

Purported Synthesis of 3,4,7,8-Tetraphenyl-1,2,5,6-tetraazocine from Benzil and Hydrazine: Competing Cyclization and Carbon–Carbon σ -Bond Scission^[†]

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The claims that 3,4,7,8-tetraphenyl-1,2,5,6-tetraazocine can be prepared by the thermal condensation of two moles of benzil monohydrazone or of an equimolar mixture of benzil and benzil dihydrazone have been thoroughly reinvestigated. When such thermolyses were conducted in moist air, neither the claimed 3,4,7,8-tetraphenyl-1,2,5,6-tetraazocine nor the precedented isomeric tetraazapentalene derivative was detected. The following products were unambiguously formed from the heating of molten benzil monohydrazone (%): benzil (10), benzaldehyde (10), benzamide (22), benzyl phenyl ketone (19), benzil bis(ketazine) (11), 3,4,5,6-tetraphenylpyridazine (9), benzil benzaldehyde azine (10), and, after column chromatography, 2,4,5-triphenylimidazole (2). This last component had a melting point and the fluorescent properties in UV light attributed by the original investigator to the mistakenly presumed 3,4,7,8-tetraphenyl-1,2,5,6-tetraazocine. Thus, the original claims for the synthesis of such a novel tetraazocine ring or even for the synthesis

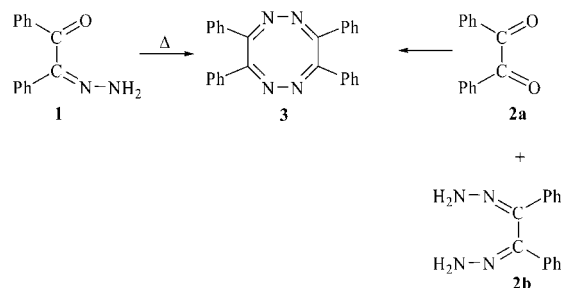
of the precedented isomeric zwitterionic tetraazapentalene have now been repudiated. The formation of 2,4,5-triphenylimidazole as a side reaction in the thermolysis of benzil monohydrazone can readily be rationalized as arising from benzil, benzaldehyde, and a source of ammonia, namely, benzamide, in the long-known Radziszewski reaction. Corroborating evidence was provided by data from the thermolysis of benzil dihydrazone. In addition, the origin of other side products is explained in terms of other possible condensations. Finally, preliminary experiments on using irreversible dehydrating agents such as titanium(IV) isopropoxide with benzil monohydrazone indicate that 3,4,7,8-tetraphenyl-1,2,5,6-tetraazocine is formed at room temperature as a transitory intermediate, which eliminates dinitrogen to produce 3,4,5,6-tetraphenylpyridazine.

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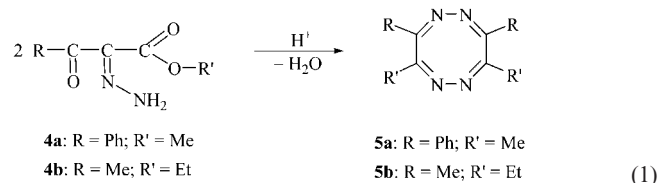
Introduction

Our long-standing interest in open-chain and cyclic conjugated imines^[1,2] has drawn our attention to two related brief communications describing the thermal autocondensation of either benzil monohydrazone (**1**)^[3] or of a 1:1 mixture of benzil (**2a**) and benzil dihydrazone (**2b**)^[4] to the purported 3,4,7,8-tetraphenyl-1,2,5,6-tetraazocine (**3**), but in very low yield and with inadequate experimental detail to support their structural assignment^[5] (Scheme 1).

Further work with the α -hydrazone of either the methyl ester of benzoylglyoxalic acid (**4a**) or of the ethyl ester of α,β -diketobutyric acid (**4b**) did provide reliable analytical data that such an autocondensation might have led to the structure of the corresponding tetraazocine (**5a** or **5b**) [Equation (1)].^[6,7] Such a finding tended to enhance the credibility of the conclusions drawn from the earlier work with benzil hydrazones **1** and **2b**.



Scheme 1.



