# Some Azo-compounds which form Spherical Micro-particles

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The present investigation will be concerned with 5-phenylazoresorcylaldehyde (I) and related compounds. I has been synthesized by Borsche.[1] He reported that the substance is prone to resinify when recrystallized, thereby preventing isolation. When he conducted the recrystallization from ethanol under a microscope, he first observed the separation of yellow needles, but they were soon covered with red-yellow resinous droplets. I was thus isolated only in the form of its phenylhydrazone.

We observed a peculiar property of the cyanoacetic ester derivative of I; it was obtained in the form of dark red spherical micro-particles and reflected the incident light fairly accurately in the opposite direction.

The present work was undertaken in order to explore the related behavior of the hydroxy derivatives of azobenzene.

I was prepared from resorcylaldehyde and, after being separated from the accompanying 3, 5 - bisphenylazoresorcylaldehyde (II), was recrystallized to yield long orange plates, m. p. 149.5—50°C. The compound, however, was apt to form spherical micro-particles in the case of recrystallization. The particles, once formed, exhibited a nature different from that of the original substance. It has no melting point and begins to carbonize, for example, above ca. 160°C and, unlike I, is hardly soluble in ethanol.

In the coupling reaction to prepare I, the 3- or 5-position of resorcylaldehyde is available for the entering phenylazo group. The assignment of the I structure is based on the following facts. I was submitted to hydrogenolysis in dioxane containing acetic anhydride. The resulting acetamidoresorcylaldehyde was identical with the acetamidoresorcylaldehyde (IV) obtained from 5-nitroresorcylaldehyde (V). However, since no rigorous determination[2] of the structure of V prepared by the nitration of resorcylaldehyde has been carried out, we methylated the nitro compound and then compared the resulting dimethoxynitrobenzaldehyde with that prepared by the nitration of 2, 4-dimethoxybenzaldehyde, which was considered to afford the 5-nitro derivative (VI) because of steric hindrance. These two specimens, prepared via alternate routes, were identical.

I, on treatment with ethyl cyanoacetate, also gave the characteristic dark red micro-particles, the composition of which varied to a certain extent;

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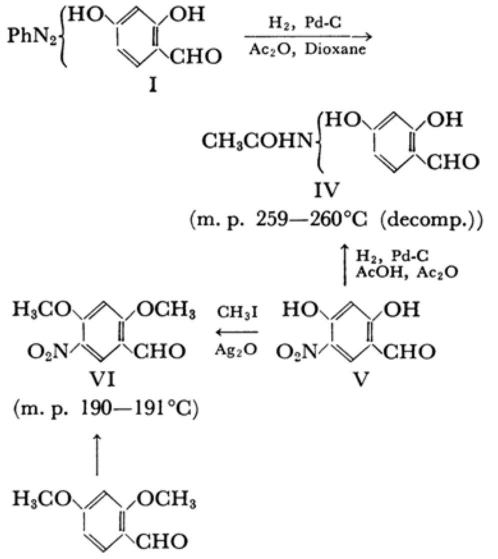
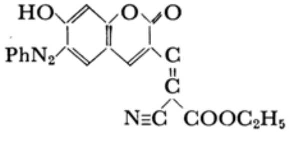
[1] W. Borsche and L. E. Bolser, *Ber.*, **34**, 2098 (1901).

[2] L. Gattermann, *Ann.*, **357**, 337 (1907)

for example, the substance was composed of a ratio of one mole of I to two moles of the ester.



The particles in this case seemed more stable than the preceding ones and began to carbonize above ca. 200°C without melting. When I was treated with the cyanoacetate a crystalline substance, brown needles, was obtained in addition to the particles. It seems from the analysis, the mode of reaction, and an analogy reported by Matsumura that this crystalline substance is of the III enamine structure.



III

3, 5-Bisphenylazoresorcylaldehyde (II), which is produced along with I in the coupling reaction, showed no tendency to form particles.

## Experimental*

**5-Phenylazoresorcylaldehyde (I).**—Into a solution of 5 g. (0.036 mol.) of resorcylaldehyde, 3.1 g. (0.033 mol.) of aniline, and 30 ml. of concentrated hydrochloric acid in 1500 ml. of water was added portionwise 4 g. of sodium nitrite over period of ca. 10 min. at ca. 7°C with stirring. After the mixtrue had stirred for an additional 20 min., 30 g. of sodium acetate was added, and then a solution of 20 g. of potassium carbonate (anhydrous) in 100 ml. of water was added over a period of 30 min. at the same temperature. Stirring was continued for further 3 hr. and then kept overnight in an ice-box. The precipitates were collected, washed with water, and dried in a desiccator. The product, which weighed ca. 7 g., consisted of a mixture of I and 3, 5-bisphenylazoresorcylaldehyde (II). The crude product was then treated with ca. 250 ml. of hot ethanol or, bester, with the same volume of cold acetone, and filtered. From the filtrate, upon the addition of water, this was obtained ca. 3.8 g. of I, which, on repeated recrystallization from acetone containing water, formed orange long plates, m. p. 149.5—150°C (slow heating) and 156°C (rapid heating).

