2-Benzoyl-5-methoxybenzoic Acid (III) from II.—2-Benzoyl-5-aminobenzoic acid (IV), m.p. 192–193°, lit.[7] 193–194° was obtained in almost quantitative yield by the hydrogenation of II (10 g., m.p. 214°, lit.[7] 212°) in ethyl acetate (300 ml.) in the presence of Raney nickel and at 50 p.s.i. Amino-acid IV was dissolved in 50% sulfuric acid, diazotized and heated on a steam-bath until the evolution of gas had ceased. The reaction mixture afforded 2-benzoyl-5-hydroxybenzoic acid, yield 40% (m.p. 191–192°), pale yellow needles from dilute acetic acid and dilute alcohol.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.83; H, 4.13. Found: C, 69.29; H, 4.38.

The hydroxyacid was methylated with methyl sulfate without difficulty and afforded III, m.p. 155–156°.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.33; H, 4.72. Found: C, 70.05; H, 4.88.

(b) **With 1-Naphthylmagnesium Bromide.**—The procedure was that of Weizmann, *et al.*,[1] and afforded 2-α-naphthoyl-4-methoxybenzoic acid, m.p. 192–193°, lit.[1] 196°. The acid was characterized by decarboxylating to 1-naphthyl-3-methoxyphenyl ketone, b.p. 260–261° at 24 mm. The ketone was fused with potassium hydroxide according to Bachmann,[8] and the cooled mass was taken up in boiling water and filtered. The precipitate did not depress the m.p. of naphthalene. The warm alkaline filtrate was acidified and the resulting solid was immediately filtered. It proved to be 1-naphthoic acid, m.p. 156–157°. The filtrate was cooled in ice and water and afforded *m*-methoxybenzoic acid, m.p. 104–105°. It did not depress the m.p. of an authentic sample of the acid.

(c) **With *m*-Methoxyphenylmagnesium Bromide.**—The Grignard reagent from *m*-bromoanisole (18.7 g.) in ether was added to a well stirred solution of the anhydride (16 g., m.p. 96°) in benzene. After refluxing for 3 hr. the reaction mixture was treated with dilute hydrochloric acid. The ether–benzene solution of the hydrolyzed reaction products was shaken with carbonate. The yield of the total acid fraction recovered from the carbonate solution was 65%, and it melted from 140 to 150°. The original ether–benzene extract contained varying amounts of neutral material (2.5–5 g.) and was not further examined.

Crystallization of the above acid mixture from 50% acetic acid yielded 9.0 g. of almost pure 2-(3′-methoxybenzoyl)-4-methoxybenzoic acid. For analysis it was crystallized three times from benzene and melted at 173°.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.1; H, 4.9. Found: C, 67.1; H, 4.9.

The keto acid (8 g.) was characterized by heating with basic copper carbonate for 1 hr. at 260°. This afforded 3,3′-dimethoxybenzophenone (6 g.), b.p. 164–168° at 2 mm. One gram of the dimethoxy compound was refluxed for 3 hr. with 10 ml. of 55% hydriodic acid. The mixture was diluted with 50 ml. of water, decolorized with sodium bisulfite and the solid material filtered. Crystallization from water afforded 0.6 g. of 3,3′-dihydroxybenzophenone, m.p. 160–161°.[9]

The keto acid was dissolved in *cold* concentrated sulfuric acid and allowed to stand at room temperature for *five* minutes. Dilution with ice and water gave a 90% yield of almost pure 2,7-dimethoxyanthraquinone, m.p. 213°. A mixed melting point determination carried out with an authentic sample of the quinone showed no change.

The acetic acid mother liquors from the crystallization of the above keto acid contained a large amount of tarry material and a small amount (1.5 g.) of what the authors believe to be impure isomeric 2-(3′-methoxybenzoyl)-5-methoxybenzoic acid. The amount was too small for characterization. It melted unsharply at 136–140°, and repeated crystallization from dilute acetic acid failed to improve the melting point. The analytical results also indicate that the material was not quite pure.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.1; H, 4.9. Found: C, 66.2; H, 5.0.