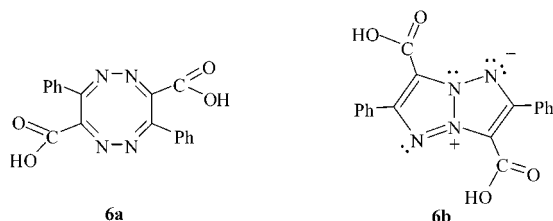
[†] Studies in Non-Pyridinoid Aza-Aromatic Systems, 7. Part 6: Ref.^[1]

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Structural assignments in these systems became more complicated after an X-ray crystallographic investigation of the diacid derived from the saponification of **5a** and subsequent acidification.^[8] This diacid was found to possess not

a tetraazocine nucleus (**6a**) but the structure of a novel aromatic zwitterionic 1,3a,4,6a-tetraazapentalene (**6b**). If tetraazocine **5a** were actually an intermediate, it must have isomerized during the reaction. Although the structures of diacid **6b** and its ester **5a** are then no longer in doubt, the crystallographic group nevertheless opined that the product from benzil monohydrazone probably is that of tetraazocine **3**.^[8]

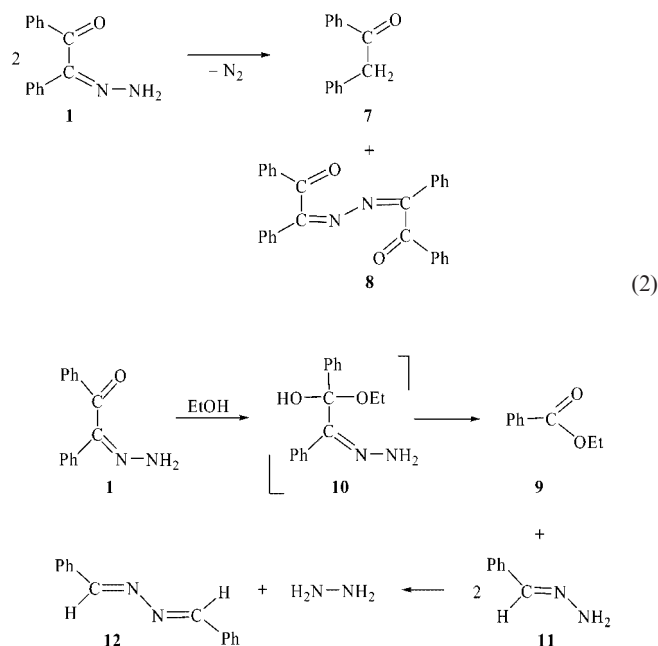


What aroused our scepticism concerning the purported tetraazocine **3** was the absence of verifiable analytical data, the lack of any color, and the high melting point (276 °C). All aryl azomethine or hydrazones we have encountered are distinctly yellow and melt under 200 °C. Therefore, we have launched a reinvestigation of the thermal reactions of hydrazones **1** and **2**. This study has led to the surprising conclusions that cyclization and carbon-carbon σ -bond scissions of such hydrazones begin as low as 50 °C and that purported **3** has neither the structure of a tetraazocine nor of a tetraazapentalene, but is the known 2,4,5-triphenylimidazole. Therewith, the joint claim of Metze and of Schlesinger to the synthesis of a tetraazocine has been decisively repudiated.

Results and Discussion

Thermal Stability of Benzil Monohydrazone (**1**)

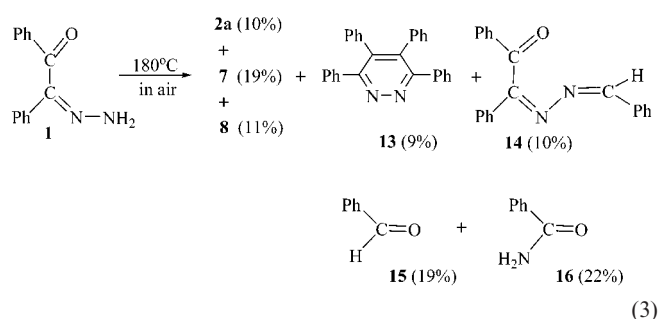
Pertinent to the thermal decomposition of **1** are two observations: (1) heating a neat sample of **1** for 2 h under reduced pressure (14 Torr) caused partial decomposition to benzyl phenyl ketone, which distilled off, and known benzil bis(ketazine) (**8**), which remained as a residue [Equation (2)];^[9] and (2) in this study, heating **1** in 95% ethanol at 110° for 17 h led to the 75% decomposition of **1** and products that consisted of 24% of **7** and 25% of **8** [cf. Equation (2)], as well as 7% of benzil (**2a**), 15% of ethyl benzoate (**9**), and 4% of *trans,trans*-benzaldehyde azine (**12**). The origin of **7** in Equation (2) can be attributed to a Wolff-Kishner reaction but the presence of ethyl benzoate (**9**) and azine **12** reveals the occurrence of a C-C bond solvolysis of **1**, possibly via **10**, to produce **9** and benzaldehyde hydrazone (**11**); the latter compound can disproportionate to azine **12** and hydrazine (Scheme 2). The source of ketazine **8** will be considered later. These reactions show that intermolecular reactions of **1** can occur at lower temperatures and that C-C bond cleavage occurs readily even in warm alcohol.



