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.

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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).

MADISON 6, WISCONSIN RECEIVED SEPTEMBER 24, 1945

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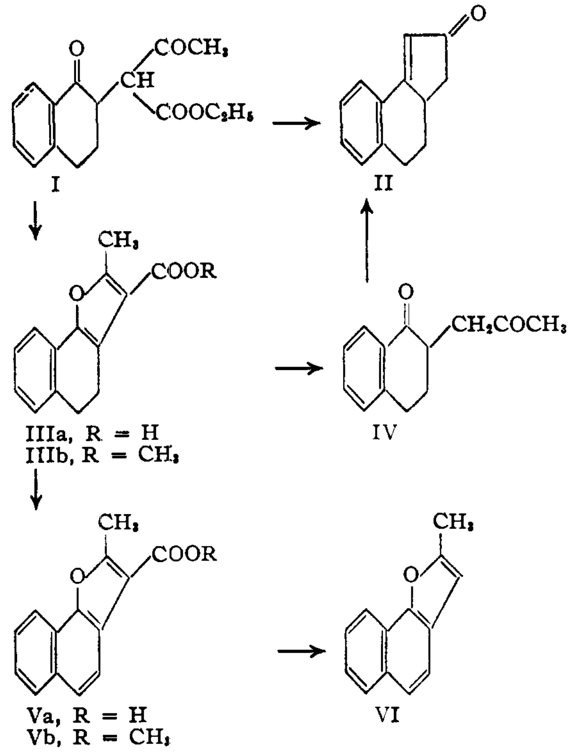
(1) U. S. N. R., now on active duty.

(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).



which was satisfactory for cyclizing the corresponding phenanthrene derivative,[3] it was possible to isolate the ketone II. The yield, however, was only 38% (over-all from 1-tetralone), and the ketone was accompanied by a considerable amount of high-boiling, neutral resin. Weidlich[4] reported obtaining no neutral material but instead a red, amorphous, acidic product of unknown composition.

Subsequently it was found that the yield could be improved considerably by use of the modified procedure[5] involving treatment first with 1% and then with 3% potassium hydroxide. In this manner the cyclic ketone II was obtained in 50–60% yields from 1-tetralone.

The behavior of the keto ester I toward some other cyclizing reagents was found to be similar to that of the corresponding phenanthrene derivatives.[3,6] Treatment with alcoholic hydrogen chloride resulted in the formation of a furan ester from which the free acid IIIa could be obtained in 76% over-all yield (from 1-tetralone). This acid was prepared previously by Weidlich (in unspecified yield).[4] The cyclization of I to an acetyl hydroxyfuran derivative by sodium ethoxide is considered in an accompanying communication.[7]

Prolonged heating of the furan acid IIIa with hydrochloric acid resulted in cleavage of the furan ring and decarboxylation to the diketone IV. This compound could also be prepared directly from the diketo ester I by a similar treatment. The diketone was cyclized to II in 80% yield by treatment with aqueous alkali.

The methyl ester of the furan acid (IIIb) was converted in good yield into the fully aromatic compounds Vb and Va by dehydrogenation with palladium-charcoal catalyst. Decarboxylation of the acid Va, in the presence of copper, gave 2-methylnaphtho[1.2-*b*]furan (VI).

Experimental[8]

2-Bromo-1-tetralone.—All of the 1-tetralone used in this work was prepared by cyclization of γ-phenylbutyric acid.[9] When the 1-tetralone was made by aerial oxidation of tetralin[10] the over-all yields in preparing the cyclic ketone and furan acid, described below, were considerably lower and the products more difficult to purify.

2-Bromo-1-tetralone was prepared from 6.92 cc. (21.5 g.) of bromine and 20 g. (2% excess) of 1-tetralone in 200 cc. of anhydrous ether by the method described previously for 2-bromo-1-ketotetrahydrophenanthrene.[3] When the addition of bromine was complete the decolorized solution was poured into ice water and the ether layer washed with water and 5% sodium bicarbonate solution. The ether was then removed and the residual crude 2-bromo-1-tetralone was dissolved in 75 cc. of thiophene-free benzene. This solution was dried over sodium sulfate, filtered and used without further purification for the reaction with sodio-acetoacetic ester. On one run the pure bromoketone was isolated, after removal of the ether, by dissolving the residue in petroleum ether and cooling in Dry Ice with scratching. Recrystallization of the resulting solid (m. p. 37–39°) from petroleum ether gave the 2-bromo-1-tetralone in the form of rods with the m. p. 39–40° (reported[11] m. p. 40°).

