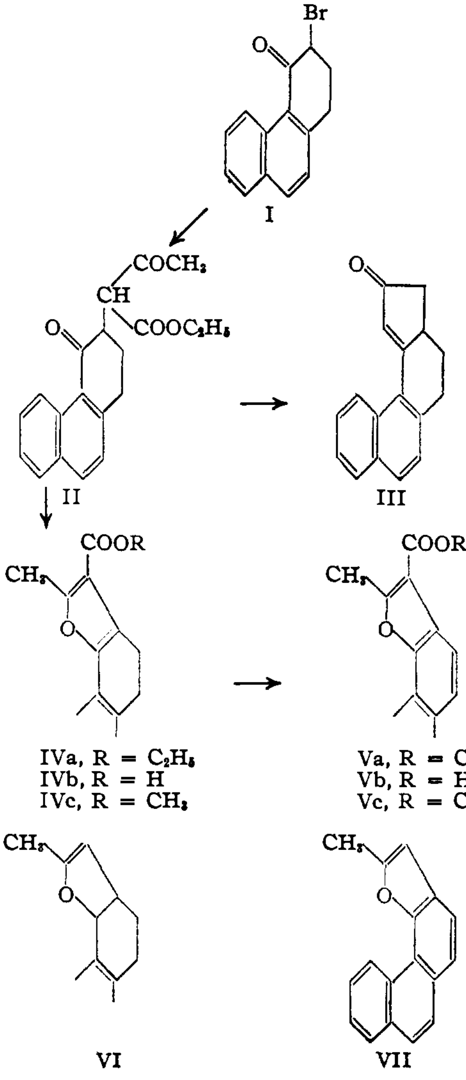
2'-Ketodihydro-3,4-cyclopentenophenanthrene and Derivatives of Phenanthro[4.3-*b*]-furan[1]

BY A. L. WILDS AND WARREN J. CLOSE

Several years ago it was shown[2] that the diketo ester resulting from reaction of 2-bromo-1-keto-tetrahydrophenanthrene with acetoacetic ester, could be cyclized in good yield either to an unsaturated ketone derived from 1,2-cyclopentenophenanthrene or to derivatives of phenanthro-[1.2-*b*]furan, depending upon the reagent used. These reactions have now been found to be applicable to the corresponding compounds prepared from 3-bromo-4-ketotetrahydrophenanthrene (I) and, in an accompanying communication, from 2-bromo-1-tetralone.[3]

The bromo ketone I, obtained in 96% yield from 4-ketotetrahydrophenanthrene, was readily converted into the diketo ester II by reaction with sodio-acetoacetic ester. As anticipated, II was cyclized by the action of aqueous potassium hydroxide to $\Delta^{4,3'}$-2'-keto-1,2-dihydro-3,4-cyclopentenophenanthrene (III). However, in contrast to the isomeric ketone prepared previously, the yield of III was affected markedly by the concentration of alkali. After a considerable number of trials the optimum conditions were found to involve preliminary treatment of II with 1% potassium hydroxide (presumably resulting in cleavage to the diketone) followed by 2.5% alkali to effect ring-closure[4,3]; the yield of III was 74%.

The structure of III was confirmed by Clemmensen reduction and dehydrogenation to the known 3,4-cyclopentenophenanthrene,[5] and a comparison was made with an authentic sample of the hydrocarbon kindly furnished by Dr. Bachmann. The picrate and trinitrobenzene derivative, prepared from the two samples of the



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[1] This work was supported in part by a grant from the Wisconsin Alumni Research Foundation.

[2] Wilds, THIS JOURNAL, **64**, 1421 (1942).

[3] Wilds and J. A. Johnson, *ibid.*, **68**, 86 (1946).

[4] Wilds and T. L. Johnson, *ibid.*, **67**, 288 (1945).

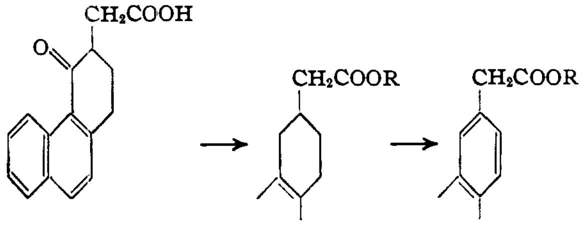
[5] Bachmann and Kloetzel, *ibid.*, **59**, 2212 (1937).

hydrocarbon also were identical. The double bond of the unsaturated ketone was shown to be conjugated with the carbonyl group and the naphthalene ring, as indicated in III, by a comparison of the ultraviolet absorption spectrum with those of closely related compounds. This will be reported in detail in the near future.

