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.

MADISON 6, WISCONSIN RECEIVED SEPTEMBER 24, 1945

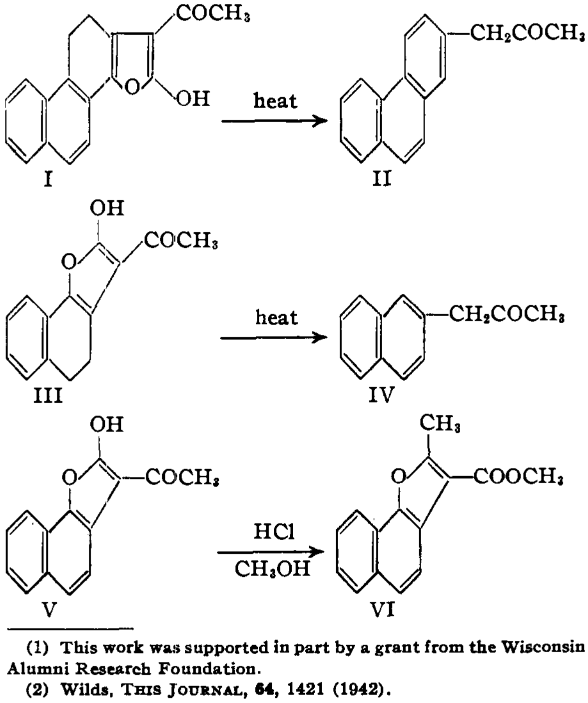
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

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).

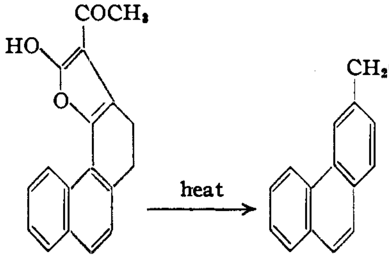
[3] Wilds and J. A. Johnson, Jr., *ibid.*, 68, 86 (1946).

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

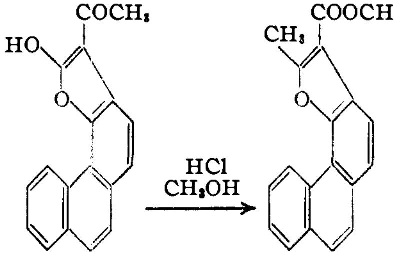
[5] For the use of this reaction in connection with the structure of I see ref. 2.

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

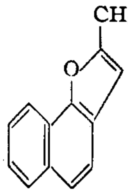
[7] Wilds and Close, THIS JOURNAL, 68, 83 (1946).



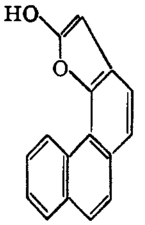
VII VIII



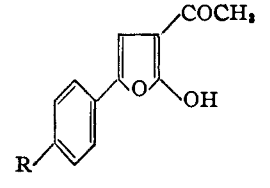
IX X



XI



XII

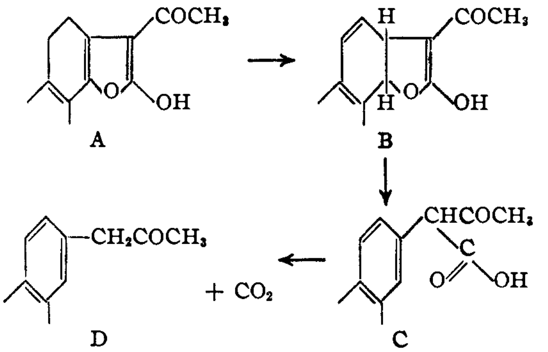


XIIIa, R = H
XIIIb, R = CH3O

hydrogenated furan derivatives IX and V, present evidence indicates that they do not arise as by-products during the formation of the aromatic ketones. Instead they seem to be the result of an entirely different type of decomposition of the dihydro derivatives VII and III, which takes place slowly even at room temperature. When the dihydro derivative VII was heated with palladium–charcoal catalyst in an effort to favor the formation of IX, little if any increase in yield was observed. On the other hand, the amount of IX that could be isolated was increased when old samples of VII were used.

