

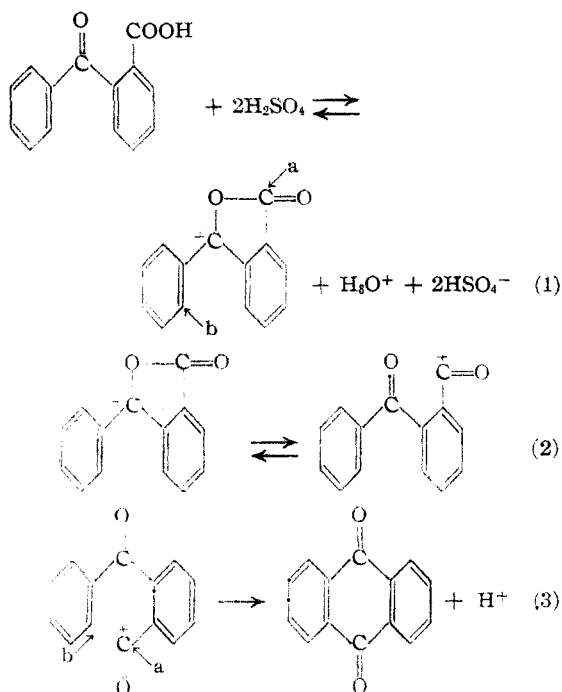
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A Mechanism for the Formation of Anthraquinone from *o*-Benzoylbenzoic Acid

BY MELVIN S. NEWMAN

The facile ring closure of *o*-benzoylbenzoic acid to anthraquinone under the influence of sulfuric acid has never been satisfactorily explained.¹ Although ring closure condensations with acids of the *o*-benzoylbenzoic and γ -arylbutyric type take place fairly readily in sulfuric acid, anthraquinone formation remains a reaction unique in organic chemistry. The ease and the high yield with which this condensation takes place ortho to a ketonic function are indeed remarkable.

It is the object of this communication to present a plausible mechanism for the formation of anthraquinone from *o*-benzoylbenzoic acid. The proposed mechanism is outlined in the following equations.



Arguments Advanced in Favor of the Proposed Mechanism

Equation 1.—The chief support for equation 1 was obtained in the following experiments.

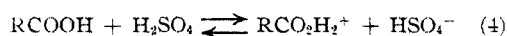
A. A solution of 5.0 g. of *o*-benzoylbenzoic acid in 98–99% sulfuric acid was poured into 500 cc. of absolute

(1) Gleason and Dougherty, *THIS JOURNAL*, **51**, 310 (1929), and Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1935, p. 189, discuss briefly the possibility of cyclic intermediates.

methanol in a one-liter Claisen flask. During this addition the flask was cooled externally by ice-water and internally by dry-ice. About 300 cc. of methanol was rapidly removed under reduced pressure at low temperature and the residue was poured on ice. The organic matter was rapidly taken into ether and separated into acid and neutral fractions by sodium carbonate extraction. From the acid fraction was isolated 1.48 g. (30%) of *o*-benzoylbenzoic acid. The neutral fraction consisted of 3.17 g. (60%) of a mixture of the normal and pseudo methyl esters of *o*-benzoylbenzoic acid. This mixture was analyzed by dissolving in 32 cc. of 98–99% sulfuric acid and pouring on ice. After such treatment it is known that the normal ester is recovered unchanged while the pseudo ester is converted into *o*-benzoylbenzoic acid.² By this means the 3.17 g. of mixed esters was converted into 1.19 g. (40%) of *o*-benzoylbenzoic acid and 1.78 g. (56%) of methyl *o*-benzoylbenzoate, thus indicating that the ester mixture consisted of 40% of pseudo ester and 56% normal ester.

B. This experiment was carried out just as experiment A, except that instead of dissolving *o*-benzoylbenzoic acid in sulfuric acid and pouring into cooled methanol, 60 cc. of 98–99% sulfuric acid was poured into a solution of 5.0 g. of the pseudo methyl ester of *o*-benzoylbenzoic acid in 500 cc. of methanol. There was then obtained 0.18 g. (3.6%) of *o*-benzoylbenzoic acid and 4.92 g. (92.5%) of mixed esters as above, was shown to consist of 35% of pseudo ester and 63% of normal ester.