Ethyl 1-Keto-1,2,3,4-tetrahydronaphthalene-2-acetoacetate (I).—To the sodio-acetoacetic ester prepared from 5.2 g. of sodium powder and 55 cc. of ethyl acetoacetate in 150 cc. of dry, thiophene-free benzene was added the dried benzene solution of crude bromotetralone prepared from 21.5 g. of bromine and 20 g. of tetralone. The mixture was refluxed for four hours, cooled, acidified with acetic acid and treated with water. The benzene layer was washed with water, dried over sodium sulfate and the benzene removed. The crude oily acetoacetic ester derivative (containing the excess ethyl acetoacetate) was employed in the subsequent reactions without purification unless otherwise indicated. When a small amount of alcohol was used with the benzene in preparing the sodio-acetoacetic ester,[3] the product gave considerably lower yields in the following reactions.

A portion of the product was freed from excess ethyl acetoacetate by washing with 2% potassium hydroxide, and was converted to ethyl 2-methyl-4,5-dihydro-1-benz[*g*]indole-3-carboxylate by treatment with ammonium acetate, as described by Weidlich and Daniels.[4] The recrystallized derivative was obtained in 21% yield (over-all from tetralone), m. p. 157.5–158° (reported,[4] 156–157°).

2-Methyl-4,5-dihydronaphtho[1.2-*b*]furan-3-carboxylic Acid (IIIa).—The crude oily acetoacetic ester derivative prepared as above (from the bromotetralone obtained from 21.5 g. of bromine and 20 g. of tetralone) was dissolved in 175 cc. of absolute alcohol which had been saturated with dry hydrogen chloride. The mixture was refluxed for two hours and then the alcohol was removed under a stream of air. The product was dissolved in benzene and washed with water and 5% sodium bicarbonate solution. Acidification of the latter gave no appreciable amount of acidic material. After drying over sodium sulfate the benzene was removed and the residue was distilled under reduced

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(5) Wilds and T. L. Johnson, THIS JOURNAL, 67, 288 (1945).

(6) Wilds and Close. *ibid.*, 68, 83 (1946).

(7) Wilds. Close and Johnson. *ibid.*, 68, 89 (1946).

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

(9) "Organic Syntheses," Coll. Vol. II, 1943. p. 569.

(10) "Organic Syntheses," 20, 94 (1940); the product was fractionated through a Vigreux column instead of a packed column of the Fenske type.

(11) Straus. Bernoully and Mautner. *Ann.*, 444, 178 (1925).

pressure. Following a forerun of ethyl acetoacetate and tetralone, 28.2 g. of the furan ester was obtained in the fraction b. p. 155–158° (0.2 mm.). The crude ester was hydrolyzed by refluxing for five hours with a solution of 45 g. of potassium hydroxide in 190 cc. of water and 60 cc. of methanol. When the clear solution was cooled and acidified with hydrochloric acid, 23.2 g. (76% over-all yield) of the furan acid was obtained; m. p. 228.5–230.5°. Recrystallization from ethyl acetate gave the pure acid in the form of long, colorless rods melting at 231.5–232.5° (reported by Weidlich and Daniels,[4] m. p. 225–226°).

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3. Found: C, 73.7; H, 5.3.

The **methyl ester (IIIb)** prepared using diazomethane was crystallized from petroleum ether; m. p. 30–31.5°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.4; H, 5.8. Found: C, 74.4; H, 6.0.