This type of decomposition was studied in more detail for the naphthofuran derivative III. From a sample which had been allowed to stand for a year at room temperature, it was possible to isolate by crystallization about 15% of the dehydrogenated derivative V. Of the remaining material approximately one-fourth no longer was soluble in alkali. However, this neutral fraction was not 2-naphthaleneacetone but contained 2-methylnaphtho[1.2-*b*]furan (XI)[8] corresponding to 12% of the original hydroxyfuran. No other crystalline material could be isolated from the decomposition products. The development of the odor of acetic acid is characteristic of this slow decomposition. This acid could not arise from the formation of either V or XI, but in the case of the decomposition of the phenanthrofuran derivative VII, there is some indication that the hydroxyfuran XII is also produced. The full nature of this slow decomposition is not yet clear, but it is characteristic (although at varying rates) not only of III, VII and I, but also of derivatives of the type of XIIIa[6] and XIIIb,[8] where the formation of a dehydrogenation product (or a ketone such as IV) is not possible.

The mechanism suggested earlier[2] to explain the possible course of the transformation of an acetylhydroxydihydrofuran derivative into the arylacetone is supported by the additional evidence presented here. This mechanism involves rearrangement of the double bond in A away from the furan ring to form an intermediate of the type B, which can undergo aromatization by opening of the furan ring. The resulting β-keto acid C would then undergo decarboxylation to the ketone D



Such a shift of the double bond is possible for all three of the compounds known to undergo this transformation (I, III and VII). For those cases in which it is not possible for the double bond to shift and allow the furan ring to be opened in this manner, the transformation does not take place. Thus, the dehydrogenated derivatives V and IX and the examples XIIIa[6] and XIIIb[8] are relatively stable toward heat. It is hoped that further work will establish more completely the general nature of this transformation and supply new examples to delineate its scope and usefulness.

In connection with the furan derivatives I, etc., we have indicated the acetylhydroxyfuran structure as the most probable. However, it is possible that these compounds may have the alternate structure of unsaturated lactones in which the acetyl group is in the enolic form, a formulation preferred by Borsche for the simpler compound XIIIa.[6] We hope to obtain evidence on this point by a comparison of the ultraviolet absorption spectra of these compounds and appropriate derivatives.

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[8] Wilds and T. L. Johnson, THIS JOURNAL, 67, 286 (1945).

Experimental[9]

3-Acetyl-2-hydroxy-4,5-dihydronaphtho[1.2-*b*]furan (III).—2-Bromotetralone was prepared from 20 g. of 1-tetralone and 21.5 g. of bromine and converted into the acetoacetic ester derivative as described previously.[3] The reaction mixture was cooled, treated with a solution of 7.5 g. of sodium in 150 cc. of absolute alcohol and allowed to stand at room temperature for thirteen hours. Water was added to the gelatinous mixture, the insoluble sodium salt of the hydroxyfuran was filtered off and washed with benzene. The dried salt was dissolved in warm 50% methanol and the solution acidified with dilute hydrochloric acid to precipitate the hydroxyfuran; 22.3 g. of material with the m. p. 133–136° was obtained, corresponding to an over-all yield of 73% (from tetralone). Recrystallization from methanol gave light yellow blades with the m. p. 137–138.5°. The compound gave a brown solution with sulfuric acid and a green color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3. Found: C, 73.6; H, 5.4.

Decomposition of III at Room Temperature.—This decomposition occurred gradually, but was appreciable in one month. After a sample (m. p. 135.5–137°) had been stored in the dark, at room temperature (20 to 35°) for one year, it had changed to a dark, red-brown mixture of liquid and semi-solid gum with a strong odor of acetic acid. Crystallization of this material (16.8 g.) from methanol gave 1.25 g. (m. p. 169–171°) and 0.85 g. (m. p. 175–177°) of a light tan solid. Upon further recrystallization from methanol the melting point of the cream-colored blades was raised to 176.5–177°. This material was stable toward heat (was unchanged upon evaporative distillation at 0.2 mm.) and agreed in analysis for the dehydrogenated 3-acetyl-2-hydroxynaphtho[1,2-*b*]furan (V). The compound gave a greenish-yellow solution with sulfuric acid and an intense blue color with alcoholic ferric chloride solution. It was soluble in dilute sodium bicarbonate.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.3; H, 4.5. Found: C, 74.4; H, 4.4.