Found: C, 64.48; H, 4.08; N, 11.60. Calcd. for $C_{13}H_{10}O_3N_2$: C, 64.46; H, 4.16; N, 11.57%.

**The 2, 4-Dinitrophenylhydrazone:** brownish red plates, m. p. 275°C (decomp.).

Found: C, 57.51; H, 3.76; N, 19.58. Calcd. for $C_{24}H_{19}O_6N_7$: C, 57.48; H, 3.82; N, 19.55%.

**The Semicarbazone:** brown needles or long plates; m. p. above 300°C.

Found: N, 21.48. Calcd. for $C_{14}H_{13}O_2N_5+C_2H_5OH$: N, 21.27%.

**3, 5-Bisphenylazoresorcylaldehyde (II).** — From the acetone-insoluble fraction, red needles or long plates, m. p. 253°C (decomp.), were obtained.

Found: C, 65.81; H, 4.10; N, 16.28. Calcd. for $C_{19}H_{14}O_3N_4$: C, 65.89; H, 4.07; N, 16.18%.

**The 2, 4 - Dinitrophenylhydrazone:** lustrous black-purple crystals, m. p. ca. 277°C (decomp.).

Found: C, 57.36; H, 3.67; N, 21.28. Calcd. for $C_{25}H_{18}O_6N_8$: C, 57.03; H, 3.45; N, 21.29%.

**The Treatment of I with Ethyl Cyanoacetate.**—To a solution of 0.1 g. (0.00041 mol.) of I in 5 ml. of ethanol were added 0.1 g. (0.00089 mol.) of ethyl cyanoacetate and one drop of piperidine; the resulting solution was then warmed on a water bath for a while. The red or dark-red micro-particles (apparently a powder) produced were more stable than those obtained in the aforesaid treatment, carbonizing at a higher temperature, e. g., above 200°C. The other properties, on the whole, were similar to those of the particles described immediately above.

**The Hydrogenolysis of I to 5-Acetamidoresorcylaldehyde (IV).**—Into a mixture of 2 ml. of acetic anhydride and 15 ml. of dioxane, 0.16 g. of I was dissolved. The resulting solution was shaken with hydrgen in the presence of palladium-on-charcoal. The yellowish solid obtained was recrystallized from acetic acid to give yellowish crystals which melted at 259—260°C (decomp.).

Found: N, 7.23. Calcd. for $C_9H_9O_4N$: N, 7.18%.

**The Reduction of 5-Nitroresorcylaldehyde (V) to IV.**—A solution of 3.5 g. of V in a mixture of 100 ml. of acetic acid and 10 ml. of acetic anhydride was shaken with hydrogen in the presence of palladium-on-charcoal. Three grams of yellowish crystals, m. p. 259—260°C (decomp.), was obtained. The melting point was undepressed on admixture with the specimen obtained by the hydrogenolysis of I.

Found: C, 55.38; H, 4.63; N, 7.18. Calcd. for $C_9H_9O_4N$: C, 55.38; H, 4.65; N. 7.18%.

**The 2, 4-Dinitrophenylhydrazone of IV.**—This melted above 300°C.

Found: C, 48.04; H, 3.19; N, 18.40. Calcd. for $C_{15}H_{13}O_7N_5$: C, 48.00; H, 3.49; N, 18.66%.

**The Preparation of 2, 4-Dimethoxy-5-nitrobenzaldehyde (VI) from V.**—Into a mixture of 1.2 g. of V, 15 ml. of dioxane and 2 g. of silver oxide was added

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3) S. Matsumura, This Bulletin, **34**, 995 (1961).

* All melting points are uncorrected.

dropwisw a solution of 11.5 g. of methyl iodide in 5 ml. of dioxane with stirring. The product was recrystallized from methanol to yield 0.15 g. of brownish yellow short needles; m. p. 190—191°C, reported 188—189°C.[4]

Found: C, 50.91; H, 4.28; N, 6.63. Calcd. for $C_9H_9O_5N$: C, 51.19; H, 4.30; N, 6.63%.

**The Preparation of VI from 2, 4-Dimethoxybenzaldehyde.**—The method used was that described by Rao al.[4] M. p. 190—191°C; reported 188—189°C[4] A mixed melting point with the preceding specimen from V was not depressed.

We are indebted to Miss Kazue Takamura and Mr. Norimichi Koizumi for their kind assistance.

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[4] M. G. S. Rao, C. Srikantia and M. S. Iyenger, *J. Chem. Soc.*, **127**, 558 (1925).