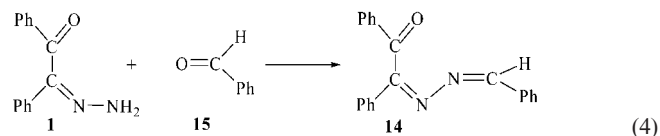
Scheme 2.

Thermal Decomposition of Benzil Monohydrazone at 180 °C in Moist Air (Presumed Metze Conditions)

Benzil monohydrazone (**1**) was heated in open air at 180 °C for 8 h. The reaction product, 95% of the original weight, consisted of 19% of **7**, 11% of **8**, 9% of 3,4,5,6-tetraphenylpyridazine (**13**), 10% of benzaldehyde benzil azine (**14**), 19% of benzaldehyde (**15**), 10% of benzil (**2a**), and, remarkably, 22% of benzamide (**16**) [Equation (3)].



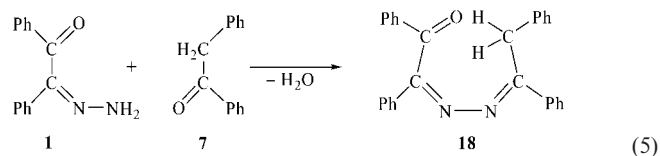
Most noteworthy are products **14**, **15**, and **16**, which must have arisen from C-C bond scission of **1**. Moreover, the formation of **16** proves that N-N bond homolysis must also have occurred. There is a straightforward explanation for the formation of **14**: when a 1:1 mixture of **1** and **15** in 95% ethanol was stored at 0 °C, a 70% yield of benzaldehyde benzil azine (**14**) was deposited [Equation (4)]. The origin of **13**, however, is puzzling and its manner of formation receives due consideration when the possible role of tetrahydrotetraazocine derivatives in these reactions is discussed (cf. *infra*).



Finally, upon column chromatography of the entire reaction mixture and the elution of all the foregoing components, a colorless, slowest-moving component (**17**) on the column or on TLC was detected by its pronounced bright-blue fluorescence. Upon isolation, 0.20 mg of compound **17** had a melting point of 274–276 °C (from ethanol). Although the properties of **17** resemble those reported for **3**, discussion of its identity will be deferred at this point until other data are presented.

Thermal Decomposition of Benzil Monohydrazone at 180 °C Under a Dry Argon Atmosphere

The decomposition of hydrazone **1**, carried out under identical conditions except that the atmosphere was anhydrous argon, gave the following array of products: 16% of **7**, 11% of **8**, 9% of **13**, 31% of **14**, and 23% of a new product, benzil (benzyl phenyl ketone) azine (**18**). The formation of **18** can readily be ascribed to the thermal condensation of **1** and **7** [Equation (5)].



Further noteworthy are the following aspects: (1) the relative amounts of **7**, **8**, and **13** formed in the two modes of decomposition, in moist air and under an argon atmosphere, are comparable: **7**: 16 vs. 19%, **8**: 18 vs. 11%, and **13**: 12 vs. 9%; (2) under an argon atmosphere the formation of **18** is accompanied by a great increase in the proportion of **14**, from 10 to 23%; and (3) under an argon atmosphere products such as benzaldehyde (**15**), benzamide (**16**), and **17** are present only in trace amounts. Because potential products such as **15**, **16**, and **17** stem from C–C, C–N, or N–N bond cleavages of **1** during decomposition, it can be concluded that the moist air present under Metzger's conditions was largely responsible for such C–C and N–N bond cleavages of **1**.

