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°.

(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 micro-melting point apparatus and are corrected.

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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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

(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).

Co.); Calcomine Diazo Brilliant Green 3GD (Calco); Rosanthrene Fast Brown RB (Ciba); 4-(p-aminobenzene-azo)-4'-nitrostilbene-2,2'-disulfonic acid (Althouse). 3% dyeings on scoured bleached cotton cloth were prepared by conventional procedures.[5]

Five-g. samples of dyed cloth were stirred at 0–10° for 20 minutes in 400 cc. of water containing 8 g. of sodium nitrite and 24 g. of concentrated hydrochloric acid. It was observed that when these diazotized samples were boiled with water for one hour they would no longer couple with β-naphthol; the boiled samples were then subjected to a second diazotization procedure and would not couple with β-naphthol. This indicated that the original diazotization was quantitative. All work following diazotization was performed in darkness to avoid possible photo effects.

Diazotized samples were immersed for three minutes in a solution of the cupro-ammonia reducing agent used in our earlier work.[6] After rinsing with dilute acid the sample would no longer couple with alkaline β-naphthol. Its color was slightly duller than the original dyeing. After rediazotizing, however, coupling with β-naphthol occurred to produce a color almost identical with a standard prepared by coupling an unreduced sample with β-naphthol. Control experiments showed that the effect produced by the reducing agent was not produced by the reducing solution when cupro-ammonia ion was omitted. Since it was demonstrated above that the original diazotization was complete, we cannot escape the conclusion that cupro-ammonia ion converted the diazo compound to the orginal amine.

Crude designs were printed on a sample of diazotized dyed cloth with the cupro-ammonia reducing reagent. When the sample was developed with β-naphthol in the usual way the printed portion failed to couple. These same portions could then be rediazotized and coupled with another developer such as phenylmethylpyrazolone. A variety of printing effects were obtained in this way.

(5) Trotman and Trotman, "The Bleaching, Dyeing and Chemical Technology of Textile Fibers," 2nd ed., Griffin, London, 1946, p. 386.

(6) E. R. Atkinson, H. J. Lawler, J. C. Heath, E. H. Kimball and E. R. Read, THIS JOURNAL, 63, 730 (1941) Method 2.

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The Absorption Spectra of I_2, I_3^-, I^-, IO_3^-, $S_4O_6^=$ and $S_2O_3^=$. Heat of the Reaction $I_3^- = I_2 + I^-$

BY ALICE D. AWTREY AND ROBERT E. CONNICK

In connection with rate studies in the thiosulfate–iodine–triiodide system[1] it was necessary to determine the molar extinction coefficients of these and other species in aqueous solution.

In Fig. 1 are given the spectra of I_2 and I_3^- in the visible and ultraviolet regions. The molar
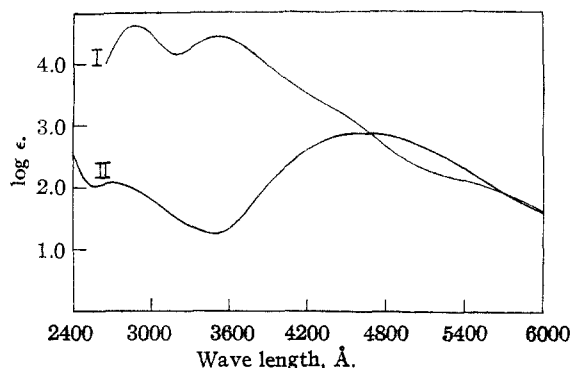

Fig. 1.—Molar extinction coefficients of triiodide ion and iodine in water: I, triiodide ion; II, iodine.

(1) A. D. Awtrey and R. E. Connick, THIS JOURNAL, 73, 1341 (1951).

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF I_3^- AND I_2 AT THE MAXIMA

	Wave length, Å.	$\epsilon_{I_3^-}$	ϵ_{I_2}
I_3^-	3530	26,400	18
	2875	40,000	95
I_2	4600	975	746
	2700	17,200	121

extinction coefficients, ϵ, at the maxima are listed in Table I. In Fig. 2 are shown the spectra of I^-, IO_3^-, $S_4O_6^=$ and $S_2O_3^=$.
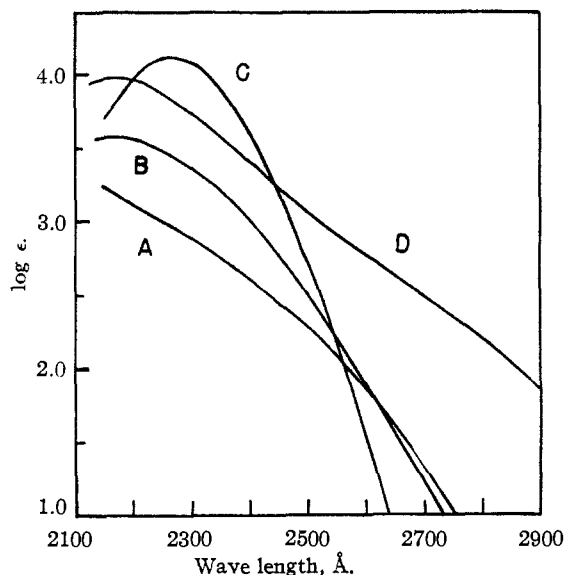

Fig. 2.—Molar extinction coefficients in water: A, IO_3^-; B, $S_2O_3^=$; C, I^-; D, $S_4O_6^=$.

The equilibrium constant for the dissociation of triiodide ion was determined spectrophotometrically at different temperatures, and ΔH was calculated to be −5100 cal.

Experimental

Absorption Spectra.—The molar extinction coefficient, ϵ, of triiodide ion was determined by measuring the optical density of solutions containing 0.049 M potassium iodide and 10^{-3} or 10^{-4} M perchloric acid; the total iodine concentrations were 1.03×10^{-5} and 6.76×10^{-5} M. A thermostated cell holder, used with the Beckman spectrophotometer, kept the temperature at 25.0°. The absorption cells were 10 and 2 cm. in length. Corrections were made for absorption due to free I_2 and to I^-; that due to perchlorate is negligible at these wave lengths and concentrations. The extinction coefficient at wave lengths lower than 2600 Å. was not obtained because of absorption due to iodide in these solutions.

For determining the spectrum of I_2, a solution was made up containing approximately 5×10^{-4} M iodine and 1.5×10^{-4} M potassium iodate, and having 0.10 M perchloric acid; the flask was sealed and put in a thermostat at 25° for ten days, to come to equilibrium. From the equilibrium constants[2]

$$\frac{(I^-)^5(IO_3^-)(H^+)^6}{(I_2)^3} = 2.7 \times 10^{-48} \text{ and } \frac{(I^-)(HOI)(H^+)}{(I_2)} = 2.58 \times 10^{-13}$$

are calculated approximate concentrations: $(I^-) = 10^{-8}$ M; $(I_3^-) = 4 \times 10^{-10}$ M; $(HOI) = 10^{-6}$ M. The maximum optical density due to triiodide, at 2875 Å., is 0.001;

(2) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.