The behavior of II toward other cyclizing reagents was found to parallel closely that of the isomeric 1-ketotetrahydrophenanthrene-2-acetoacetate derivative.[2] The action of alcoholic hydrogen chloride converted it in nearly quantitative yield into the furan ester IVa. The corresponding acid (IVb) and methyl ester (IVc) were prepared readily from IVa. Treatment of II with alcoholic sodium ethoxide gave the acetyl hydroxy derivative of the furan in as high as 86% yield. This compound and its reactions are considered in an accompanying communication.[6]

The dihydro furan ester IVa could be dehydrogenated with palladium–charcoal catalyst in 93% yield to the fully aromatic phenanthro[4.3-*b*]furan ester Va. Both of the acids IVb and Vb underwent decarboxylation in the presence of copper to the corresponding furans VI and VII. Of these 2-methylphenanthro[4.3-*b*]furan (VII) is of especial interest since it is a furan analog of the carcinogenic hydrocarbon 3,4-benzophenanthrene.

The bromo ketone I also served as an intermediate for preparing derivatives of 3-phenanthreneacetic acid. By means of the malonic ester synthesis the keto acid VIII was prepared in 76% yield. Clemmensen reduction to the tetrahydro acid IXa and dehydrogenation (as the methyl ester IXb) gave 3-phenanthreneacetic acid (Xa), m. p. 183–184°, in good over-all yield.



VIII IXa, R = H Xa, R = H
IXb, R = CH_3 Xb, R = CH_3

Experimental[7]

4-Keto-1,2,3,4-tetrahydrophenanthrene.—Succinic anhydride (200 g.) was condensed with naphthalene (400 g.) by the procedure of Haworth[8] and the products were isolated as described by Robinson and Slater,[9] except after hydrolysis the nitrobenzene layer was washed several times with water by decantation and then heated to 45° for one hour before filtering. The solid was washed with benzene and dried to give 35 to 40% yields of β-2-naphthoylpropionic acid, m. p. 169–172°, which was satisfactory for reduction.[10] From the nitrobenzene filtrate was obtained 65 to 55% of crude β-1-naphthoylpropionic acid, m. p. 119–127°. Clemmensen–Martin[11] reduction of the 2-isomer (50 g. as obtained above) gave γ-2-naphthylbutyric acid in 90–95% crude yield. After vacuum distillation and recrystallization from benzene–petroleum ether, the yield of material melting at 98.5–101° was 76%. Cyclization using phosphorus pentachloride, followed by stannic chloride[12] gave the ketone in 89% yield, m. p. 67–69°.

3-Bromo-4-keto-1,2,3,4-tetrahydrophenanthrene (I).—Twenty grams of the ketone was brominated in absolute ether by the method described for the 1-keto isomer.[2] When the reaction was complete, water was added and 21.4 g. of nearly pure crystalline bromo ketone was obtained; m. p. 107–109°. The ether layer of the filtrate was evaporated and the residue recrystallized from acetone–alcohol, giving another 5.4 g. of material with the m. p. 106–110°, for a total yield of 96%. Further recrystallization from acetone–alcohol gave colorless plates melting at 108–109.5°. Mosettig and Burger[13] obtained the compound in 87% yield and reported the m. p. 104–105°.

Ethyl 4-Keto-1,2,3,4,-tetrahydrophenanthrene-3-acetoacetate (II).—To the sodio-acetoacetic ester prepared from 3.3 g. (0.14 equivalent) of powdered sodium, 55 cc. (0.43 mole) of ethyl acetoacetate and 100 cc. of dry, thiophene-free benzene was added 20 g. (0.073 mole) of 3-bromo-4-ketotetrahydrophenanthrene and 50 cc. of benzene. After heating to reflux for five hours, the mixture was cooled, 10 cc. of acetic acid and then water were added. The benzene layer was washed with 2% sodium hydroxide solution and water, the solvent was removed and the residue recrystallized from alcohol, to give 15.83 g. of a light tan solid melting at 92–102°. From the filtrate, after several recrystallizations, was obtained an additional 0.6 g. (m. p. 93–103°) bringing the total yield to 70%. The remainder of the material was a red oil (5.5 g.), from which only a small amount (0.81 g. corresponding to 5%) of the unsaturated ketone III could be obtained by treatment with dilute alkali as described below.

