[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

THE REDUCTION OF PARA-DIMETHYLAMINOBENZIL[1]

BY SANFORD S. JENKINS[2] WITH JOHANNES S. BUCK AND LUCIUS A. BIGELOW

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The work described in this paper is a continuation of that reported in an earlier communication[3] which dealt with the catalytic reduction of a number of symmetrical α-diketones by means of a modified form of the Adams apparatus, using hydrogen under pressure in the presence of a platinum-black platinum oxide catalyst. It seemed desirable to extend this study to include the reduction of the unsymmetrical α-diketone, *p*-dimethylaminobenzil, and this has led to some interesting and not altogether expected results.

The starting material was obtained conveniently by oxidizing *p*-dimethylaminobenzoin, which in turn was prepared in the usual manner by condensing *p*-dimethylaminobenzaldehyde with benzaldehyde in the presence of potassium cyanide according to the method of Staudinger.[4]

Upon reduction by the method already described, the benzil readily took up either one or two molecules of hydrogen, yielding in the one case the corresponding benzoin, and in the other, the analogous *p*-dimethylaminohydrobenzoin, melting at 112°, which has not previously been reported. It was possible either to isolate the intermediate product, or not, as desired, without affecting the ultimate result.

The hydrobenzoin, on treatment with a mixture of acetic and hydrochloric acids, was readily dehydrated, with the production of *p*-dimethylaminodesoxybenzoin, melting at 128°, and this, on further catalytic reduction, was converted without difficulty into the corresponding *p*-dimethylaminostilbene hydrate, melting at 78°. The hydrate lost a molecule of water in the presence of the acetic–hydrochloric acid mixture, forming the related stilbene, already known,[5] and this on final catalytic reduction yielded, as would be expected, the saturated *p*-dimethylaminodiphenylethane, which melted at 63°.

Up to this point, the results obtained did not differ in any essential respect from what might have been expected from the earlier work. When, however, an attempt was made to reduce the benzoin with tin and hydrochloric acid in alcohol solution, *two* isomeric *desoxy* derivatives were obtained, and none whatever of the hydro compound, which is the sole

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[1] This paper is constructed from portions of a thesis presented by Sanford S. Jenkins in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences, Duke University.

[2] Angier B. Duke Memorial Fellow, 1929–1930.

[3] Buck and Jenkins, THIS JOURNAL, **51**, 2163 (1929).

[4] Staudinger, *Ber.*, **46**, 3537 (1913).

[5] F. and L. Sachs, *ibid.*, **38**, 515 (1905).

product of the direct hydrogenation. The existence of these isomers is possible, of course, upon theoretical considerations, but as the benzoin itself gave every evidence of being a single substance, the appearance of the two desoxy compounds at this point was not particularly expected. They are very easily separated, as one is quite soluble in dilute acid while the other is relatively insoluble in this reagent. The first, or *α-p*-dimethylaminodesoxybenzoin melted at 128°, and was identical with the material obtained by catalytic dehydration of the hydro compound, while the other, or *β*-desoxy derivative, melted at 164°.

Each of these substances, upon further reduction with hydrogen, yielded a corresponding stilbene hydrate. The *α*-derivative, as mentioned above, showed a melting point of 78°, and the *β*-compound, which has been described in the literature,[5] fused at 60°. Both lost water under the influence of the acetic and hydrochloric acid mixture, forming one and the same stilbene, identical with that already described.

A sample of *β-p*-dimethylaminostilbene hydrate was prepared by the Sachs method. It melted at 60°, and when mixed with some of the corresponding material prepared by reducing the desoxy compound, the melting point was not depressed. From this it follows that the structures of the two isomers are as follows

$(CH_3)_2NC_6H_4CH_2CHOHC_6H_5$	$(CH_3)_2NC_6H_4CHOHCH_2C_6H_5$
α-p-Dimethylaminostilbene hydrate, m. p. 78°	*β-p*-Dimethylaminostilbene hydrate, m. p. 60°

Furthermore, the desoxybenzoins from which these compounds are derived by reduction may reasonably be assumed to possess corresponding structures, in which the (CHOH) group is replaced by (CO).

