dissolved in 2500 ml. of water. The mixture was stirred for 30 min. more and vacuum-filtered. The residue was suspended into 10% hydrochloric acid, refiltered, and washed with water to give, upon drying, 114 g. (76.5% yield) of 4′-chloro-5-nitro-2-furanacrylanilide, m.p. 212–213.5° (lit.,[8] m.p. 214°). A portion was crystallized from alcohol to give orange crystals, m.p., 216°.

Anal. Calcd. for $C_{13}H_9ClN_2O_4$: C, 53.34; H, 3.09. Found: C, 53.56; H, 3.14.

BEN VENUE LABORATORIES, INC.
BEDFORD, OHIO

Dienone-Phenol Rearrangement of 2-Phenyl-*o*-quinolacetate[1]

H. BUDZIKIEWICZ AND W. METLESICS

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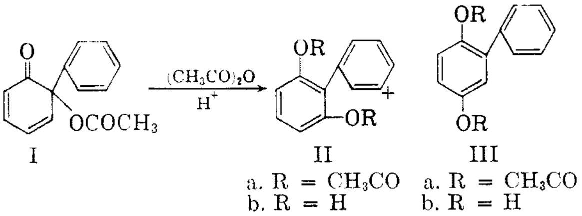
In preceding papers[2,3] it has been shown that *o*-quinol acetates, when treated with acetic anhydride and a catalytic amount of concentrated acid or BF_3-etherate, are readily rearranged to acetylated phenols.

Under these conditions 2-methyl-*o*-quinol acetate yields 85% of 2,6-diacetoxytoluene and a trace of 2,5-diacetoxytoluene. In analogy to this result we expected to get mainly 2,6-diacetoxybiphenyl by subjecting 2-phenyl-*o*-quinol acetate (I) to this reaction:

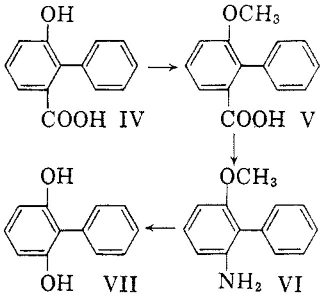


From the crude product an acetate, m.p. 91–93°, was obtained in 90% yield. Hydrolysis gave a phenol, m.p. 117–119°.

These melting points differ greatly from the figures given by Kubota and his co-workers[4] who described 2,6-dihydroxybiphenyl as having a melting point of 138° (m.p. of the diacetate 111°), a substance which we can hardly believe to be identical with our phenol IIb.

As infrared absorption, chromatographic behavior, and color reactions are consistent with the assumed structure of II, we have secured this result by an independent synthesis.

6-Hydroxybiphenyl-2-carboxylic acid (IV)[5] was transformed into 2,6-dihydroxybiphenyl as shown in the illustrated scheme.



The resulting phenol was identical with our rearrangement product IIb, as shown by mixed melting point and paper chromatography.

In the mother liquor of IIb some trace of a second phenol was found by paper chromatography. Color reaction and R_f value were the same as observed with a sample of 2,5-dihydroxybiphenyl[6] which had been prepared for comparison.

EXPERIMENTAL[7]

2-Phenyl-o-quinol acetate, I, was prepared by lead tetraacetate oxydation of 2-hydroxybiphenyl according to the directions of Wessely and his co-workers.[8]

Rearrangement of 2-phenyl-o-quinol acetate, I. Two-tenths of a gram of I was added in portions while stirring to a mixture of 2 ml. acetic anhydride and 2 drops of perchloric acid. The mixture was allowed to stand for 2 hr., then it was poured into 20 ml. of water. Having thus stood during the night, crystals had separated in 90% yield. The analytical sample, which was recrystallized from methanol and a mixture of ether and ligroin, resulted in 2,6-diacetoxybiphenyl, IIa, m.p. 91–93°, $\gamma^{CS_2}_{max}$ 1770 (C═O), 734, 696 (monosubstituted benzene ring), 762 (1,2,3-trisubstituted benzene ring).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.1; H, 5.2. Found: C, 71.3; H, 5.4.

Hydrolysis of the crude rearrangement product with a mixture of 10% sulfuric acid and methanol (1:1) yielded crystals which were recrystallized to give 2,6-dihydroxybiphenyl, IIb, m.p. 117.5–119°. IIb with an ethanolic solution of ferric chloride did not show any color reaction.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.4; H, 5.4. Found: C, 78.0; H, 5.5.

Paper chromatography of the products of hydrolysis was carried out by descending the upper phase of a mixture of benzene, glacial acetic acid, and water (4:1:5). IIb having been sprayed with diazotized sulfanilic acid solution and treated with ammonia vapors, formed a reddish brown spot. The mother liquors of IIb showed a second spot with the same R_f value and color reaction as observed with a sample of *2,5-dihydroxybiphenyl,* IIIb.

2,6-Dihydroxybiphenyl, VII, has been synthesized as follows:

6-Methoxybiphenyl-2-carboxylic acid, V. 6-Hydroxybiphenyl-2-carboxylic acid, IV,[5] treated with dimethylsulfate

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[1] Paper III on Dienone-Phenol-Rearrangement of Quinols.

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[3] W. Metlesics, F. Wessely, and H. Budzikiewicz, *Tetrahedron* . . . . (1959).

[4] B. Kubota, Y. Fujimura, K. Akashi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo),* **2,** 185 (1925); *Chem. Abstr.,* **19,** 2334 (1925).

[5] C. Graebe, P. Schestakow, *Ann.,* **284,** 316 (1894).

[6] W. Borsche, *Ann.,* **312,** 221 (1900).