1-Keto-1,2,3,4-tetrahydronaphthalene-2-acetone (IV). (*a*) *From the Acetoacetic Ester Derivative I.*—The crude acetoacetic ester derivative (prepared using the bromo ketone from 21.5 g. of bromine and 20 g. of tetralone), 200 cc. of acetic acid, 200 cc. of hydrochloric acid and 70 cc. of water were refluxed for forty-eight hours under a carbon dioxide atmosphere. At the end of the period of heating the mixture was cooled, diluted with water and extracted thoroughly with benzene. The combined extract was washed with dilute alkali, water and dried. After removal of the solvent the ketone was isolated by distillation, giving 15.7 g. of material in the fraction boiling at 142–145° at 0.7 mm. Recrystallization from petroleum ether gave 10.6 g. (39% over-all yield) of material with m. p. 51–53°.

(*b*) *From the Furan Acid IIIa.*—A mixture of 10 g. of the furan acid, 200 cc. of acetic acid, 200 cc. of hydrochloric acid and 70 cc. of water was refluxed under a carbon dioxide atmosphere for forty-seven hours. At the end of five hours an additional 100 cc. of acetic acid and 75 cc. of hydrochloric acid were added and another 50 cc. of hydrochloric acid after twenty-six hours. The diketone was isolated as before giving 7.91 g. (89%) of crude material, m. p. 42–46°. One recrystallization from petroleum ether gave 5.92 g. (67%) melting at 50.5–52.5°.

The analytical sample, purified by evaporative distillation at 0.5 mm. and two recrystallizations from petroleum ether, was obtained as colorless prisms with the m. p. 52.5–53°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.2; H, 7.0. Found: C, 77.3; H, 7.1.

$\Delta^{1,1'}$-2'-Keto-3,4-dihydro-1,2-cyclopentenonaphthalene (II). (*a*) *From the Acetoacetic Ester Derivative I.*—The oily acetoacetic ester derivative was prepared as described above from bromotetralone (obtained from 21.5 g. of bromine and 20 g. of tetralone). This was placed in a 3-liter, three-necked flask fitted with a Hershberg stirrer, dropping funnel and reflux condenser to which was attached a mercury trap. The system was evacuated, filled with nitrogen and 1140 cc. of freshly boiled water was added. To the boiling, stirred suspension was added 200 cc. of 20% potassium hydroxide over a period of forty-five minutes and heating was continued for another forty-five minutes. An additional 158 cc. of 20% potassium hydroxide was then added over fifteen minutes (final alkali concentration about 3%) and stirring and refluxing were continued for six hours. The system was allowed to cool under a stream of nitrogen and the reaction mixture was extracted with benzene. After washing with water and twice with 5% hydrochloric acid, the benzene solution was dried over sodium sulfate and the solvent removed. The residue was distilled under reduced pressure and 15.4 g. (62%) of crude product was collected in the fraction boiling at 151–155° (0.4 mm.); m. p. 62–72°. Recrystallization from petroleum ether gave 10.2 g. of m. p. 73–74° and a second crop of 2.4 g. of m. p. 70–73.5° for an over-all yield of 51%. From the filtrate after evaporative distillation at 0.5 mm. was obtained 1.1 g. of material with the m. p. 35–60°.

(*b*) *From the Diketone IV.*—To a refluxing and stirred mixture of 3 g. of the diketone IV and 255 cc. of freshly boiled water under an atmosphere of nitrogen was added 45 cc. of 20% potassium hydroxide over a period of fifteen minutes and the reaction mixture was refluxed for an additional five and one-half hours. When the product was extracted as above and evaporatively distilled twice at 0.5 mm., 2.20 g. (80%) of the cyclic ketone was obtained with the m. p. 70–72.5°. Similar results were obtained with 5% aqueous potassium hydroxide. However, when the diketone was heated with 5% methanolic potassium hydroxide for five hours the product was an orange-yellow, high-boiling, amorphous solid, presumably the result of condensation. When the reaction in either (a) or (b) was not carried out in an inert atmosphere, the product was very dark in color and difficult to purify.

For analysis a sample of the ketone was evaporatively distilled at 0.5 mm. and recrystallized twice from petroleum ether. Colorless prisms were obtained with the m. p. 74–75°.

Anal. Calcd. for $C_{13}H_{12}O$: C, 84.7; H, 6.6. Found: C, 84.9; H, 6.8.