The original filtrate from the solid was dissolved in benzene and ether and extracted five times with 5% sodium bicarbonate solution, five times with 5% potassium hydroxide and then washed with water. Acidification of the bicarbonate extract and treatment of the resulting oil with methanol gave an additional 0.45 g. of the dehydrogenated acetyl hydroxyfuran, m. p. and mixed m. p. 174–176°, bringing the total yield of this material to 15%. No additional solid could be isolated from the remaining 3.5 g. of this fraction, even after evaporative distillation (approximately one-half was non-volatile at 250° and 0.4 mm.). Acidification of the potassium hydroxide fraction gave 7.0 g. of a dark colored oil which decomposed to a non-volatile pitch when heated.

The neutral fraction contained 3.6 g. of a dark oil which gave 2.0 g. of a yellow liquid upon evaporative distillation at 105–120° (0.2 mm.). This could not be crystallized directly, but upon treatment with picric acid in absolute alcohol gave a total of 3.7 g. of an orange picrate, m. p. 113–114°. This proved to be the picrate of 2-methylnaphtho[1.2-*b*]furan XI[3] (mixed m. p. 113–114°) and corresponded to a 12% yield. A sample of the free naphthofuran was prepared from the picrate and recrystallized from methanol (using Dry Ice); m. p. 22.5–23°. The trinitrobenzene derivative, obtained as light yellow needles, had the m. p. and mixed m. p. 132.5–133.5°.[3]

Conversion of V to Methyl 2-Methylnaphtho[1.2-*b*]furan-3-carboxylate (VI).—Methanol (30 cc.) containing 0.3 g. of the dehydrogenated acetylhydroxynaphthofuran V was saturated with hydrogen chloride and refluxed for three days. The mixture was treated with benzene and the extract washed with water and 5% potassium hydroxide. The neutral fraction crystallized readily from methanol to give a total of 0.26 g. (82%) of the methyl ester of the furan acid VI, m. p. 61–62.5°. Recrystallization gave colorless prisms of m. p. 63–64.5° which did not depress the m. p. of the sample prepared previously.[3]

Similar treatment of the dihydroacetylhydroxyfuran derivative III for four hours followed by alkaline hydrolysis gave the corresponding dihydrofuran acid[3] in 50% yield, m. p. and mixed m. p. 230–232°.

2-Naphthaleneacetone (IV). (*a*) *From the Hydroxy Furan III.*—Four grams of the hydroxynaphthofuran III was melted in a 10-cc. Claisen flask and heated in an oil-bath at 210–220° under slightly reduced pressure for one and one-half hours. Then the pressure was lowered slowly until the product began to distill and finally was lowered to 0.5 mm. until a higher boiling fraction began to appear. The distillate amounted to 2.72 g. (84%) of solid with the m. p. 32–35.5°. After two recrystallizations from petroleum ether the melting point of the colorless leaflets was 37–37.5°. The material gave no color with sulfuric acid.

Anal. Calcd. for $C_{13}H_{12}O$: C, 84.7; H, 6.6. Found: C, 84.5; H, 6.5.

Evaporative distillation (at 0.5 mm.) of the residue in the distillation flask gave 0.1 g. of solid melting at 167–200°. This material appeared to contain some of the dehydrogenated acetylhydroxyfuran and gave a blue-green color with alcoholic ferric chloride solution.

When 5 g. of the hydroxydihydronaphthofuran III was heated under reflux with 200 cc. of acetic acid[3] in a carbon dioxide atmosphere for eighteen hours, the main product again was 2-naphthaleneacetone. The mixture was diluted with water, extracted with benzene and the latter washed with dilute alkali and water. The residue after removal of the benzene was crystallized from petroleum ether giving 2.48 g. of material melting at 34.5–36°. From the filtrate after evaporative distillation at 0.5 mm. and recrystallization from petroleum ether was obtained an additional 0.52 g., m. p. 33–34.5°, bringing the total yield to 74%. Acidification of the alkaline wash gave 0.4 g. of solid melting at 152–158°. The melting point was raised to 167–170° by purification through the sodium salt (using bicarbonate solution). A mixture of this material with the dehydrogenated hydroxyfuran V obtained above (m. p. 175–176°) melted at 171–173.5°.