The changes which have been described may conveniently be represented by the diagram.

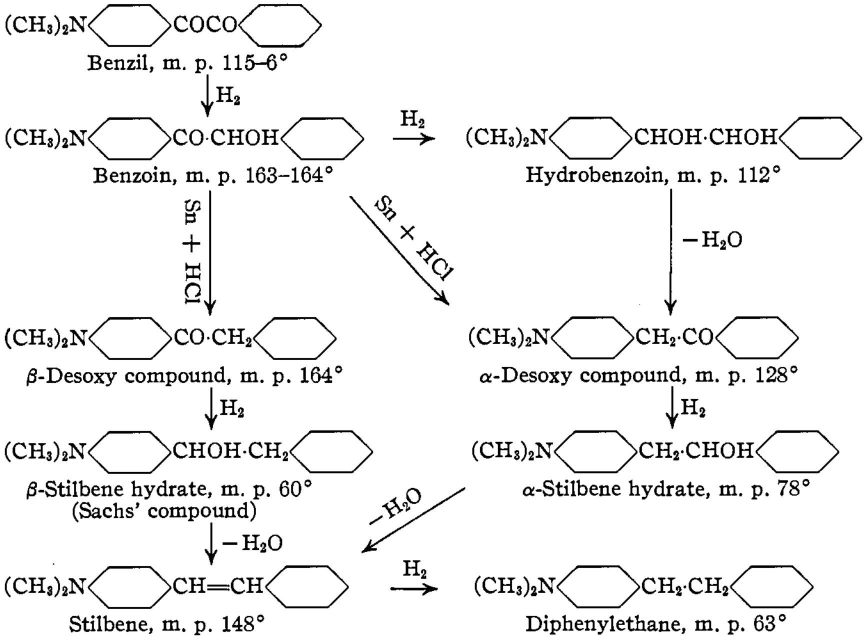
It will be noticed that in this scheme one formula has been assigned arbitrarily to the benzoin, which itself is capable of existing in two isomeric modifications. The reasons for this will be set forth in another paper, which will deal with the structure of this benzoin. It may be stated at this point, however, that while the appearance of two desoxy derivatives made it seem likely that the benzoin itself might be a mixture of isomers, repeated efforts to separate it into *α*- and *β*-components have not been successful.

Experimental

***p*-Dimethylaminobenzoin.**—This substance was prepared according to the method of Staudinger, already cited. It crystallized in prisms melting at 163–164°.

***p*-Dimethylaminobenzil.**—This compound resulted from the oxidation of the corresponding benzoin with concentrated Fehling's solution as recommended by Staudinger. Ten grams of the benzoin yielded 9.0 g. of benzil (90% of calcd.), which, after crystallization from alcohol, melted at 115–116°.

***p*-Dimethylaminobenzoin by the Catalytic Reduction of the Benzil.**—In this procedure, the modified form of the Adams apparatus, already described, was used. An



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accurate calibration showed that when 0.01 mole of pure benzoin (unsubstituted) took up 0.01 mole of hydrogen, forming hydrobenzoin, the gage showed a drop in pressure of 12 lb. Glacial acetic acid was found, after a number of trials, to be the best solvent. Accordingly, 2.50 g. (0.01 mole) of *p*-dimethylaminobenzil, 0.05 g. of platinum oxide and 50 cc. of glacial acetic acid were placed in the apparatus, and the reduction carried on at room temperature until the requisite drop in pressure was obtained. It should be noted that in mixing the reagents it is best to add the solvent last, to prevent spontaneous ignition of the mixture. After filtering off the catalyst, the solution was diluted with an equal volume of water and the precipitated benzoin filtered and dried. It weighed 1.62 g. (68% of calcd.), and, after one crystallization from alcohol, was obtained as white prisms which melted at 163–164° (corr.). A mixed melting point with a sample prepared by Staudinger's method showed no depression.

***p*-Dimethylaminohydrobenzoin.**—This material was prepared in a manner similar to that described above, except that absolute alcohol proved to be the best solvent, and the reduction was allowed to proceed until the gage registered a drop in pressure of 25 lb., which required about thirty minutes. After removal of the catalyst, the solvent was evaporated under reduced pressure, and the product crystallized twice from ligroin (b. p. 60–70°). Two and one-half grams of the benzil yielded 2.3 g. of the hydro derivative (90% of the theoretical), as snow white prisms, melting at 112° (corr.).