When a small amount of alcohol was used with the benzene in forming the sodio-acetoacetic ester,[2] the yields were reduced to 50–62%. A smaller excess of acetoacetic ester also was less favorable; thus, a 4:2:1 molar ratio of ester, sodium and bromide resulted in a 58% yield and a 3:2:1 ratio, in a 50% yield.

The analytical sample of the substituted acetoacetic ester, obtained as colorless prisms, after several recrystallizations from alcohol, still melted over the wide range 93–105°. The material gave only a tan color with alcoholic ferric chloride. The solid gave an initial yellow color with sulfuric acid, turning to a deep red upon standing.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.0; H, 6.2 Found: C, 74.3; H, 6.2

$\Delta^{4,3'}$-2′-Keto-1,2-dihydro-3,4-cyclopentenophenanthrene (III).—In a 1-liter, three-necked flask fitted with a dropping funnel, Hershberg stirrer and reflux condenser attached to a mercury trap was placed 5 g. of the substituted acetoacetic ester II and the system was filled with nitrogen (necessary to minimize the formation of colored by-products). To this was added 300 cc. of water previously boiled to remove dissolved air, and then a solution of 4 g. of potassium hydroxide (85%) in 100 cc. of boiled water was added over a period of ten minutes to the refluxing suspension. After heating for two hours, 11 g. of potassium hydroxide in 100 cc. of boiled water was added to make the concentration of alkali about 2.5% and the mixture was heated for six hours longer. The orange mixture was cooled under nitrogen and extracted with benzene. After washing the extract with water and dilute acid, the benzene was evaporated and the residue was crystallized from alcohol, giving 2.1 g. of orange crystals with the m. p. 114–121°. When the solid was inserted in a bath preheated to 114° the crystals melted partially, resolidified and remelted at 120–122°, indicating the existence of two

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(6) Wilds, Close and Johnson, This Journal, **68**, 89 (1946).

(7) All melting points are corrected unless otherwise indicated.

(8) Haworth, *J. Chem. Soc.*, 1129 (1932).

(9) Robinson and Slater, *ibid.*, 381 (1941).

(10) We wish to acknowledge the aid of Mr. Kenneth H. Anderson in carrying out and developing some improvements in the preparation of the keto acids.

(11) Martin, This Journal, **58**, 1438 (1936).

(12) See Bachmann and Cortes, *ibid.*, **65**, 1331 (1943); also ref. 2, p. 1426, for a similar procedure for the 1-keto isomer.

(13) Mosettig and Burger, *ibid.*, **57**, 2191 (1935).

crystallographic forms. A second crop of 0.58 g. (m. p. 119–120°) obtained from the filtrate by evaporative distillation at 180–200° (0.1 mm.) and recrystallization from alcohol, brought the total yield to 74%. Similar treatment of the first crop gave the analytical sample as colorless needles with the m. p. 122.5–123.5°. Occasionally a sample melted originally at 112–114°, resolidified and remelted at 121–122°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 86.9; H, 6.2.

From the original alkaline layer was obtained 0.53 g. (14%) of the crude keto acid VIII (m. p. 156–165°), which after recrystallization from ethyl acetate melted at 170–172°. When the substituted acetoacetic ester was heated with a fixed concentration of alkali, instead of building up the concentration gradually as above, the yields of III were lowered; the optimum yield in this case was 60% using 2% potassium hydroxide solution. With 5% potassium hydroxide the yield dropped to 34%, and considerable high-boiling, red, resinous material was formed.

The **oxime** of the ketone was obtained in quantitative yield by the alcohol-pyridine method as yellow needles of m. p. 176–179° (dec.). Further recrystallization from alcohol did not change the m. p.

Anal. Calcd. for $C_{17}H_{15}ON$: C, 81.9; H, 6.1. Found: C, 82.1; H, 6.2.

