fluorescence. The ether layer was separated, the ether removed and the yellow, oily residue treated with methyl alcohol, whereupon it became crystalline. After recrystallization from a mixture of methyl alcohol and acetone the furan melted at 125–126°;[19] yield 22 g. The oxidation of the furan has been described previously.

Summary

Compounds described erroneously in the literature as (a) 3,9-dihydroxy-9-(4′-hydroxyphenyl)-anthrone-10, (b) 3-chloro-9-hydroxy-9-(4′-chlorophenyl)-anthrone-10, (c) 3-chloro-9-(4′-chlorophenyl)-anthrone-10 and (d) 3-chloro-9-(4′-chlorophenyl)-10-hydroxy-9,10-dihydroanthracene are, in reality, (a) 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone, (b) 2-(4″-chlorobenzoyl)-4′-chlorobenzophenone, (c) 2,4-di-(*p*-chlorophenyl)-3,4-benzofuran and (d) 2,5-di-(*p*-chlorophenyl)-2,5-dihydro-3,4-benzofuran, respectively.

A few derivatives of 3,9-dichloro-9-(4′-chlorophenyl)-anthrone-10, including the free radical 3-chloro-9-(4′-chlorophenyl)-anthronyl-10, have been studied.

Two additional syntheses of 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone, in the form of its dimethyl ether, have been described.

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[19] Mixed with a sample (m. p. 126–127°) prepared by another method [Blicke and Weinkauff, THIS JOURNAL, **54**, 1458 (1932)] the melting point was found to be that recorded above.

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

The Action of Sulfuric Acid on Diarylphthalins. I[1]

BY F. F. BLICKE AND R. A. PATELSKI[2]

It was stated by Baeyer[3] that treatment of tetrabromophenolphthalin with sulfuric acid yields 2,4-dibromo-3-hydroxy-9-(3′,5′-dibromo-4′-hydroxyphenyl)-anthrone-10 ("tetrabromophenolphtalidin") and that this compound, when oxidized, is converted into 2,4-dibromo-3,9-dihydroxy-9-(3′,5′-dibromo-4′-hydroxyphenyl)-anthrone-10 ("tetrabromophenolphtalideïn"). The reaction product actually obtained by the use of sulfuric acid is 2,5-di-(*m,m*′-dibromo-*p*-hydroxyphenyl)-3,4-benzofuran and this, upon oxidation, yields 2-(3″,5″-dibromo-4″-hydroxybenzoyl)-3′,5′-dibromo-4′-hydroxybenzophenone. The deep yellow color of the furan, its intense yellow-green fluorescence when dissolved and its conversion, by oxidation, into a 2-benzoylbenzophenone, furnish proof of its structure.

The constitution of 2-(4″-hydroxybenzoyl)-2′-hydroxybenzophenone has been established definitely.[4] Upon bromination of this substance the resulting tetrabromo substitution product which could hardly be any other than the 3′,3″,5′,5″-tetrabromo derivative, was found to be identical with the material obtained by oxidation of the tetrabromofuran mentioned above.

When the dimethyl ether of isophenolphthalin (2′,4″-dimethoxytriphenylmethane-2-carboxylic acid) reacts with sulfuric acid a compound, undoubtedly 2-(2′-methoxyphenyl)-5-(4″-methoxyphenyl)-3,4-benzofuran, forms but not in crystalline state. Upon oxidation the material yields 2-(2″-methoxybenzoyl)-4′-methoxybenzophenone.

In order to prove the structure of this ketone it was synthesized by interaction of 4′-methoxyphenylphthalide with 2-anisylmagnesium iodide and oxidation of the furan, formed as an intermediate product.

It has been stated[5] that tetrabromophenolphthalin can be prepared by reduction of tetrabromophenolphthalein with zinc and sodium hydroxide solution; we found, however, that under these conditions the bromine is removed practically quantitatively[6] and phenolphthalin is produced.

Potassium ferricyanide is a satisfactory agent for the oxidation of alkali-soluble 2,5-diaryl-3,4-benzofurans to 2-benzoylbenzophenones.