This keto acid, unlike its isomer, did not undergo ring closure in cold concentrated sulfuric acid. However, heating for 3 hr. on a steam-bath afforded a good yield of yellow 2,6-dimethoxyanthraquinone, m.p. 250°.[10]

(d) **With *p*-Methoxyphenylmagnesium Bromide.**—The reaction between the Grignard reagent from *p*-bromoanisole and 4-methoxyphthalic anhydride has been shown to yield approximately a 3:1 ratio of the 4-methoxy-2-aroylbenzoic acid to the 5-methoxy isomer.[11]

---

[8] W. E. Bachmann, THIS JOURNAL, **57**, 737 (1935).

[9] L. Gattermann and H. Rudt (*Ber.*, **27**, 2293 (1894)) have reported a m.p. of 162–163°.

[10] E. Schunck and H. Roemer (*Ber.*, **9**, 379 (1876)) report yellow needles, m.p. 250°; L. H. Briggs and G. A. Nichols (*J. Chem. Soc.*, 1138 (1951)) report almost colorless plates, m.p. 257°.

[11] Unpublished work by the authors.

EDMONTON, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA]

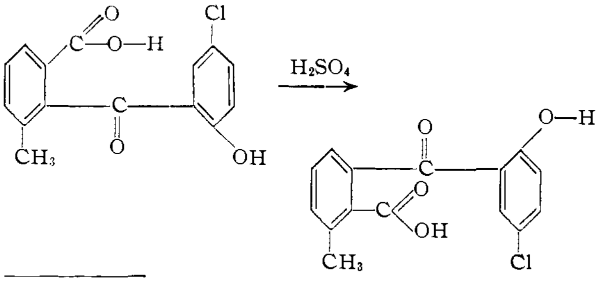
The Hayashi Rearrangement of Substituted o-Benzoylbenzoic Acids

BY REUBEN B. SANDIN, RUSSELL MELBY, ROBERT CRAWFORD AND DONALD MCGREER

RECEIVED MARCH 12, 1956

The rearrangement of some substituted *o*-benzoylbenzoic acids in concentrated sulfuric acid has been studied. It has been proposed that the rearrangement involves the rearrangement of an acyl carbonium ion in such a way that there is an increase in conjugation. It is also suggested that a non-classical phenonium cation type of structure is involved.

Hayashi,[1] in 1927, was the first to report the occurrence of a molecular rearrangement in the course of the ring closure of certain substituted *o*-benzoylbenzoic acids



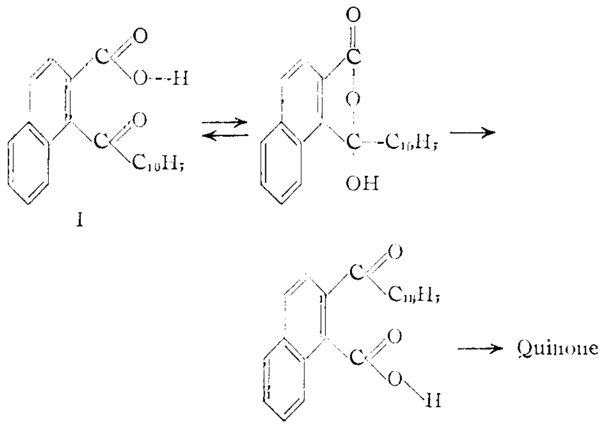
Since 1927, several instances of this remarkable rearrangement have been recorded.[2] Cook[2b] working with 1-(1-naphthoyl)-2-naphthoic acid (I) found that on cyclization, instead of the expected 1,2,7,8-dibenzanthraquinone, compound I gave only 1,2,5,6-dibenzanthraquinone. Cook suggested that the rearrangement proceeded through the hydroxy lactone form of the keto acid.[3]

---

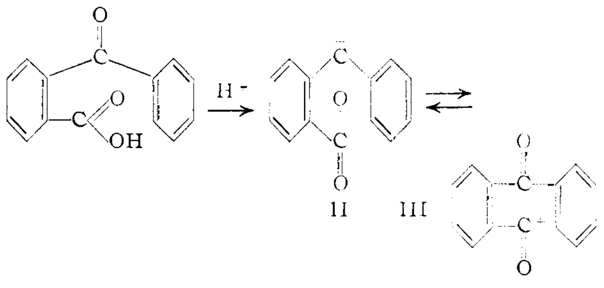
[1] M. Hayashi, *J. Chem. Soc.*, 2516 (1927).