Anal. Calcd. for $C_{16}H_{19}NO_2$: N, 5.44. Found: N (Kjeldahl), 5.44, 5.50.

α-*p*-Dimethylaminodesoxybenzoin. (First Method.)—The α-desoxy compound was formed without difficulty by dehydrating the hydrobenzoin just described. Accordingly, 5.1 g. (0.02 mole) of the substance was heated for twenty minutes with 40 cc. of a mixture of glacial acetic acid and hydrochloric acid. (sp. gr. 1.19) 4:1 by volume. After adding 200 cc. of water, the solution was neutralized with sodium carbonate and the yellow precipitate filtered off and recrystallized from alcohol. The product was obtained in white prisms melting at 128° (corr.), and weighed 3.5 g. which is 70% of the theoretical.

Anal. Calcd. for $C_{16}H_{17}NO$: N, 5.85. Found: N (Kjeldahl), 5.82, 5.95.

β-*p*-Dimethylaminodesoxybenzoin.—It is interesting to note that while this isomer is formed readily in the reduction of the benzoin with tin and hydrochloric acid, not a trace of it appeared in the dehydration of the hydrobenzoin just described. A mixture of 20 g. of *p*-dimethylaminobenzoin, 16 g. of mossy tin, 30 cc. of hydrochloric acid (sp. gr. 1.19), 80 cc. of alcohol and 0.5 g. of $CuSO_4 \cdot 5H_2O$ was heated under a reflux condenser for five hours, after which the unchanged tin was filtered off, the solution diluted with 100 cc. of water, and allowed to cool somewhat. After a short time crystals began to form and another 100 cc. of water was added. The mixture was allowed to stand in a cool place for two hours, and the product finally filtered off and recrystallized from alcohol. A yield of 9.0 g. was obtained, which consisted of white or at times cream-colored plates, melting at 164° (corr.). A mixed melting point with the original benzoin, which also melted at 163–164°, showed a large depression.

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.85. Found: C, 80.34; H, 7.22; N (Kjeldahl), 5.78.

α-*p*-Dimethylaminodesoxybenzoin. (Second Method.)—The solution from which the β-desoxy compound had been filtered (see above) was made alkaline with sodium carbonate, and a large precipitate obtained. This was separated, washed well with water, sucked as dry as possible and extracted twice with boiling alcohol. The combined extracts were evaporated to a volume of 50 cc. and allowed to cool. The crystals which separated weighed 7.0 g. and, after recrystallization from alcohol, formed white prisms, melting at 128°. A mixed melting point with a sample of the α-desoxybenzoin obtained by the dehydration of the hydro compound showed no depression. The combined yield of the α- and β-isomers was 16.0 g., which is 85% of the theoretical.

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.85. Found: C, 80.31, 80.55; H, 7.27, 7.36; N (Kjeldahl), 5.92.

α-*p*-Dimethylaminodesoxybenzoin Oxime.—This compound was prepared by dissolving 2.0 g. of the corresponding desoxybenzoin, and 1.0 g. of hydroxylamine hydrochloride in 10 cc. of pyridine and heating the mixture on the water-bath for three hours. After this, 100 cc. of water was added and the solution allowed to crystallize. The product was filtered, washed with water, dried, and recrystallized from ligroin (b. p. 95–98°). It separated in long white needles melting at 139° (corr.).

Anal. Calcd. for $C_{16}H_{18}N_2O$: N, 11.02. Found: N (Kjeldahl), 11.00, 11.20.

β-*p*-Dimethylaminodesoxybenzoin Oxime.—This oxime was formed in exactly the same manner as the corresponding α-compound. It separated from alcohol in white prisms melting at 142° (corr.). A mixed melting point with the α-oxime showed a large depression.

Anal. Calcd. for $C_{16}H_{18}N_2O$: N, 11.02. Found: N (Kjeldahl), N, 10.90, 11.02.