The **2,4-dinitrophenylhydrazone,** prepared using an alcoholic solution of the reagent and an equivalent amount of hydrochloric acid, was obtained in 91% yield. Recrystallization from a mixture of benzene and toluene gave dark red needles m. p. 250.5–251° dec., and lighter red plates, m. p. 247.5–248° dec.

Anal. Calcd. for $C_{19}H_{16}O_4N_4$: C, 62.6; H, 4.4. Found: C. 62.6; H, 4.5.

Methyl 2-Methylnaphtho[1.2-*b*]furan-3-carboxylate (Vb).—The methyl ester, prepared from 3 g. of the dihydro acid IIIa (m. p. 231–232°) by means of diazomethane, was dehydrogenated by heating with 0.3 g. of palladium-charcoal catalyst[12] at 200° for five minutes and then at 300° for a total of forty-five minutes. The product crystallized readily from methanol to give a total of 2.62 g. (83%) of the methyl ester, m. p. 61.5–63.5°. Another recrystallization gave colorless prisms melting at 62–63.5°.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.0; H, 5.0. Found: C, 74.9; H, 4.9.

2-Methylnaphtho[1.2-*b*]furan-3-carboxylic Acid (Va).—The methyl ester (2.3 g.) was hydrolyzed by heating for sixteen hours with 5 cc. of 45% potassium hydroxide and 30 cc. of methanol. Acidification gave 2.1 g. (97% yield) of the colorless acid (dried at 100°); m. p. 248–250° (uncor.), with previous sintering at 243°. After recrystallization from a mixture of dioxane and ethyl acetate the m. p. of the colorless crystals was 248.5–249.5° (uncor.).

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.3; H, 4.5. Found: C, 74.3; H, 4.5.

2-Methylnaphtho[1.2-*b*]furan (VI).—A mixture of 1 g. of the acid Va, 0.5 g. of copper powder and 5 cc. of redistilled quinoline was refluxed for one and one-half hours. The neutral fraction was evaporatively distilled at 115–130° (0.3 mm.) giving a colorless oil which could be crystallized from methanol at Dry Ice temperature; m. p. 21.5–22.5°.

Anal. Calcd. for $C_{13}H_{10}O$: C, 85.7; H, 5.5. Found: C, 85.5; H, 5.7.

The product from the above run was isolated as the **picrate,** which crystallized from absolute alcohol as orange-red needles, m. p. 113–113.5°. The total yield was 1.58 g. or 87%.

Anal. Calcd. for $C_{13}H_{10}O \cdot C_6H_3O_7N_3$: N, 10.2. Found: N, 10.0.

The **trinitrobenzene derivative,** prepared by using slightly less than one equivalent of the reagent, crystallized from absolute alcohol as clusters of light yellow needles, m. p. 132.5–133.5°.[13]

Anal. Calcd. for $C_{13}H_{10}O \cdot C_6H_3O_6N_3$: C, 57.7; H, 3.3. Found: C, 57.7; H, 3.5.

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

[13] When an excess of trinitrobenzene was used another addition compound was obtained corresponding in analysis to 1.5 molecules of reagent per molecule of the furan; m. p. 111.5–113°.

Decarboxylation of the dihydro acid IIIa gave the corresponding dihydro furan derivative as a colorless oil which could not be crystallized.

Summary

Conditions have been developed for the cyclization of ethyl 1-keto-tetrahydronaphthalene-2-acetoacetate (I) by alkali to $\Delta^{1,1'}$-2'-keto-3,4-dihydro-1,2-cyclopentenonaphthalene (II).

Derivatives of naphtho[1.2-*b*]furan-3-carboxylic acid also were prepared from the keto ester I by means of acid cyclization.