Conversion of III to 3,4-Cyclopentenophenanthrene.—One gram of the ketone was heated with 5 g. of amalgamated zinc, 20 cc. of hydrochloric acid, 1 cc. of water, 1 cc. of acetic acid and 2 cc. of toluene for twenty-four hours, during which time an additional 10 cc. of hydrochloric acid was added. Evaporative distillation of the product isolated with benzene gave 0.51 g. of an oil (190–200° at 0.1 mm.) which was dehydrogenated by heating at 300–310° for fifteen minutes with 0.15 g. of palladium–charcoal catalyst.[14] By evaporative distillation at 150–170° (0.1 mm.) and recrystallization from alcohol–acetone, 0.29 g. of material, m. p. 61–62°, was obtained as a mixture of needles and hexagonal plates. A second crop of 0.11 g., m. p. 59–61°, brought the total yield to 43%. Bachmann and Kloetzel[6] obtained 3,4-cyclopentenophenanthrene as octahedra melting at 73.5–75° (uncor.), but reported that the material remelted at 60°, indicating the existence of the second polymorphic modification obtained above. Further recrystallization of the lower melting form of the hydrocarbon did not change the melting point until the solution was seeded with a sample of the higher melting form (m. p. 73–74°) kindly sent by Dr. W. E. Bachmann; the material then was obtained as prismatic needles of m. p. 73.5–74.5° which showed no depression in melting point when mixed with the authentic specimen.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.5; H, 6.5. Found: C, 93.8; H, 6.5.

The picrate was obtained as orange-red needles, m. p. 137–137.5°, undepressed when mixed with the picrate of the same melting point prepared from the authentic sample of hydrocarbon.

The **trinitrobenzene derivative**, which crystallized from absolute alcohol as yellow needles of m. p. 153–154°, also was identical with a specimen prepared from the Bachmann–Kloetzel sample of the hydrocarbon.

Anal. Calcd. for $C_{17}H_{14} \cdot C_6H_3O_6N_3$: C, 64.0; H, 4.0. Found: C, 64.2; H, 4.1.

Ethyl 2-Methyl-4,5-dihydrophenanthro[4.3-*b*]furan-3-carboxylate (IVa).—Dry hydrogen chloride was passed for a short time into a solution of 4 g. of the substituted acetoacetic ester II in 50 cc. of absolute alcohol, and the mixture was heated to reflux for three hours. The alcohol was evaporated and the yellow oil taken up in benzene, washed with water and dilute ammonium hydroxide and the benzene removed. The residue was crystallized from alcohol to give a total of 3.64 g. (96%) of the colorless furan ester, m. p. 68–70°. Further recrystallization from alcohol gave a mixture of fine, silky needles melting at 70.5–71.5° and plates melting at 71.5–72°.

Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.4; H, 5.9. Found: C, 78.4; H, 5.8.

The free **acid IVb** was obtained by hydrolyzing 5 g. of the ethyl ester with a mixture of 25 cc. of 45% potassium hydroxide and 250 cc. of methanol, refluxing for twenty-two hours. Most of the methanol was evaporated, the salt was dissolved in warm water and acidified with dilute hydrochloric acid. The yield of acid (dried at 100°) was 4.51 g. (99%); m. p. 259–261° (Pyrex melting point tube). In a soft glass melting point tube the compound melted over a 10° range. The analytical sample, obtained as colorless prisms from dioxane, had the m. p. 262–263° (uncor., Pyrex melting point tube).

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.7; H, 5.1. Found: C, 77.9; H, 5.1.

The **methyl ester (IVc)**, prepared in quantitative yield by means of ethereal diazomethane, was obtained as colorless needles from methanol; m. p. 87.5–88°.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 78.3; H, 5.6.

Ethyl 2-Methylphenanthro[4.3-*b*]furan-3-carboxylate (Va).—The ethyl dihydrofuran ester (1.0 g.) was dehydrogenated by heating with 0.1 g. of palladium–charcoal catalyst[14] at 160–170° for ten minutes and then at 190–200° for another ten minutes. After removal of the catalyst and crystallization of the product from alcohol, 0.92 g. (93%) of the ester was obtained; the crystals melted at 127°, resolidified and remelted at 135–136°. Further recrystallization from alcohol gave colorless plates melting originally at 129°, and then resolidifying and remelting at 135–136°.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.9; H, 5.3. Found: C, 79.0; H, 5.4.