[2] (a) M. Hayashi, *ibid.*, 1513, 1520, 1524 (1930); (b) J. W. Cook, *ibid.*, 1472 (1932); (c) M. Hayashi, S. Tsuruoka, T. Morikawa and H. Namikawa, *Bull. Chem. Soc. Japan*, **11**, 184 (1936); (d) R. B. Sandin and L. F. Fieser, THIS JOURNAL, **62**, 3098 (1940); (e) R. Goncalves, M. R. Kegelman and E. V. Brown, *J. Org. Chem.*, **17**, 705 (1952).

[3] L. F. Fieser, "The Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1936, p. 95.



The very interesting work of Newman,[4] on the behavior of *o*-benzoylbenzoic acid in solvent sulfuric acid has shown that intramolecular acylation occurs through the cyclic carbonium ion II which on heating cleaves to yield the acyl carbonium ion III.[5]



In view of these findings, the present authors consider that a plausible mechanism for the Hayashi rearrangement involves the rearrangement of an acyl carbonium ion. The rearrangement of a carbonium ion usually takes place in such a way that there is an increase in conjugation or hyperconjugation. Using the reversible change between 2-(5′-chloro-2′-hydroxybenzoyl)-4-methylbenzoic acid (VI) and 2-(5′-chloro-2′-hydroxybenzoyl)-5-methylbenzoic acid (VII) recorded by Hayashi,[2a] the rearrangement may be accounted for by the following equilibria in which the present authors suggest that the non-classical "phenonium" cationic type structure IV is involved.[6,7]

The elegant work of Winstein,[8] Cram,[9] Roberts[10] and Collins[11] and their co-workers has done much to establish the extent of importance or non-importance of the "ethyleneonium" cationic intermediate in carbonium ion type reactions. Reaction rate and stereochemical techniques have been used, and where these procedures have not been applicable, Roberts and co-workers[10] and Collins and co-workers[11] have obtained valuable information by the isotopic tracer technique. In the present study there is no experimental evidence to indicate the role of IV in the Hayashi rearrangement. It is possible that IV is simply a transition state through which the acylcarbonium ions are interconverted.

It is significant that Hayashi[2a] found that 2-benzoyl-5-methylbenzoic acid did not rearrange in concentrated sulfuric acid at room temperature whereas 2-(5′-chloro-2′-hydroxybenzoyl)-5-methylbenzoic acid rearranged under the same conditions. Similarly Goncalves, *et al.*,[2e] found that the rearrangement of 2-(2-thenoyl)-6-nitrobenzoic acid and 2-(2-thenoyl)-4-nitrobenzoic acid could be effected in boiling acetic acid but even more satisfactorily by the action of warm concentrated sulfuric acid. In the present work it has been found that 2-benzoyl-4-methoxybenzoic acid does not rearrange in concentrated sulfuric acid at 65° but instead undergoes a ring closure without rearrangement. In contrast to this behavior it has been found that 2-(4′-methoxybenzoyl)-4-methoxybenzoic acid (VIII) under the same conditions rearranges to 2-(4′-methoxybenzoyl)-5-methoxybenzoic acid (IX) without ring closure.[12] One possible interpretation of these observations is that the "phenonium" ion is stabilized by the delocalization of the unshared electron pairs on oxygen of the 4′-methoxy and 2′-hydroxyl groups. Similarly the 2-thienyl group might be expected to be favorable because of its nucleophilic properties.[13]

Experimental

2-Benzoyl-4-methoxybenzoic Acid.—This was prepared by the method of Weizmann, Bergmann and Bergmann[14] who reported the compound to be 4(5?)-methoxy-2-benzoylbenzoic acid. Weizmann's compound has now been characterized as 2-benzoyl-4-methoxybenzoic acid, m.p. 172°.[15]

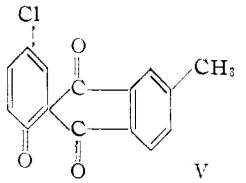
2-(4′-Methoxybenzoyl)-4-methoxybenzoic Acid (VIII).—The Grignard reagent from *p*-bromoanisole (18.7 g.) in ether (200 ml.) was added to a well stirred solution of 4-methoxyphthalic anhydride (17.8 g., m.p. 96°) in benzene

---

(4) M. S. Newman, THIS JOURNAL, **64**, 2324 (1942).

