The Pinacol–Pinacolone Type Rearrangement of 4,4′-Bis-dimethylaminohydrobenzoin

By Milton J. Allen

Clemo and Smith[1] reported their unsuccessful attempts to rearrange 4,4′-bis-dimethylaminohydrobenzoin. In our laboratory the rearrangement was attempted with satisfactory results. The high and low melting forms of the hydrobenzoin were prepared by electrolytic reduction of dimethylaminobenzaldehyde.[2] Each form was treated with a 50% solution of concentrated hydrochloric acid in water. The resultant compounds melted at 195–196° and the elementary analyses indicated that a molecule of water had been eliminated.

Structurally the rearranged product could have been either 4,4′-bis-dimethylaminodesoxybenzoin or 1,1-bis-dimethylaminophenyl acetaldehyde. The compound gave a negative Schiff test but a positive phenylhydrazine reaction, which indicated the desoxybenzoin structure.

An infrared spectrum of a nujol paste was obtained[3] and it was found that the first band was at 6.03 microns. According to Randall, *et al.*,[4] the wave length range for an aldehyde group is 5.78 to 5.88 microns, for a ketone group 5.81 to 5.99 microns. In the aldehyde structure there is no conjugation or resonance between the aromatic rings and the aldehyde group and, therefore, if the compound were an aldehyde, one would expect a band in the stipulated range. However, in the ketone structure, owing to resonance and conjugation between the ketone group and the aromatic rings, it is likely that there would be a shift of the ketone band to a higher wave length. In view of the evidence, it can be assumed that 4,4′-bis-dimethylaminohydrobenzoin undergoes a pinacol–pinacolone type rearrangement to 4,4′-bis-dimethylaminodesoxybenzoin. The shift of the hydrogen is consistent with previous work on symmetrical pinacols. The work of Bachmann and Sternberg,[5] Allen and Corwin[6] and Price and Mueller[7] has demonstrated that it is the most strongly electron releasing group which migrates. In this case it is the $\overset{+}{N}H(CH_3)_2$ attached to a benzene ring which makes this a relatively strong electron attractor and, therefore, a non-migratory group.

Experimental[8]

4,4′-Bis-dimethylaminodesoxybenzoin.—One-half gram of 4,4′-bis-dimethylaminohydrobenzoin, m.p. 178–179°, was refluxed for two hours with 2 ml. of concentrated hydrochloric acid and 2 ml. of water. The solution was then diluted with water and made alkaline. The precipitate was washed with water and recrystallized from ethyl cellosolve; yield 0.45 g. (95.8%); m.p. 196–197°.

Anal. Calcd. for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85. Found: C, 76.43; H, 7.90.

A sample of this compound gave a positive phenylhydrazine test and a negative Schiff test.

The low melting form, m.p. 112–113°, of 4,4′-bis-dimethylaminohydrobenzoin was treated in the same manner; yield 0.43 g. (91.5%); m.p. 196–197°. A mixed melting point with the previous rearranged product showed no depression.

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(1) Clemo and Smith, *J. Chem. Soc.*, 2423 (1928).

(2) Allen, *J. Org. Chem.*, **15**, 435 (1940).

(3) The spectral analysis was performed by S. P. Sadtler & Son, Inc., of Philadelphia, Pa.

(4) Randall, Fowler, Fuson and Dangl, "Infrared Determination of Organic Structures," Van Nostrand Co., Inc., New York, N. Y., 1949.

(5) Bachmann and Sternberg, THIS JOURNAL, **56**, 170 (1934).

(6) Allen and Corwin, *ibid.*, **72**, 117 (1950).

(7) Price and Mueller, *ibid.*, **66**, 634 (1944).

(8) All melting points reported were obtained with a Koefler micromelting point apparatus and are corrected.

The Reduction of Diazotized Amines on Cotton

By Edward R. Atkinson and Albert G. Hoyle

Our earlier work with the reduction of diazotized amines to biaryls and azo compounds by cuproammonia ion[1,2] was confined to diazo compounds derived from relatively simple amines. In extending the scope of this reaction we chose to study diazo compounds derived from those primary amines belonging to the class of Direct and Developed dyestuffs.[3] We postulated that if the biaryl were produced in this reaction the resulting dyestuff would have a chromophore system approximately twice as long as the starting material and a molecular weight approximately double that of the starting material. Such changes might cause significant changes in the color and dyeing properties of the dye. If the azo compound were produced the above considerations would hold; in addition a new azo chromophore would be introduced.

It was suggested that the molecular weights of the reduction products would be sufficiently high to result in colloidal behavior. We, therefore, chose to use dyestuffs affixed to the fiber for our study.

Using seven representative dyes of the Direct and Developed class as 3% dyeings on cotton we observed in each case that the chief reduction product of their diazotized forms was the original amine. This result is reasonable in view of the fact that the diazo molecules attached to the fiber do not possess a mobility sufficient to permit their coupling to biaryl or azo compound during reduction. A similar type of reaction was observed by us earlier[4] when we reduced the hindered diazo compound derived from 3,5-dichloro-2-aminobenzoic acid; in this case 50% yields of the biaryl were obtained but 20% of the starting material was recovered as a true reduction product.

Experimental Part

The following Direct and Developed dyestuffs were kindly supplied by the manufacturers: Primuline (C.I. 812, du Pont); Diazo Brilliant Orange GGA Extra Concentrated CF (General Dyestuff Corp.); Diazo Bordeaux BACF (General); Calcomine Brown M (C.I. 420, Calco Chemical

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(1) E. R. Atkinson, C. R. Morgan, H. H. Warren and T. J. Manning, THIS JOURNAL, **67**, 1513 (1945).

(2) E. R. Atkinson, D. N. Reynolds and D. M. Murphy, *ibid.*, **72**, 1397 (1950).

(3) Direct and Developed dyestuffs are azo dyes which may be applied to the fiber from a neutral salt-bath and which have diazotizable amino groups in their structure.

(4) E. R. Atkinson and H. J. Lawler, THIS JOURNAL, **62**, 1704 (1940).