The **acid Vb** was obtained in quantitative yield by alkaline hydrolysis as described above for the dihydro derivative; m. p. 305–308° (Pyrex melting point tube). Recrystallization from dioxane gave colorless prisms melting at 308–309° (uncor., Pyrex melting point tube).

Anal. Calcd. for $C_{18}H_{12}O_3$; C, 78.3; H, 4.4. Found: C, 78.1; H, 4.3.

The **methyl ester (Vc)**, obtained in 87% yield by means of diazomethane, crystallized from methanol as colorless needles with the m. p. 136–136.5°. A mixture with the ethyl ester melted at 118–126°.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.6; H, 4.9. Found: C, 78.3; H, 4.9.

2-Methyl-4,5-dihydrophenanthro[4.3-*b*]furan (VI).—One gram of the dihydrofuran acid IVb was decarboxylated by heating with 0.5 g. of copper powder and 5 cc. of redistilled quinoline at 220–225° for sixty minutes and at 230–235° for ten minutes. The material was extracted with benzene and the neutral fraction was evaporatively distilled at 160–180° (0.1 mm.) to give a total of 0.64 g. (76% yield) of yellowish prisms, m. p. 40.5–42°. The analytical sample was obtained as nearly colorless prisms from methanol, m. p. 42–43°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 86.9; H, 6.0.

2-Methylphenanthro[4.3-*b*]furan (VII).—A similar decarboxylation of the dehydrogenated furan acid Vb gave the corresponding furan in 89% yield. The compound crystallized from methanol as colorless needles, m. p. 85–85.5°.

Anal. Calcd. for $C_{17}H_{12}O$: C, 87.9; H, 5.2. Found: C, 87.9; H, 5.3.

4-Keto-1,2,3,4-tetrahydrophenanthrene-3-acetic Acid (VIII).—To the sodio derivative prepared from 0.55 g. of sodium powder and 5.5 cc. of diethyl malonate in 25 cc. of dry, thiophene-free benzene was added 5 g. of 3-bromo-4-ketotetrahydrophenanthrene and 10 cc. of benzene. After the mixture was refluxed for four hours, acetic acid and water were added and the benzene layer was washed with water. The benzene was removed and the residue hydrolyzed and decarboxylated by heating with 75 cc. of ace-

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[14] Linstead and Thomas, *J. Chem. Soc.*, 1130 (1940).

tic acid, 75 cc. of concentrated hydrochloric acid and 30 cc. of water for twenty-four hours under an atmosphere of carbon dioxide.[15] When the reaction mixture was poured into water, the product was obtained as a solid; recrystallization from ethyl acetate gave 3.5 g. (76%) of pink crystals with the m. p. 167–171°. Further recrystallization, using Norit, gave colorless prisms melting at 171–172°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.5. Found: C, 75.6; H, 5.7.

When a small amount of alcohol was used to prepare the sodiomalonic ester[3] the yields were lowered (40–55%) and the product was accompanied by an oily by-product. After evaporative distillation at 0.1 mm. and recrystallization from ethyl acetate, colorless needles, m. p. 184–185°, were obtained in 5% yield. The fact that the compound is soluble in warm dilute sodium hydroxide solution, coupled with the analytical data, suggests that this material is **2-hydroxyphenanthro[4.3-*b*]furan** resulting from ring closure, dehydrogenation and decarbethoxylation of the intermediate malonic ester derivative. A pyridine solution of the compound gave a blue-violet color with alcoholic ferric chloride.

Anal. Calcd. for $C_{16}H_{10}O_2$: C, 82.0; H, 4.3. Found: C, 82.1; H, 4.5.

The **methyl ester of 4-ketotetrahydrophenanthrene-3-acetic acid** was prepared in 96% yield by the action of diazomethane upon the acid; the colorless plates obtained from methanol had the m. p. 66–67°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 76.1; H, 6.2.

1,2,3,4-Tetrahydrophenanthrene-3-acetic Acid (IXa).—Clemmensen–Martin reduction of 2 g. of the keto acid was carried according to the procedure of Bachmann and Struve for β-2-phenanthroylbutyric acid.[16] After thirty-six hours of refluxing, the product was isolated as described for the 2-isomer,[3] and recrystallized from ethyl acetate to give a total of 1.66 g. (88%) of acid melting at 127–128°. Further recrystallization did not raise the m. p. of the colorless prisms.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 80.1; H, 6.9.