Before drawing any conclusions from these experiments, it is desirable to point out certain facts. From the studies cited by Hammett,³ it seems well established that most organic acids behave as monoacid bases on ionization in solvent sulfuric acid, as follows



When sulfuric acid solutions of such acids are poured into absolute methanol, no appreciable amount of esterification occurs other than the slow normal acid catalyzed esterification.⁴ Likewise, when sulfuric acid solutions of the methyl esters of such acids are poured into water, the methyl esters are recovered almost completely unchanged.^{4,5} The normal methyl ester of *o*-benzoylbenzoic acid represents such an ester.

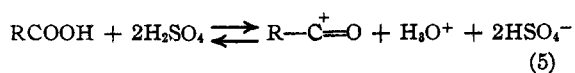
Certain acids, chiefly 2,4,6-trialkylbenzoic acids, ionize in sulfuric acid in a more complex way,^{3b} as follows

(2) Newman and McCleary, *ibid.*, **63**, 1539 (1941).

(3) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, (a) pp. 45–47, (b) pp. 54–56.

(4) Newman, *THIS JOURNAL*, **63**, 2431 (1941).

(5) Treffers and Hammett, *ibid.*, **59**, 1708 (1937).



When sulfuric acid solutions of such acids are poured into methanol, almost complete esterification takes place.⁴ Similarly when sulfuric acid solutions of the methyl esters of such acids are poured into water the free acid is obtained.^{4,5} The pseudo methyl ester of *o*-benzoylbenzoic acid represents such an ester.

Since *o*-benzoylbenzoic acid is largely esterified by dissolving in sulfuric acid and pouring into methanol (experiment A) it seems quite likely that in sulfuric acid solution *o*-benzoylbenzoic acid ionizes according to equation 1. The cyclic form of the positive ion is the preferred structure as indicated because the pseudo methyl ester is formed on pouring the sulfuric acid solution into methanol. The fact that the ester isolated after such treatment contains a large amount of normal ester should not confuse the picture because experiment B shows that during the isolation of the reaction products considerable isomerization of pseudo ester to normal ester occurs. Furthermore, no cyclic ester could have been formed from the normal ester or from free *o*-benzoylbenzoic acid because the normal ester is stable in acid methanol and is the ester formed on acid catalyzed esterification of *o*-benzoylbenzoic acid.^{2,6} To summarize briefly, then, the fact that *o*-benzoylbenzoic acid is largely esterified on pouring its sulfuric acid solution into methanol constitutes evidence that *o*-benzoylbenzoic acid undergoes a complex ionization in solvent sulfuric acid. Furthermore, the fact that the pseudo ester is first formed on pour-

ing a sulfuric acid solution of *o*-benzoylbenzoic acid into methanol indicates that the positive ion present in the sulfuric acid solution is cyclic in nature, as shown in equation 1.

Equations 2 and 3.—Since great chemical reactivity is generally associated with positive ions in organic molecules, it would appear strange that such an ion as indicated in equation 1 did not immediately react to form anthraquinone. However, it is a fact that sulfuric acid solutions of *o*-benzoylbenzoic acid must be heated before anthraquinone is formed to any appreciable extent. Recourse to atomic models shows that in a cyclic form carbon atom *a* is far removed from carbon atom *b* with which it must join to form anthraquinone. It seems necessary, therefore, to postulate that the cyclic positive ion on heating absorbs energy and cleaves to a new open chain acyl ion of higher energy content (equation 2). This acyl ion can then rotate so that carbon atom *a* approaches carbon atom *b*. At some stage a proton is lost from carbon *b*, a new carbon-carbon link is formed between carbons *a* and *b*, and anthraquinone results (equation 3).

With the above mechanism as a working hypothesis, it is proposed to study the rate of anthraquinone formation under various conditions and to study, if possible, the effect of substituents on steps 1, 2 and 3.

Summary

A mechanism for the formation of anthraquinone from *o*-benzoylbenzoic acid in sulfuric acid is proposed. Experimental evidence in favor of the proposed mechanism is presented.

COLUMBUS, OHIO

RECEIVED JULY 8, 1942

(6) Plaskuda, *Ber.*, **7**, 987 (1874); Haller and Guzot, *Bull. soc. chim.*, (3) **25**, 54 (1901); H. Meyer, *Monatsh.*, **25**, 475 (1904).