α-*p*-Dimethylaminostilbene Hydrate.—Two and four-tenths grams (0.01 mole) of α-*p*-dimethylaminodesoxybenzoin, 0.10 g. of platinum oxide and 50 cc. of absolute alcohol were heated to 60° and shaken with hydrogen until the pressure had dropped 13 lb., which required two hours. The catalyst was filtered off, and the solvent removed under reduced pressure. The crude product was crystallized from ligroin (b. p. 95–98°) and separated in long colorless needles, weighing 2.25 g. (93% of calcd.) and melting at 78° (corr.).

Anal. Calcd. for $C_{16}H_{19}NO$: N, 5.80. Found: N (Kjeldahl), 5.79, 5.87.

β-*p*-Dimethylaminostilbene Hydrate. (First Method.)—Considerable difficulty was experienced in the catalytic reduction of β-*p*-dimethylaminodesoxybenzoin, as slight amounts of impurities appeared to inhibit the reaction entirely. However, after repeated crystallization from alcohol, a pure white product was obtained which would reduce slowly. Two and four-tenths grams (0.01 mole) of the desoxy derivative, 0.10 g. of platinum oxide and 100 cc. of absolute alcohol were shaken with hydrogen at 60° for four hours, after which the catalyst was filtered off and the solvent evaporated under reduced pressure. The product crystallized from ligroin (b. p. 95–98°) in clusters of colorless needles weighing 2.10 g. (85% of calcd.) and melting at 60° (corr.).

β-*p*-Dimethylaminostilbene Hydrate. (Second Method.)—As this stilbene hydrate has been described in the literature, the writers have prepared a sample of it by Sachs' method, already cited, in which *p*-dimethylaminobenzaldehyde is reacted with benzylmagnesium bromide. The product separated in 62% yield from ligroin (b. p. 95–98°) as white needles, melting at 60° (corr.). When the material of known structure was mixed with that prepared by catalytic reduction, the melting point was not depressed.

***p*-Dimethylaminostilbene.**—To prepare this substance, 5.0 g. of β-*p*-dimethylaminostilbene hydrate was heated for twenty minutes with a mixture of glacial acetic acid and hydrochloric acid (sp. gr. 1.19) 4:1 by vol., after which the solution was diluted with 200 cc. of water, neutralized with sodium carbonate and the precipitated product filtered. This was recrystallized from alcohol and separated in colorless scales, weighing 4 g. (90% of calcd.) and melting at 148°. α-*p*-Dimethylaminostilbene hydrate, treated in exactly the same manner, gave an 80% yield of the stilbene, which melted at 148°, and a mixture of the two also fused at 148°.

***p*-Dimethylaminodiphenylethane.**—To prepare this compound, 2.23 g. (0.01 mole) of *p*-dimethylaminostilbene, 0.05 g. of platinum oxide and 50 cc. of glacial acetic acid were shaken with hydrogen at room temperature for twenty minutes, after which time the pressure had dropped 12 lb The catalyst was filtered off, the mixture diluted with 200 cc. of water and neutralized with sodium carbonate. The precipitated product was filtered, washed and recrystallized from 60% alcohol. It weighed 1.80 g. (80% of calcd.) and formed nearly white flakes melting at 63° (corr.).

Anal. Calcd. for $C_{16}H_{19}N$: N, 6.22. Found: N (Kjeldahl), 6.35, 6.52.

Addition Product of Methyl Iodide to *p*-Dimethylaminodiphenylethane.—This substance resulted when methyl iodide was added to a solution of *p*-dimethylaminodiphenylethane in absolute ether. The mixture was allowed to stand overnight and the product crystallized out in white plates melting at 260–262° (uncorr.).

Anal. Calcd. for $C_{17}H_{22}NI$: I, 34.6. Found: I (Pringsheim), 34.3.

Summary

1. The complete series of reduction products of *p*-dimethylaminobenzil has been studied.

2. The corresponding benzoin, which seems to be a single substance, yielded the two theoretically possible desoxy derivatives upon reduction under suitable conditions. These compounds in turn can be reduced further to form two isomeric stilbene hydrates. Seven new substances have been prepared and characterized.

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