melting point and mixed melting point, crystallized in long slender needles. On attempted recrystallization from alcohol, the substance invariably came out as slightly yellow plates, characterized by a greenish fluorescence.

Anal.[c] Calcd. for $C_{25}H_{16}O_7N_3Cl$: N, 8.31. Found: N, 8.16. [b] Calcd. for $C_{19}H_{13}Cl$: Cl, 12.81. Found: Cl, 12.60, 12.68.

Two attempts were made to oxidize IV and obtain 5-chloro-1,2-benzanthraquinone. However, only a trace of a yellow crystalline material, m. p. 175–176°, was isolated and analysis showed that this was not the desired compound.

5-Cyano-10-methyl-1,2-benzanthracene, V.—The conversion of IV into a nitrile by heating with cuprous cyanide in pyridine gave variable results. In the best experiment, 0.51 g. of IV, 0.50 g. of cuprous cyanide, and 1 cc. of pyridine were heated in a sealed tube at 260 ± 3° for forty-eight hours. The reaction mixture was worked up as in a similar case.[1] The nitrile V crystallized in shining yellow plates from benzene–alcohol and the yield of material melting at 182.8–183.2° was 0.21 g. or 43%. An additional quantity of V, m. p. 179–181°, raised the yield to 62%.

Anal.[c] Calcd. for $C_{20}H_{13}N$: N, 5.24. Found: N, 5.16.

The Amide of 5-Carboxy-10-methyl-1,2-benzanthracene, VI.—Various attempts at hydrolysis of the nitrile to the acid gave crystalline products obviously impure and melting over a wide range. In the best experiment, 0.229 g. of nitrile was dissolved in 20 cc. of hot acetic acid and 2 cc. of 65% sulfuric acid was added. This solution was refluxed for eleven hours, diluted with hot water, and allowed to stand overnight at 0°. The solids were collected and weighed 0.237 g. The melting point was fairly sharp at 303–305°, uncorr. On recrystallization from dioxane–alcohol or from acetic acid the amide was obtained as fine yellow needles with little loss in weight. The highest melting point was 308–310°, uncorr. Several other runs were made but rarely did the yield exceed 50%.

Anal.[c] Calcd. for $C_{20}H_{15}ON$: C, 84.18; H, 5.30; N, 4.91. Found: C, 84.21; H, 5.12; N, 5.07.

Summary

A rather general method for the synthesis of chloro derivatives of 10-methyl-1,2-benzanthracenes is illustrated by the synthesis of 5-chloro-10-methyl-1,2-benzanthracene. The method involves: reaction of *o*-chlorophenylmagnesium bromide with 1,2-naphthalic anhydride; addition of methylmagnesium bromide to the ketone group of the resulting 2-*o*-chlorobenzoyl-1-naphthoic acid; reduction of the resulting lactone to an acid; and cyclization and reduction to 5-chloro-10-methyl-1,2-benzanthracene. The conversion of this compound into the corresponding 5-cyano compound and into the amide of the 5-carboxy compound is also described.

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[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

Arsenated Derivatives of Mixed Ketones. II. Arsenicals of Peonol

BY C. KENNETH BANKS[1] AND CLIFF S. HAMILTON

In a previous paper[2] it was shown that, although 2,4-dimethoxyacetophenone formed a stable arsonic acid, no stable arsenic derivative of the unmethylated ketone was isolable. In an effort to retain a free hydroxyl group in the molecule, one of the monomethyl ethers of resacetophenone, 2-hydroxy-4-methoxyacetophenone,[3] peonol, was investigated.

Direct arsonation of the ketone with arsenic acid failed to give even a trace of an arsonic acid. In order to introduce the arsono group through the diazo reaction,[4] it was necessary to prepare the amine of the ketone. Adams[5] obtained a mononitropeonol in low yields but did not prove the structure of the compound. Baker[6] prepared the same compound in 60% yields and proved it to be 2-hydroxy-4-methoxy-5-nitroacetophenone. By a modification of the nitration process of Omer and Hamilton,[2] 80% yields of this nitro compound were obtained.

The corresponding amine was also isolated by Adams with difficulty. By using Raney catalyst,[7] nitropeonol was reduced quantitatively to the amine in an acetone solution with molecular hydrogen. After removing the catalyst, the free amine could be isolated by evaporation of the solvent in an inert atmosphere. As the amine was unstable, it was generally isolated as the stable hydrochloride.

Arsonation of the amine hydrochloride proceeded smoothly, giving good yields of 2-hydroxy-4-methoxy-5-arsonoacetophenone. This product was then reduced to 2-methoxy-4-hydroxy-5-

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(1) Parke, Davis and Company Fellow.

(2) Omer and Hamilton, THIS JOURNAL, **59**, 642 (1937).

(3) Hoesch, *Ber.*, **48**, 1122 (1915).

(4) Bart, *Ann.*, **429**, 55 (1922).

(5) Adams, THIS JOURNAL, **41**, 247 (1919).

(6) Baker, *J. Chem. Soc.*, 1684 (1934).

(7) Raney, U. S. Patent 1,638,190 (1927).

acetylphenylarsine oxide with sulfur dioxide, using sodium iodide as a catalyst. Reduction of the arsonic acid with hypophosphorous acid gave 2,2′-dimethoxy-4,4′-dihydroxy-5,5′-diacetylarsenobenzene.

