Summary

1. A new method for the preparation of 1,4-diketones is described.
2. A number of new 1,4-diketones have been prepared and characterized.
3. The mechanism of the formation of the 1,4-diketones is discussed.

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NOTES

Studies on the Mechanism of the Sulfonation of Aromatic Amines. III. Rearrangement of Barium Phenylsulfamate

BY ELLIOT R. ALEXANDER

In earlier communications, it has been shown that freezing point data and kinetic data[1] support a bimolecular mechanism for the sulfonation of aromatic amines rather than an intramolecular rearrangement of phenylsulfamic acid which has been postulated as an intermediate. There is one fact, however, that appears to be an anomaly: The dihydrate of barium phenylsulfamate can be transformed into sulfamic acid on heating at 180°.[2] It therefore seemed advisable to repeat Bamberger's experiments with carefully purified materials and to determine whether the reaction would proceed with the anhydrous salt.

On heating the dihydrate of barium phenylsulfamate in a closed vessel four and one-half hours at 175–185°, sulfonation of the aromatic nucleus was indeed found to have occurred to the extent of 26%. When the reaction was carried out with *anhydrous* barium sulfamate, however, no sulfonation occurred.

While these facts do not necessarily preclude an intramolecular rearrangement of the hydrate (since the water of hydration might have weakened and labilized certain bonds in the molecule permitting rearrangements which would not be possible in the anhydrous material), nevertheless it is interesting that this reaction is not characteristic of the anhydrous salt.

Experimental

Rearrangement of the Dihydrate of Barium Phenylsulfamate.—Barium phenylsulfamate dihydrate[3] (5.0 g., 0.00965 mole) was crushed into a fine powder and heated for four and one-half hours at 175–185° in a stoppered round-bottomed flask partially immersed in a metal heating bath. At the beginning of the heating moisture could be seen to condense on the cooler portion of the flask. As heating was continued the solid became streaked with purple but did not melt. After the heating period was completed, the flask was cooled and a mixture of 15 ml. of concentrated hydrochloric acid in 100 ml. of water was added. This mixture was digested fifteen minutes on a steam-bath and attached to a Kjeldahl apparatus. The solution was then made basic with sodium hydroxide solution and steam distilled quantitatively into 10 ml. of concentrated hydrochloric acid and 25 ml. of distilled water. The aromatic amine content of the distillate and the non-volatile portion was determined by titrating with standard sodium nitrite solution.[4] The steam-volatile portion required 28.91 ml. of 0.484 *N* sodium nitrite solution (72.6%) while the non-volatile portion required 10.38 ml. (26.1%).

Attempted Rearrangement of Anhydrous Barium Phenylsulfamate.—Anhydrous barium phenylsulfamate was prepared by drying the dihydrate for eight hours at 100° and 1 mm. It was analyzed by titration with sodium nitrite solution.[4]

Anal. Calcd. for $C_{12}H_{12}N_2S_2O_6Ba$: NH_2, 6.58. Found: NH_2, 6.55.

This salt (5.0 g., 0.00104 mole) was treated exactly as described above. Three drops of the sodium nitrite solution was required for the non-volatile portion while 42.87 ml. (99.6%) was required for the portion volatile with steam.

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[1] Alexander, THIS JOURNAL, **68**, 969 (1946); **69**, 1599 (1947).

[2] Bamberger and Hinderman, *Ber.*, **30**, 655 (1897).

[3] Traube, *ibid.*, **23**, 1654 (1890).

[4] Kolthoff and Stenger, "Volumetric Analysis," Interscience Publishers, Inc., New York, N. Y., 1942, p. 240.

The Preparation of 2-Amino-4-hydroxy-6-keto-5,5-dichlorodihydropyrimidine

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In connection with the investigation of the synthesis of pteroylglutamic acid[1] the compound, 2-amino-4-hydroxy-6-keto-5,5-dichlorodihydropyrimidine (III), became of some interest. The corresponding 2,4-dihydroxy-6-keto-5,5-dichlorodihydropyrimidine (IV) has been prepared by several methods[2,3,4] including the direct chlorination of barbituric acid (II) in water solution.[4] Several attempts to chlorinate 2-amino-4,6-dihydroxypyrimidine (I) by the use of chlorine in a water solution were unsuccessful. A good deal of decomposition occurred and the small yield of product usually obtained was apparently a mixture of the starting material and the monochloro and dichloro substitution products. When a potassium chlorate and hydrochloric acid mixture was used as a chlorinating agent a reasonably pure

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[1] Waller, *et al.*, THIS JOURNAL, **70**, 19 (1947).

[2] Behrend, *Ann.*, **236**, 64 (1886).

[3] Blitz and Hamburger, *Ber.*, **49**, 639 (1916).

[4] Bock, *ibid.*, **56B**, 1222 (1923).