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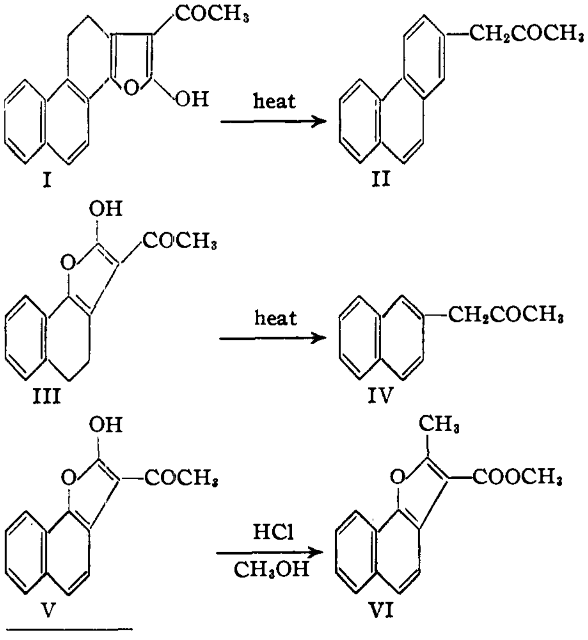
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Derivatives of Acetyl Hydroxy Furans and Their Conversion into Substituted Acetones[1]

BY A. L. WILDS, WARREN J. CLOSE AND JAMES A. JOHNSON, JR.

Several years ago the observation was made[2] that 1-acetyl-2-hydroxydihydrophenanthro[1.2-*b*] furan (I) was converted by heat into 2-phenanthreneacetone (II) in 79% yield. In view of the unusual nature and facility of this transformation, we became interested in determining if the reaction could be extended to other acetyl hydroxyfurans. The present paper describes the results obtained with the compounds III and VII.

The naphtho[1.2-*b*]furan derivative III was prepared from 1-tetralone in 73% yield by reactions similar to those used for the synthesis of I, namely, condensation of 2-bromo-1-tetralone with sodio-acetoacetic ester[3] and cyclization to III by means of sodium ethoxide. The naphthofuran derivative, like I, underwent a smooth reaction upon heating at 210–220° and gave 2-naphthaleneacetone (IV) in 84% yield. This transformation also proceeded in good yield (74%) when III was heated in acetic acid solution.



The structure of the ketone was established by synthesis from 2-naphthaleneacetic acid by conversion into the acid chloride and condensation with sodio-malonic ester. Hydrolysis and decarboxylation of the product by means of acid gave 2-naphthaleneacetone (IV),[4] identical with the sample obtained from the furan derivative III, as shown by the melting points and mixed melting points of the ketone, 2,4-dinitrophenylhydrazone and picrate.

In the conversion of the furan III to the ketone IV by either procedure the ketone was accompanied by a small amount (2 to 8%) of an alkali-soluble by-product which proved to be the dehydrogenated acetyl hydroxyfuran derivative V. Unlike the dihydro derivative, V was stable toward heat. Its structure follows from the analytical results and from the fact that it was converted into the methyl ester of 2-methylnaphtho[1.2-*b*]furan-3-carboxylic acid (VI)[3] by long heating with methanol containing hydrogen chloride. A similar reaction has been found to take place in the dihydro series.[5,6]

The phenanthro[4.3-*b*]furan derivative VII was prepared from 4-ketotetrahydrophenanthrene by a series of reactions similar to those used for I and III. The conversion to 3-phenanthreneacetone (VIII) was found to go smoothly in this case, too; by heating VII to 200° the ketone was formed in 81% yield, and by the acetic acid procedure, in 71% yield. The structure of the ketone VIII was proved by synthesis from the acid chloride of 3-phenanthreneacetic acid and malonic ester in a manner similar to the preparation of IV.

In this series, too, a small amount of the dehydrogenated acetylhydroxyfuran IX accompanied the ketone when the latter was prepared from the furan VII. The structure of IX was supported by its conversion into the methyl ester of the corresponding furan acid X,[7] when heated with methanol and hydrogen chloride.

In connection with the formation of the de-

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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, Jr., *ibid.*, 68, 86 (1946).

[4] For this series of reactions compare Wilds and Beck, *ibid.*, 66, 1688 (1944).

[5] For the use of this reaction in connection with the structure of I see ref. 2.

[6] Borsche and Fels, *Ber.*, 39, 1809 (1906).

[7] Wilds and Close, THIS JOURNAL, 68, 83 (1946).