Experimental

2-Hydroxy-4-methoxy-5-nitroacetophenone.—Twenty grams of 2-hydroxy-4-methoxyacetophenone was added to 250 cc. of nitric acid (1.42) cooled in an ice-bath to 15°, with constant stirring. The stirring was continued for two hours, during which time the temperature was lowered to 10°, and the mixture then poured into 4 liters of chipped ice and water. This material was sufficiently pure for reduction. The pure nitro compound was obtained by recrystallization from hot water and decolorization with charcoal, giving an 80% yield of light tan orthorhombic crystals, m. p. 155°.

2-Hydroxy-4-methoxy-5-aminoacetophenone Hydrochloride.—Ten and five-tenths grams of 2-hydroxy-4-methoxy-5-nitroacetophenone was dissolved in 50 cc. of reagent acetone, 3 g. of Raney catalyst added and reduced with electrolytic hydrogen. After the reduction was complete, the catalyst was filtered off and half the acetone removed by evaporation in a partial vacuum. An equal volume of anhydrous ether was added and, on saturation with dry hydrogen chloride, an almost quantitative yield of the white, triclinic amine hydrochloride needles was obtained: m. p. 250°.

Anal. Calcd. for $C_9H_{11}O_3N \cdot HCl$: Cl, 16.32. Found: Cl, 16.42, 16.27.

2-Hydroxy-4-methoxy-5-aminoacetophenone.—Five grams of 2-hydroxy-4-methoxy-5-nitroacetophenone, which had been recrystallized from alcohol and water, was reduced as in the preparation of the amine hydrochloride. After removing the catalyst, the solution, in an evaporating dish, was placed in a vacuum desiccator in a carbon dioxide atmosphere and the majority of the acetone removed by evaporation. The amine crystallized in 80% yields as light yellow, orthorhombic crystals: m. p. 115°.

Anal. Calcd. for $C_9H_{11}O_3N$: N, 7.74. Found: N, 7.71, 7.65.

2-Hydroxy-4-methoxy-5-arsonoacetophenone.—Eight and one-tenth grams of 2-hydroxy-4-methoxy-5-aminoacetophenone hydrochloride was dissolved in water and 6 cc. of 12 *N* hydrochloric acid added. The solution was cooled to 0° and diazotized by adding 40 cc. of *N* sodium nitrite slowly with stirring. After the diazotization was completed, a solution of 1.5 g. of sodium hydroxide was added to the diazonium solution slowly to prevent heating. The diazonium solution was then added to a mixture of 11 g. of arsenic trioxide, 9 g. of sodium hydroxide and 1.5 g. of copper sulfate in 150 cc. of water and 150 cc. of ice with vigorous stirring. Nitrogen was evolved rapidly and the stirring was continued for two hours. After standing overnight, the mixture was heated to 60° and filtered. The filtrate was acidified with hydrochloric acid until neutral to litmus and concentrated to one-half its former volume. Charcoal was added to the hot solution and the coagulated material filtered off. The filtrate was made acid to Congo red paper and, on cooling, the arsonic acid separated. The product was recrystallized from water, giving white, orthorhombic needles in 58% yields; m. p. 225° (dec).

Anal.[8] Calcd. for $C_9H_{11}O_6As$: As, 25.83. Found: As, 25.87, 25.86.

2-Methoxy-4-hydroxy-5-acetylphenylarsine Oxide.—Five grams of 2-hydroxy-4-methoxy-5-arsonoacetophenone was dissolved in 50 cc. of warm water, 10 cc. of 12 *N* hydrochloric acid and 0.25 g. of sodium iodide were added. Sulfur dioxide gas was passed into the solution until saturated. The solution was allowed to stand for one hour, sufficient alkali added to give a *N* solution and filtered. The filtrate was made neutral to litmus, whereupon the arsine oxide precipitated. The compound was filtered off and recrystallized from hot water, giving a white powder on drying at 110° containing a molecule of water, in 85% yields; m. p. 260° (dec):

Anal. Calcd. for $C_9H_9O_4As \cdot H_2O$: As, 27.33. Found: As, 27.26, 27.24.

2,2′-Dimethoxy-4,4′-dihydroxy-5,5′-diacetylarsenobenzene.—Five grams of 2-hydroxy-4-methoxy-5-arsonoacetophenone was dissolved in 35 cc. of hypophosphorous acid by heating gently. The heating was continued for five minutes after gentle boiling occurred. An equal volume of hot water was added and the solution filtered while hot. The precipitate was washed well with alcohol and ether giving 85% yields of the yellow arseno compound; m. p. 228° (dec.).

Anal. Calcd. for $C_{18}H_{18}O_6As_2$: As, 31.21. Found: As, 31.25, 31.22.

Summary

1. 2-Hydroxy-4-methoxy-5-arsonoacetophenone was prepared from the corresponding amino derivative by diazotization followed by coupling with sodium arsenite.
2. 2-Methoxy-4-hydroxy-5-acetylphenylarsine oxide was obtained from the corresponding arsonic acid by reduction with sulfur dioxide in acid solution, using sodium iodide as a catalyst.
3. 2,2′-Dimethoxy-4,4′-dihydroxy-5,5′-diacetylarsenobenzene was prepared by the hypophosphorous acid reduction of the corresponding arsonic acid.
4. Several intermediate compounds were prepared in good yields by new methods, namely, 2-hydroxy-4-methoxy-5-nitroacetophenone, the corresponding amine and amine hydrochloride.

LINCOLN, NEBRASKA

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[8] The potentiometric method of Cislak and Hamilton, THIS JOURNAL, **52**, 638 (1930), was used for the quantitative determination of arsenic in all arsenic containing compounds prepared.