The **methyl ester (IXb)**, obtained in 89% yield with diazomethane, crystallized from methanol as colorless needles melting at 47–48°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1. Found: C, 80.1; H, 7.0.

3-Phenanthreneacetic Acid (Xa).—The methyl ester of the tetrahydro acid was dehydrogenated by heating 0.6 g. with 0.06 g. of palladium–charcoal catalyst[14] under nitrogen first at 240° for thirty minutes, then at 280° and finally at 300° for thirty minutes each. At the end of this time the evolution of hydrogen had ceased. The catalyst was removed, using benzene to dissolve the dehydrogenated ester, but the latter could not be crystallized even after evaporative distillation (or preparation from the pure crystalline acid). The weight of the nearly colorless oil was 0.55 g. (93%).

The ester (0.52 g.) was hydrolyzed with methanolic potassium hydroxide to give 0.47 g. (96%) of the crude acid; m. p. 165–175°. Recrystallization from ethyl acetate gave colorless leaflets melting at 183–184° (80% recovery, the over-all yield from the tetrahydro ester was 71%). Mosettig and Van de Kamp[17] reported the m. p. 177–177.5° for the acid and the corresponding methyl ester as an oil. From another dehydrogenation using unpurified methyl ester and heating at 270–300° for two hours, approximately 25% of 3-methylphenanthrene was obtained in addition to 55% of the crude acid. The hydrocarbon had the m. p. 63–65° and gave a picrate of m. p. 139–140° (reported[8] 62–63° and 137–138°, respectively).

Summary

Ethyl 4-ketotetrahydrophenanthrene-3-acetoacetate (II) has been prepared and converted in good yield to $\Delta^{4,3'}$-2′-keto-1,2-dihydro-3,4-cyclopentenophenanthrene (III) by treatment with alkali. Reduction and dehydrogenation of the ketone afforded 3,4-cyclopentenophenanthrene.

Cyclization of II with alcoholic hydrogen chloride afforded a route to a number of derivatives of phenanthro[4.3-*b*]furan, which are of interest as analogs of the carcinogenic 3,4-benzophenanthrene and its derivatives.

The malonic ester derivative analogous to II was also prepared as an intermediate to derivatives of 3-phenanthreneacetic acid.

MADISON 6, WISCONSIN RECEIVED SEPTEMBER 24, 1945

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[15] This method of hydrolysis has been used by W. E. Bachmann and Leonard Miller (private communication) to prepare the 1-keto-2-acetic acid isomer. In the present case this method has proved to be superior to alkaline hydrolysis followed by decarboxylation.

[16] Bachmann and Struve, *J. Org. Chem.*, **4**, 459 (1939).

[17] Mosettig and Van de Kamp, THIS JOURNAL, **55**, 2995 (1935).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

2′-Ketodihydro-1,2-cyclopentenonaphthalene and Derivatives of Naphtho[1.2-*b*]furan

BY A. L. WILDS AND JAMES A. JOHNSON, JR.[1]

A few years ago it was shown that the Paal–Borsche method[2] of preparing cyclopentenone derivatives from 1,4-diketones and related substituted acetoacetic esters could be extended, under the proper conditions, to the synthesis of cyclic unsaturated ketones, such as $\Delta^{1,1'}$-2′-keto-3,4-dihydro-1,2-cyclopentenophenanthrene.[3] It then became of interest to see if $\Delta^{1,1'}$-2′-keto-3,4-dihydro-1,2-cyclopentenonaphthalene (II) could be prepared similarly from 1-tetralone. An unsuccessful attempt to accomplish this has been reported by Weidlich and co-workers.[4]

1-Tetralone was converted into the 2-bromo ketone and the latter was condensed with the sodium derivative of acetoacetic ester to give I. This diketo ester was used without purification for the subsequent reactions. When I was heated with 5% potassium hydroxide, a procedure

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[1] U. S. N. R., now on active duty.

[2] (a) Paal, *Ber.*, **16**, 2865 (1883); **17**, 2756 (1884); (b) Borsche and Fels, *ibid.*, **39**, 1809, 1922 (1906); Borsche and Menz, *ibid.*, **41**, 190 (1908).

[3] Wilds, THIS JOURNAL, **64**, 1421 (1942).

[4] Weidlich, Daniels, Knauber and Kübler, *Ber.*, **72**, 1598 (1939).