Experimental Part

Tetrabromophenolphthalin.—To 20 g. of phenolphthalin, dissolved in 100 cc. of boiling acetic acid, there was added 40 g. of bromine, dissolved in 20 cc. of the same solvent. The mixture was heated for ten minutes, cooled and the precipitate filtered. More material was obtained upon

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[1] This paper represents part of a dissertation to be submitted to the Graduate School by R. A. Patelski in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] The Upjohn Company Fellow.

[3] Baeyer, *Ann.*, **202**, 93 (1880).

[4] Blicke and Weinkauff, THIS JOURNAL, **54**, 1454 (1932); Blicke and Patelski, *ibid.*, **58**, 273 (1936).

[5] Baeyer, *Ann.*, **202**, 85 (1880).

[6] Zinc dust and alkali also remove nuclear bromine from 2′-hydroxy-5′-bromodiphenylphthalide [Blicke and Swisher, THIS JOURNAL, **56**, 924 (1934)]; see also Jacobson and Adams, *ibid.*, **46**, 2790 (1924); *ibid.*, **47**, 2011, 2012 (1925).

concentration of the acetic acid filtrate; yield 30 g. The product was recrystallized four times from benzene; m. p. 130–135°. When heated for some time at 120° the material melted and then solidified; the compound now melted at 209–210°.[7]

In order to acetylate the compound 5 g. of the bromo derivative was heated with 15 cc. of acetic anhydride for one hour at 140°, the cold mixture poured into water and the compound recrystallized from acetic acid; m. p. 186–187° with decomposition.[8]

Anal. Calcd. for $C_{24}H_{16}O_6Br_4$: Br, 44.44. Found: Br, 44.22.

When the diacetyl derivative was treated with sulfuric acid in the manner described in this paper 2,5-di-(*m,m'*-dibromo-*p*-hydroxyphenyl)-3,4-benzofuran was obtained.

When a mixture of 15 g. of tetrabromophenolphthalein, m. p. 294–295°,[9] three hundred and fifty cubic centimeters of 10% sodium hydroxide solution and 80 g. of zinc dust was stirred and heated on a steam-bath for four hours, filtered, the filtrate acidified and the crystalline precipitate recrystallized from dilute alcohol, there was obtained 7.4 g. or 98% of the calcd. amount of phenolphthalin; mixed m. p. 233–234°.

2,5 - Di - (*m,m'* - dibromo - *p* - hydroxyphenyl) - 3,4-benzofuran.—A mixture of 20 g. of finely powdered tetrabromophenolphthalin and 120 cc. of concd. sulfuric acid was stirred until all of the phthalin had dissolved. The green-brown solution was poured into 1000 cc. of water and the yellow, crystalline precipitate recrystallized from acetone; m. p. 240–242° with decomposition. The compound exhibited an intense yellow-green fluorescence in organic solvents and dissolved in sodium hydroxide solution to form an orange solution.

Anal. Calcd. for $C_{20}H_{10}O_3Br_4$: Br, 51.78. Found: Br, 51.42.

The diacetyl derivative was obtained when 5 g. of the furan and 30 cc. of acetic anhydride were heated for one hour at 140°. The yellow, crystalline compound is very insoluble and melted at 264–266°[10] with decomposition after recrystallization from acetic acid. This derivative also possesses a yellow-green fluorescence in solution.

Anal. Calcd. for $C_{24}H_{14}O_5Br_4$: Br, 45.59. Found: Br, 45.36.

2-(3″,5″-Dibromo-4″-hydroxybenzoyl)-3′,5′-dibromo-4′-hydroxybenzophenone.—Four grams of the furan, dissolved in 30 cc. of 10% sodium hydroxide solution, was stirred and 7 g. of potassium permanganate, dissolved in 40 cc. of water, added. After fifteen minutes the mixture was filtered, the filtrate acidified with dilute sulfuric acid and the extremely insoluble, crystalline precipitate purified by boiling it with acetone; yield 3.5 g.; m. p. 298–301°[11] with decomposition.

To 23 g. of 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone and 120 cc. of absolute alcohol, heated to the boiling point of the solution, there was added, gradually, 47 g. of bromine. The crystalline tetrabromo derivative was purified by treatment with boiling acetone; mixed with a sample of the product described above the material melted at 298–300° with decomposition.

Anal. Calcd. for $C_{24}H_{14}O_6Br_4$: Br, 44.57. Found: Br, 44.58.