(5) See the work of W. H. Stevens and D. A. Crowder (*Can. J. Chem.*, **32**, 792 (1954)) for evidence in favor of the mechanism proposed by Newman.

(6) Hayashi[2a] has suggested the formation of an intermediate V which, although it does not carry a positive charge, does however involve a phenyl group which has one carbon atom attached to two outside atoms at once. From a structural standpoint IV is a protonated V.



V

(7) As far as the authors are aware, all rearrangements of substituted benzoylbenzoic acids and like compounds recorded in the literature are consistent with this mechanism. It is noticeable that the acids derived from 3-methylphthalic anhydride rearrange so that a less hindered acid becomes a more hindered acid[2a] and the acid from 3-nitrophthalic anhydride yields a less hindered acid.[2e]

(8) As a leading reference to a number of papers, see S. Winstein, C. R. Lindgren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953); (b) S. Winstein and D. Trifan, *ibid.*, **71**, 2953 (1950); **74**, 1147, 1154 (1952).

(9) D. J. Cram, *ibid.*, **71**, 3863 (1949); **74**, 2129, 2159 (1952), and later papers.

(10) (a) As a leading reference to a number of papers, see J. D. Roberts and J. A. Yancey, *ibid.*, **77**, 5558 (1955); (b) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953).

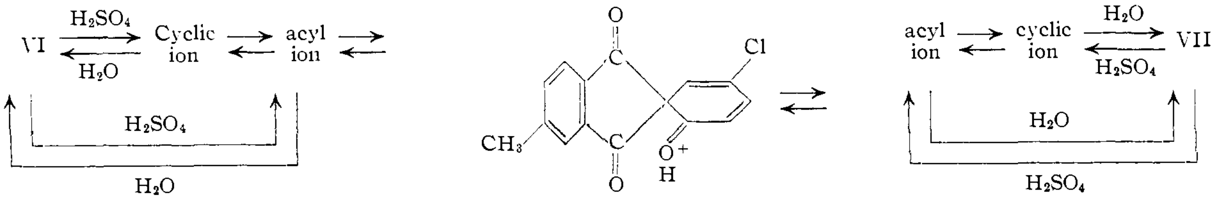
(11) (a) C. J. Collins and W. Bonner, *ibid.*, **75**, 5372 (1953); **77**, 72, 99 (1955); (b) Collins, *ibid.*, **77**, 5517 (1955).

(12) The acyl ion from VIII would be expected to be more stable than the acyl ion from IX. It is interesting, therefore, that the rearrangement VIII → IX takes place. This may be explained on the basis of the cyclic ion X from IX. The ion X should be relatively stable because of two methoxyl groups in favorable positions.

(13) In this connection see particularly the work by Roberts and Regan.[10b]

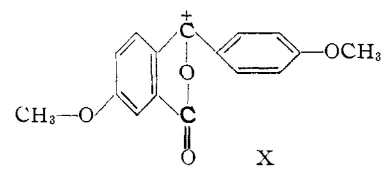
(14) C. Weizmann, E. Bergmann and F. Bergmann, *J. Chem. Soc.*, 1367 (1935).

(15) R. Melby, R. Crawford, D. McGreer and R. B. Sandin, THIS JOURNAL, **78**, 3816 (1956).



IV

(300 ml.). After refluxing for 3 hr., the reaction mixture was decomposed with 150 ml. of saturated ammonium chloride and 10 ml. of dilute hydrochloric acid. The ether-benzene solution of hydrolyzed reaction products was shaken with carbonate. The carbonate extract was acidified with acetic acid and yielded 11.5 g. of keto acid, m.p. 198–206°. After crystallization from benzene and from alcohol, it melted at 210–211°.



X

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.1; H, 4.9. Found: C, 67.05; H, 4.90.

The keto acid was characterized by heating with basic copper carbonate for 1 hr. at 260°. This afforded the dimethoxy compound which was refluxed with 55% hydriodic acid. The demethylated material was crystallized twice from water and yielded yellow crystals of 3′,4-dihydroxybenzophenone, m.p. 196–198°.