[7] Infrared spectrum was measured using a Perkin-Elmer Model 21 spectrophotometer. Maxima are expressed in cm.$^{-1}$ Melting points are determined on a Kofler micro hot stage.

[8] F. Wessely, L. Holzer, and H. Vilcsek, *Monatsh. Chem.,* **83,** 1253 (1952).

formed V, which was then recrystallized from methanol m.p. 175–176°.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3. Found: C, 73.3; H, 5.4.

2-Amino-6-methoxybiphenyl, VI. Schmidt degradation of V was carried out according to the directions of Briggs and Lyttleton.[9] Concentrated sulfuric acid (0.15 ml.) was added to a mixture of 0.4 mmoles of V, 0.5 ml. of about 1*N* HN_3 in $CHCl_3$, and 1 ml. of $CHCl_3$ and the mixture was stirred until the evolution of gas had ceased. By treating the reaction mixture as described above a yellow oil was isolated being 2-amino-6-methoxybiphenyl, VI. It showed a positive reaction with Duke's reagent for primary amines. It was benzoylated by means of benzoyl chloride and pyridine to form a benzoate m.p. 106–107°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: N, 4.6. Found: N, 4.5.

2,6-Dihydroxybiphenyl, VII. 2-Amino-6-methoxybiphenyl, VI, was diazotized and the diazonium salt decomposed in the usual way. By distillation 2-hydroxy-6-methoxybiphenyl could be isolated in the form of a yellowish oil which was cleaved by refluxing with a mixture of HBr (d = 1.38) and glacial acetic acid for 3 hr. to give white crystals of 2,6-dihydroxybiphenyl, VII, which recrystallized from a mixture of ether and ligroin. M.p. 118.5–119.5°, undepressed on admixture with the saponified rearrangement product. Identity was further proved by paper chromatography.

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II. CHEMISCHES INSTITUT
UNIVERSITÄT WIEN
VIENNA, AUSTRIA

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Reactions of Several 4-Pyrones Catalyzed by Potassium Acetate and Trifluoroacetic Acid

L. L. WOODS[1] AND P. A. DIX

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In a previous communication[2] the reaction of aryl aldehydes with 2,6-dimethyl-4-pyrone in the presence of potassium hydroxide was described. The product in each of the cases reported was a vinyl derivative.

This Note is, in part, the description of the reaction of aryl aldehydes with 4-pyrones, some of which are methylated at positions 2 and 6, whereas others have these positions open or blocked with other groups. The only common denominator in the pyrones used in these experiments is that position 3 is unoccupied.

Since none of the various pyrones failed to react with the aryl aldehydes under the influence of fused potassium acetate, the point of ring attachment to form a secondary alcohol was probably position 3. The infrared absorption spectrum of the simplest compound of the I series (I_G), gives an absorption band at 3502 cm.$^{-1}$ indicating the presence of a hydroxyl radical. Chromanone formed unsaturated derivatives due to the presence of an extra ring hydrogen in position 3, which made possible the elimination of water. The compounds formed by the reaction of 4-pyrones with aldehydes under the catalytic influence of potassium acetate are given as I_{A-I} series of Table I.

A part of the study of the effect of certain catalysts on the reactive nature of 4-pyrones was the examination of the use of trifluoroacetic acid with acylating compounds on such substances.

It was found that the use of trifluoroacetic acid as a solvent would permit acyl halides to react with 4-pyrones in a clean reaction giving good yields in a short reaction time. The product was not contaminated with large amounts of polymeric substances as was encountered in some of the preparations by the zinc chloride method.[2,3]

Benzoylation of kojic acid diacetate gave the compound II_B which was quite different in its physical constants from 2-acetoxymethyl-5-acetoxy-6-benzoyl-4-pyrone which had been prepared earlier.[4] The fact that these two compounds are different means that the point of the attachment of the benzoyl group to the pyrone ring is position 3 when kojic acid diacetate is acylated under the influence of trifluoroacetic acid.

In order to prove that II_B has the benzoyl group in position 3 it was postulated that such a compound would form a pyronopyrone[5] under the rearranging and cyclizing influence of fused potassium acetate and acetic anhydride, since no such compound should be formed from 2-acetoxymethyl-5-acetoxy-6-benzoyl-4-pyrone.

Unfortunately the cyclized product from II_B was a liquid. Efforts to purify the compound by distillation have been unsuccessful.

Compound II_F has been reported previously[6] elsewhere but the method gave a polymeric mixture. The above procedure gave superior results in every respect.

Compound II_C was chosen as representative of the II_{A-G} series so the malononitrile derivative and the 2,4 dinitrophenylhydrazone of the pyridone of II_C were prepared as proof of the ketonic nature of the substances formed during the reaction.

EXPERIMENTAL[7]

Preparation of compounds of I_{A-I} series. One-tenth mole of the aldehyde was mixed with 0.1 mole of the pyrone and 0.1 mole of powdered fused potassium acetate in a 500-ml. flask and the mixture was heated for 2 hr. at 120–130° in a

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[1] The person to whom all communications concerning this article are to be directed.

[2] L. L. Woods, *J. Am. Chem. Soc.*, **80**, 1440 (1958).

[3] L. L. Woods, *J. Org. Chem.*, **22**, 341 (1957).

[4] L. L. Woods, *J. Am. Chem. Soc.*, **74**, 1105 (1952).

[5] L. L. Woods, *J. Org. Chem.*, submitted for publication.

[6] L. L. Woods, *Texas Jour. Sci.*, **11**, 28 (1959).

[7] All analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J. All melting points were determined on a Fisher-Johns apparatus.