The compound was acetylated according to Baeyer's directions and recrystallized from acetone; m. p. 165–166°.[12]

Isophenolphthalein.[13]—A mixture of 150 g. of 2-(2′-hydroxybenzoyl)-benzoic acid, 150 g. of phenol and 150 g. of fused zinc chloride was stirred and heated at 90–100° for twelve hours, poured into 2000 cc. of hot water, the precipitate washed with water, digested with 10% sodium hydroxide solution and filtered; the alkali-insoluble fluoran weighed 15 g. and melted at 182–183°. The filtrate was acidified and the precipitate triturated with sodium bicarbonate solution to dissolve unchanged 2-(2′-hydroxybenzoyl)-benzoic acid. The crystalline residue, isophenolphthalein, weighed 160 g.; after several recrystallizations from acetic acid it melted at 201–202°.

2′,4″-Dimethoxydiphenylphthalin (Isophenolphthalin Dimethyl Ether).—A solution of 5 g. of isophenolphthalin[14] in 70 cc. of 10% sodium hydroxide solution was stirred with 12 cc. of dimethyl sulfate for one-half hour at 80–90°; 4 g. of sodium hydroxide was added and the mixture heated for three hours longer in order to hydrolyze the methyl ester of 2′,4″-dimethoxytriphenylmethane-2-carboxylic acid. The filtered solution was acidified and the crystalline precipitate recrystallized from acetic acid; yield 5 g.; m. p. 211–212° after four recrystallizations from acetic acid.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.83; H, 5.79. Found: C, 75.45; H, 5.84.

2-(2″-Methoxybenzoyl)-4′-methoxybenzophenone.—A mixture of 10 g. of finely powdered 2′,4″-dimethoxydiphenylphthalide and 12 cc. of concd. sulfuric acid was stirred for five minutes and the green-brown solution poured into 200 cc. of water. The green, solid precipitate, which showed an intense greenish fluorescence when dissolved, soon turned into a dark green gum. This substance, the furan, was dissolved in 90 cc. of acetic acid, 15 g. of sodium dichromate dissolved in 90 cc. of acetic acid added and the mixture heated for fifteen minutes on a steam-bath; 200 cc. of water was added and, after twelve hours, the brown, gummy precipitate was recrystallized from alcohol; m. p. 109–110°; yield 4 g.

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.27; H, 5.24. Found: C, 75.90; H, 5.27.

According to a second method 2-anisylmagnesium iodide was prepared from 11.8 g. of 2-iodoanisole, 45 cc. of ether, 45 cc. of benzene and 1.2 g. of magnesium. The Grignard reagent was added to 12 g. of 4′-methoxyphenyl-

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[7] Baeyer [*Ann.*, **202**, 86 (1880)] reported 205° and Acree and Slagle [*Am. Chem. J.*, **42**, 136 (1909)] 208–209° as the melting point.

[8] According to Baeyer [*Ann.*, **202**, 87 (1880)] the compound melts at 165–166°.

[9] Other recorded melting points are 220–230° [Baeyer, *Ann.*, **202**, 78 (1880)], 286° [Thiel and Diehl, *Sitzber. Ges. Beförder. ges. Naturw. Marburg*, **62**, 537 (1927)], 295–297° [Blicke, Smith and Powers, THIS JOURNAL, **54**, 1470 (1932)].

[10] Baeyer [*Ann.*, **202**, 95 (1880)] reported 256°.

[11] Baeyer [*ibid.*, **202**, 107 (1880)] stated that the compound melts above 280°.

[12] Baeyer [*ibid.*, **202**, 108 (1880)] reported 182–183°.

[13] Orndorff and Barrett, THIS JOURNAL, **46**, 2488 (1924). The description of the preparative method of these investigators is inadequate.

[14] Orndorff and Barrett, *ibid.*, **46**, 2495 (1924). We found the melting point to be 193–194° instead of 189–190°.

phthalide[15] dissolved in 50 cc. of benzene. The mixture was heated for two hours, decomposed with ice and ammonium chloride and the colorless benzene layer separated; the latter rapidly turned yellow and acquired a green fluorescence due to the formation of the furan. The benzene was removed under diminished pressure and the green, gummy furan oxidized with sodium dichromate; the ketone melted at 109–110°.