2-(4-Methoxybenzoyl)-5-methoxybenzoic Acid (IX).—The acetic acid acidified filtrate from the above keto acid was treated with hydrochloric acid. This afforded 3.5 g. of keto acid, m.p. 165–173°. The acid was crystallized from benzene and alcohol and melted at 174–175°.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.1; H, 4.9. Found: C, 66.82; H, 4.96.

It was characterized by heating with basic copper carbonate which yielded 4,4′-dimethoxybenzophenone, m.p. 144–145°.

Reactions of Keto Acids with Concentrated Sulfuric Acid.—The acid (1 g.) was dissolved in concentrated sulfuric acid (6 ml.) and heated at 65° for 1 hr., at which time it was cooled and diluted with ice and water. The reaction mixture was made basic with sodium hydroxide and any cyclized material was separated. The filtrate was acidified to yield unchanged or rearranged keto acid. Under these conditions 2-benzoyl-4-methoxybenzoic acid afforded 0.8 g. of unchanged acid and 0.2 g. of 2-methoxyanthraquinone, m.p. 195°. Compound VIII (0.5 g.) in 3 ml. of concentrated sulfuric acid at 65° for 6 hr. gave 0.5 g. of IX, m.p. 170–172°, and after crystallization from dilute alcohol afforded 0.45 g. of keto acid, m.p. 173–175°.

The following acids were found not to rearrange under the above conditions: 2-benzoyl-4-hydroxybenzoic, 2-benzoyl-5-hydroxybenzoic and 2-benzoyl-5-methoxybenzoic.

Acknowledgment.—The authors wish to express their appreciation to Dr. John D. Roberts of the California Institute of Technology for his kindly interest and the excellent suggestions which he has made in connection with this work.

EDMONTON, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA]

Synthesis of Some Cyclic Iodonium Salts

BY JOHN COLLETTE, DONALD MCGREER, ROBERT CRAWFORD, FRANCIS CHUBB AND REUBEN B. SANDIN

RECEIVED MARCH 12, 1956

The facile ring closure of the iodoso compounds from 2-iodobiphenyl, (*o*-iodophenyl)-phenylmethane, 1-(*o*-iodophenyl)-2-phenylethane and 1-(*o*-iodophenyl)-3-phenylpropane to yield the corresponding iodonium salts has been carried out.

In order to find a convenient method for the preparation of cyclic iodonium compounds such as the diphenyleneiodonium salts, which in turn might prove useful for bringing about a carbon-to-carbon ring closure, the elegant method of Beringer, Drexler, Gindler and Lumpkin[1] was investigated.

Beringer and co-workers have shown that an iodoso compound will condense with an aromatic compound in the presence of sulfuric acid to yield an iodonium salt. Unsymmetrical as well as symmetrical diaryliodonium compounds have thus been made available. According to Beringer, *et al.*, it seems likely that the reaction mechanism involves electrophilic substitution by the conjugate acid formed by the action of sulfuric acid on the iodoso compound.

Diphenyleneiodonium iodide has been made by the tetrazotization of 2,2′-diaminobiphenyl and subsequent treatment with potassium iodide.[2] Lothrop[2b] was the first to use diphenyleneiodonium iodide for the purpose of bringing about a carbon-to-carbon ring closure and so was the first to prepare the interesting hydrocarbon biphenylene. In the present work it has been found that diphenyleneiodonium salts can be made in high yield (99%) from 2-iodosobiphenyl by the reaction of Beringer, *et al.* The starting material is the available 2-aminobiphenyl (Eastman Kodak Co.) which is readily converted into 2-iodobiphenyl. The latter compound is oxidized with peracetic acid to the iodoso compound without difficulty.[3] The addition of concentrated sulfuric acid to the iodoso com-

---

(1) F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

(2 (a) L. Mascarelli and G. Benati, *Gazz. chim. ital*, **38**, 627 (1908); (b) W. C. Lothrop, THIS JOURNAL, **63**, 1187 (1941); (c) W. Baker, M. P. V. Boarland and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954); Baker and co-workers report a 69% yield.

(3) (a) J. Böeseken and G. C. Schneider, *Proc. Acad. Sci. Amsterdam*, **33**, 827 (1930); (b) J. Böeseken and E. Wicherlink, *Rec. trav. chim.*, **55**, 936 (1936).