The **2,4-dinitrophenylhydrazone of 2-naphthaleneacetone** was obtained in nearly quantitative yield by heating the ketone (by either procedure above) with a solution of the reagent in alcohol containing an equivalent of hydrochloric acid. Recrystallization from a mixture of ethyl acetate and alcohol gave orange hexagonal plates with the m. p. 172.5–173°.

Anal. Calcd. for $C_{19}H_{16}O_4N_4$: C, 62.6; H, 4.4. Found: C, 62.7; H, 4.4.

The **picrate** of the ketone was obtained from absolute alcohol as yellow rectangular plates melting at 79.5–80°.

Anal. Calcd. for $C_{13}H_{12}O \cdot C_6H_3O_7N_3$: N, 10.2. Found: N, 10.0.

(*b*) *From 2-Naphthaleneacetic Acid.*—2-Naphthaleneacetic acid (m. p. 141.5–143°) was prepared from 2-acetylnaphthalene by the modified Willgerodt procedure described by Schwenk and Bloch.[10] The acid chloride was prepared from 7 g. of the acid, condensed with sodiomalonic ester and hydrolyzed with acid following the procedures used for 1-keto-2-methyltetrahydrophenanthrene-2-acetone.[4] Evaporative distillation of the neutral fraction at 0.5 mm. followed by recrystallization from petroleum ether gave a total of 3.9 g. (56%) of 2-naphthaleneacetone, m. p. 35.5–37.5°; 14% of the starting acid was recovered from the bicarbonate extract. Further recrystallization of the ketone raised the m. p. to 37–37.5°. The 2,4-dinitrophenylhydrazone melted at 172.5–173° and the picrate at 79.5–80°. The melting points of the ketone and its derivatives were undepressed when mixed with the corresponding samples prepared in (*a*).

3-Acetyl-2-hydroxy-4,5-dihydrophenanthro[4.3-*b*]furan (VII).—A solution of 5 g. of ethyl 4-keto-1,2,3,4-tetra-

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

(10) Schwenk and Bloch, THIS JOURNAL, **64**, 3051 (1942); Newman, *J. Org. Chem.*, **9**, 521 (1944).

hydrophenanthrene-3-acetoacetate[7] in 20 cc. of dry benzene was added to a solution of 1 g. of sodium in 20 cc. of absolute alcohol. The red-orange mixture was allowed to stand for twelve hours at room temperature, during which time only a small amount of solid separated. The mixture was acidified with 5% hydrochloric acid and the yellow solid filtered, giving 3.67 g. (86%) of VII, m. p. 173–175° (gas). No pure material was obtained from the benzene layer. Recrystallization of a portion of the solid from benzene gave the analytical sample as fine, yellow needles with the m. p. 172.5–174° (gas). A pyridine solution of the compound gave a green color with alcoholic ferric chloride and the solid gave a deep brown color with concentrated sulfuric acid. Upon standing for several months the compound became dark and underwent decomposition.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.7; H, 5.1. Found: C, 77.4; H, 5.2.

3-Phenanthreneacetone (VIII). (*a*) *From the Acetylhydroxyfuran VII.*—One gram of VII was heated at 180–200° for ten minutes and then was evaporatively distilled at 0.1 mm. and the same temperature. The oily distillate solidified and was recrystallized from methanol to give 0.61 g. of the ketone melting at 70–71.5° and an additional 0.07 g. melting at 64–68° for a total yield of 81%.

Following the oily distillate was a small amount of solid sublimate (200–225° at 0.1 mm.) which melted at 222.5–223.5° after recrystallization from alcohol or benzene. More of this material was isolated when crude hydroxyfuran was used. This is shown below to be 3-acetyl-2-hydroxyphenanthro[4.3-*b*]furan (IX).

