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ON THE OXIDATION PRODUCTS OF BENZALDEHYDE PHENYLHYDRAZONE AND THE ISOMERS OF BENZIL OSAZONE

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The publication of a recent review(1) prompts us to communicate the results, fully described in a doctoral dissertation,(2) of a study of the oxidation products of benzaldehyde phenylhydrazone. Although observations not dissimilar to ours in some respects have been reported by others,(3) we should like to make the following points.

The compounds isolated by early workers, who used amyl nitrite(4) or mercuric oxide(5) as oxidizing agents, were the very insoluble *meso* **1** (whose structure is as written,(2,6) *not* **7**), and compound **4**. When a more powerful oxidant, such as iodine in sodium ethoxide,(7) was used, then **3** (benzil osazone) was also found. Compound **2** was not isolated. Presumably *meso* **1** is saved from tautomerization because it precipitates from solution.(8)

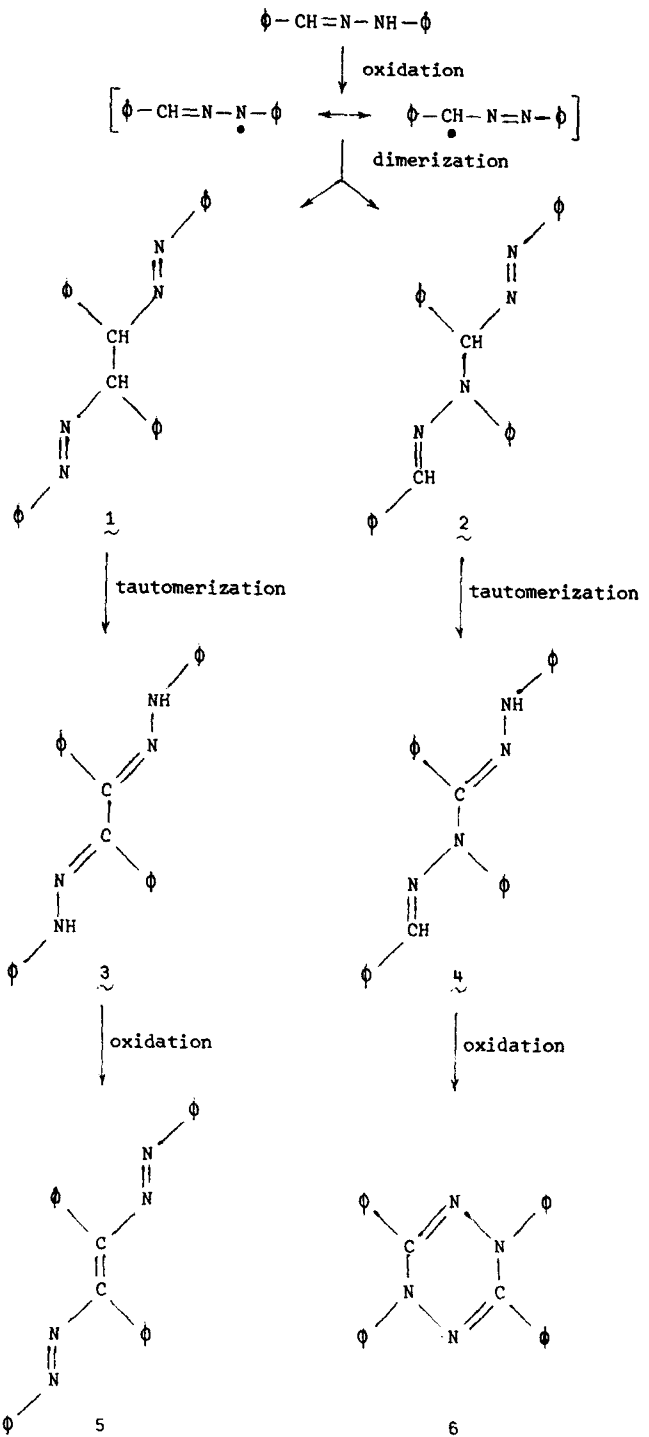
Much confusion has stemmed from reports(7,10,11) of a *syn* osazone **8** obtained in some oxidations. Reported melting points range from 204° to 218°. The structure was regarded as *syn* on the basis of the observation that the substance afforded small amounts of 2,4,5-triphenyl-1,2,3-triazole, **9**, when it was treated with sulfuric acid.(7) The benzil osazone, m.p. 234°, obtained from benzil and phenylhydrazine or from tautomerization of **1**, yielded no triazole on treatment with sulfuric acid. It is generally regarded as the *anti* osazone **3** (see below).