In order to obtain the di-(*p*-bromophenyl)-hydrazone 1.7 g. of the ketone, 50 cc. of alcohol, 5.4 g. of *p*-bromophenylhydrazine and two drops of acetic acid were refluxed for twenty-four hours; the crystalline precipitate was boiled with 150 cc. of methyl alcohol to remove impurities, then washed three times with small amounts of cold acetic acid and recrystallized from a mixture of methyl alcohol and ethyl acetate; m. p. 163–165° with decomposition.

Anal. Calcd. for $C_{34}H_{22}O_2N_4Br_2$: Br, 23.59. Found: Br, 23.41.

Oxidation of 2,5-Di-(*p*-hydroxyphenyl)-3,4-benzofuran with Potassium Ferricyanide.—The gummy benzofuran obtained from 9.6 g. of phenolphthalin was dissolved in 100 cc. of 10% sodium hydroxide solution and treated with 22 g. of potassium ferricyanide, dissolved in 100 cc. of water. After five minutes the clear solution was acidified, whereupon 5 g. of 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone precipitated; m. p. 225–226°.

Summary

Tetrabromophenolphthalin and 2′,4″-dimethoxydiphenylphthalin, when treated with sulfuric acid, yield 2,5-diaryl-3,4-benzofurans which upon oxidation are converted into 2-benzoylbenzophenones.

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[15] Nourrisson, *Ber.*, **19**, 2105 (1886).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Photolysis of the Aliphatic Aldehydes. III. Hydrogen from Acetaldehyde

BY FRANCIS E. BLACET AND JACK G. ROOF

The primary process in the photochemical decomposition of the aliphatic aldehydes in the vapor phase has been assumed by Norrish[1] and others to be represented principally by

$$(1) \quad RHCO + h\nu \longrightarrow RH + CO$$

Pearson considers this to be the initial act even though he has shown recently[2] that free radicals are produced in acetaldehyde photolysis. If this is the initial process, no subsequent reactions are probable and in the continuous region of absorption a quantum yield of unity is to be expected. Leighton and Blacet have shown that the quantum yield of decomposition is not always unity in this region.[3] In the case of propionaldehyde, they found hydrogen among the decomposition products. These facts along with the work of Herzberg on formaldehyde[4] led them to postulate the initial process to be

$$(2) \quad RHCO + h\nu \longrightarrow R + HCO$$

The free radicals thus liberated enter into secondary reactions in which R_2 and H_2 are probable products as well as RH. However, because of experimental difficulties they were not able to confirm the presence of hydrogen in the photolytic products of acetaldehyde.[3b] This fact has been taken by Norrish[1] as added proof of his primary mechanism. Leermakers,[5] however, studying the photolysis of this compound at elevated temperatures obtained results in agreement with Reaction 2. Since the results of Leighton and Blacet on acetaldehyde were published, a method of microanalysis for hydrogen has been developed which permits the analysis for this gas in the presence of a mixture of saturated hydrocarbons.[6] This development has permitted a re-examination of the products of photolysis of acetaldehyde with the object in view of determining which of the primary processes postulated above is correct.

Experimental Method and Results

The apparatus used for the photolysis was essentially the same type as that previously described.[3] The light sources were the λ 3130, 2804 and 2537 lines of mercury, obtained from a high pressure mercury arc and a crystal quartz monochromator. The absorption of radiant energy took place in an all fused silica cell and the aldehyde vapor was not allowed to contact any substances except fused silica, Pyrex glass and mercury. The average pressure in the cell dur-

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[1] (a) Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934); (b) Kirkbride and Norrish, *ibid.*, **27**, 404 (1931); (c) W. West, THIS JOURNAL, **57**, 1931 (1935).

[2] Pearson and Purcell, *J. Chem. Soc.*, 1151 (1935).

[3] (a) Leighton and Blacet, THIS JOURNAL, **54**, 3165 (1932); (b) *ibid.*, **55**, 1766 (1933).

[4] Herzberg, *Trans. Faraday Soc.*, **27**, 378 (1931).

[5] Leermakers, THIS JOURNAL, **56**, 1537 (1934).

[6] Blacet and MacDonald, *Ind. Eng. Chem., Anal. Ed.*, **6**, 334 (1934).