Recrystallization of the 3-phenanthreneacetone from alcohol gave colorless leaflets with the m. p. 70.5–71.5°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 87.0; H, 6.0.

3-Phenanthreneacetone also was obtained in 71% yield, m. p. 70–72°, by refluxing a solution of the hydroxyfuran VII in acetic acid, as described above for the naphthofuran derivative.

The ketone gave a **2,4-dinitrophenylhydrazine derivative** in 99% yield; m. p. 253–254° dec. uncor. When this derivative was recrystallized from toluene, the product gave high analytical values for carbon (found: C, 68.0, 68.2; H, 4.6, 4.6) because of retention of the solvent even after drying at 80° and 0.5 mm. for twelve hours. A satisfactory analytical sample was obtained by recrystallization from a large volume of *n*-butyl alcohol; in each case the melting point of the orange prisms was unchanged.

Anal. Calcd. for $C_{23}H_{18}N_4O_4$: C, 66.7; H, 4.4. Found: C, 66.5; H, 4.3.

(*b*) *From 3-Phenanthreneacetic Acid.*—Eight-tenths gram of this acid[7] was converted into 0.36 g. (45% yield) of the ketone by the method described earlier[4] for an analogous transformation; 34% of the crude starting acid was recovered. The ketone had the m. p. 70.5–71.5° alone or when mixed with the sample prepared in (*a*). The 2,4-dinitrophenylhydrazone (m. p. 253–254° dec.) similarly showed no depression in melting point upon admixture with the derivative described above.

3-Acetyl-2-hydroxyphenanthro[4.3-*b*]furan (IX).—An attempt was made to increase the amount of dehydrogenation of VII to IX by heating 1 g. of the material (nine months old, m. p. 165–168°) and 0.1 g. of palladium-charcoal catalyst[11] to 200–300° for one-half hour. The amount of IX isolated by extraction with sodium hydroxide and sublimation at 220–230° (0.1 mm.) was 0.08 g. (8%), m. p. 220–222°. Although this was somewhat more than was obtained from the pure furan derivative, it was not significantly larger than that resulting from heating an aged sample.

The analytical sample was obtained as colorless needles, m. p. 222.5–223.5°. The solid gave only a pale yellow color with sulfuric acid but a solution in pyridine gave an intense green color with alcoholic ferric chloride.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.3; H, 4.4. Found: C, 78.5; H, 4.3.

From the "neutral" fraction a small amount of material believed to be 2-hydroxyphenanthro[4.3-*b*]furan (XII) could be isolated by heating the oil repeatedly with 5% sodium hydroxide and recrystallizing the acidic material several times from alcohol; yield 0.03 g. (3%), m. p. 183–184°. The material gave no depression in melting point when mixed with the sample obtained previously.[7]

Conversion of IX to the Furan Ester X.—Forty milligrams of IX was heated for three and one-half days with methanol saturated with hydrogen chloride. Evaporative distillation of the neutral fraction gave 18 mg. (43%) of the furan ester X; m. p. 133–135°. The recrystallized product had the m. p. 135–136° alone and when mixed with a sample of the material prepared previously.[7] Alkaline hydrolysis gave the corresponding furan acid with the m. p. and mixed m. p. 308–309°, uncor. (Pyrex tube).

Summary

The earlier observation that 1-acetyl-2-hydroxy-10,11-dihydrophenanthro[1.2-*b*]furan (I) was converted by heat into 2-phenanthreneacetone (II) has now been extended to 3-acetyl-2-hydroxy-4,5-dihydronaphtho[1.2-*b*]furan (III) and 3-acetyl-2-hydroxy-4,5-dihydrophenanthro[4.3-*b*]furan (VII). These derivatives gave 2-naphthaleneacetone (IV) and 3-phenanthreneacetone (VIII) in 84 and 81% yields, respectively.

Small amounts of the corresponding dehydrogenated furan derivatives were formed by a slow decomposition of III and VII at room temperature. The fact that these dehydrogenated compounds are stable toward heat provides additional support for the mechanism suggested for the conversion of the acetylhydroxyfurans into substituted acetones.

Madison 6, Wisconsin Received September 24, 1945

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