It was our finding that the so-called *syn* osazone, prepared according to the old procedures, was a mixture of three compounds: **3**, **4**, and **5**. Compound **3**, m.p. 234°, and compound **4**, m.p. 204°, are isomorphous (identical X-ray powder photographs(12)) and form a continuous series of solid solutions melting from 204° to 234°, depending on the composition. Such mixed crystals can be produced by simply dissolving in the same solvent appropriate quantities of each compound and then allowing crystallization to take place. In this manner any desired mixture, of constant melting point regardless of subsequent recrystallization, can be obtained. Mixtures of **3** and **4** are separable by chromatography. Thin layer chromatograms (silica gel, 50% pentane/50% benzene), when developed with a spray of concentrated sulfuric acid, display two brilliant spots, yellow (3, rf 0.78) and azure blue (4, rf 0.70). Under various oxidative conditions, mixtures differing in percentage composition are obtained; hence, the variety of observed melting points. It is noteworthy that 3 and 4 have substantially identical ultraviolet spectra,(2,6) in keeping with their similar molecular shapes and electronic structures.

Neither 3 nor 4 yields triazole 9 on treatment with sulfuric acid. However, 5(11) is cyclized to 9 in the presence of acid. Compound 5 is obtained from 3 by the action of iodine in sodium ethoxide, and it occurs as an impurity in the oxidation of benzaldehyde phenylhydrazone with the same reagent, although careful crystallization from benzene/ethanol does suffice to separate it from the mixture of 3 and 4. To complete the picture, we have confirmed that oxidation of 4 with iodine in sodium ethoxide yields 6.(11,13,14) Although other workers(3) have recently reported the isolation of compound 7, we have not found evidence for its formation.

Finally, we wish to call attention to the hitherto neglected extraordinary experimental work of Spasov(11) on the isomers of benzil osazone. Three benzil osazones are possible: *anti* (3), *syn* (8), and *amphi* (10). Spasov had in hand *four* osazones. Two of these were the authentic 234° osazone and the old so-called *syn* osazone. However, the two missing isomers had actually been prepared by Spasov, and we were able to reproduce his work in every detail. By heating the 234° osazone with trichloroacetic acid, he obtained a "γ-benzil osazone" as needles which crystallized in a characteristic pinwheel formation; these needles melted at 175° (we found 172°), resolidified, and melted again at 234°. The resolidified material was the starting osazone. By treating the 234° osazone with concentrated sulfuric acid in ethyl acetate, Spasov obtained a "rhombic osazone" in rhombic plates which melted at 196° (we found 192°), followed by resolidification and remelting at 234° (again, starting osazone).

In the absence of evidence to the contrary, it seems not unreasonable to assume that the 234° osazone (uv $\lambda\lambda\ \max_{\mathrm{EtOH}}$ 240 mμ (ε 33,500), 298 mμ (ε 18,000), 341 mμ (ε 34,500); ir 3.0 μ) is the *anti* osazone 3. Spasov's "γ-osazone" shows a doublet in the N—H stretch region of the infrared spectrum, indicative of intramolecular hydrogen bonding. Such bonding is likely only in the *amphi* case, so that the 175° osazone (uv $\lambda\lambda\ \max_{\mathrm{EtOH}}$ 242 mμ (ε 20,500), 322 mμ (ε 19,000), 399 mμ (ε 12,000); ir 3.0 μ, 3.1 μ) is the best candidate for the structure 10. Spasov's 196° "rhombic osazone" (uv $\lambda\lambda\ \max_{\mathrm{EtOH}}$ 298 mμ (ε 14,000), 368 mμ (ε 37,500); ir 3.0 μ) would then be the true *syn* osazone 8.(15)



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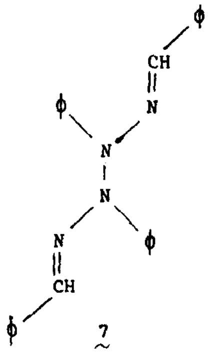

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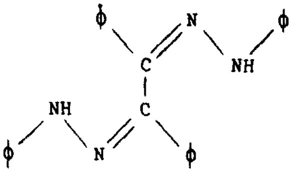

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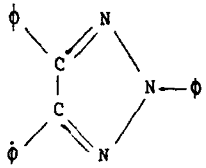

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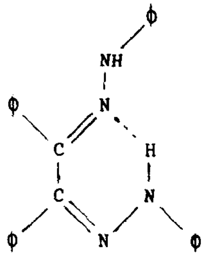

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(8) Recently, by using gentle conditions, evidence for the existence of the soluble and sensitive compounds **2** and *dl* **1** has been obtained.(9)

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(12) We thank Professor W. N. Lipscomb.

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