Thermal Decomposition of Benzil Dihydrazone at 180 °C in Moist Air

The decomposition of dihydrazone **2b** at 180 °C in moist air was cleaner and more informative. The reaction product dissolved in 95% ethanol deposited very small amounts of compound **17** with a melting point of 274–276 °C.

Recrystallization from ethanol gave a melting point of 275–276 °C.

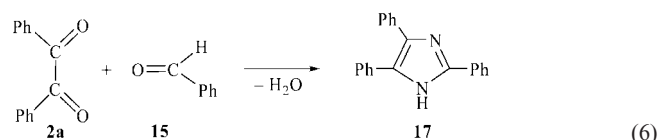
The original ethanolic filtrate was evaporated and analyzed by ¹H and ¹³C NMR spectroscopy. The presence of 62% of benzyl phenyl ketone (**7**), 5% of *trans,trans*-benzaldehyde azine, and 33% of **2b** was established.

When an identical thermolysis of **2b** was carried out, but in the presence of a threefold excess of benzaldehyde, about a 3.5% yield of **17** was achieved.

Identity and Origin of Compound 17

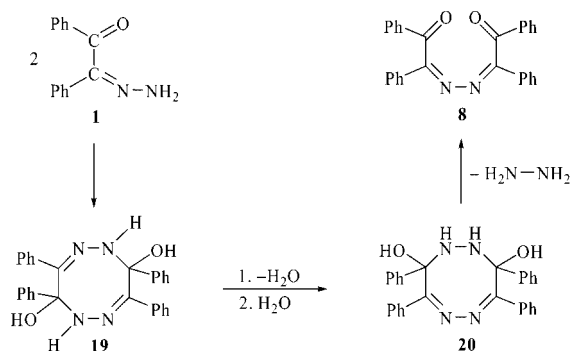
The melting point, migration on TLC plates, and infrared, ¹H and ¹³C NMR spectra of compound **17** isolated from the foregoing experiments was compared with an authentic sample of 2,4,5-triphenylimidazole (m.p. 275–276 °C), and it was found to be identical in all respects. The melting point of a mixture of **17** and the authentic imidazole was not depressed.

The origin of 2,4,5-triphenylimidazole (**17**) in the pyrolysis of benzil monohydrazone (**1**) or of benzil dihydrazone (**2b**) conducted in moist air is not difficult to trace. As shown in Equation (3), monohydrazone **1** produces benzil (**2a**), benzaldehyde (**15**), and benzamide (**16**), a source of ammonia. More than 125 years ago, Radziszewski demonstrated that passing ammonia into an ethanolic solution of **2a** and **15** at 50 °C leads to a quantitative formation of 2,4,5-triphenylimidazole (**17**) [Equation (6)].^[10]



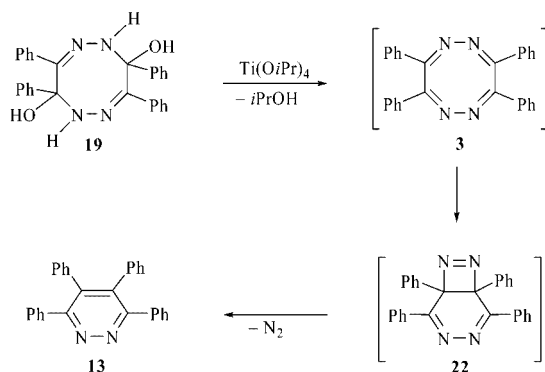
Origins of Benzil Bis(ketazine) (**8**) and 3,4,5,6-Tetraphenylpyridazine: Transitory Formation of Tetrahydrotetraazocine Intermediates

As mentioned above (Scheme 2), ketazine **8** forms readily from benzil monohydrazone (**1**) even in warm ethanol. Most likely **1** undergoes cyclic dimerization to the tetrahydrotetraazocine derivative **19**, which by consecutive loss and readdition of H₂O would isomerizes to conjugated isomer **20**. Structure **20** could readily eliminate hydrazine to yield **8** (Scheme 3). The complete loss of H₂O from **19** or **20** to produce **3** would undoubtedly involve a high activation energy, because as molecular models show, **3** would assume a nonplanar, highly strained tub-shaped conformation, like cyclooctatetraene itself. We conclude, therefore, that the prospects of synthesizing tetraazocine **3** by the ordinary dehydration of **1** are unpromising, as the water eliminated would be available for the reversible rehydration of intermediates, such as in steps **19** → **20** (Scheme 3).



Scheme 3.

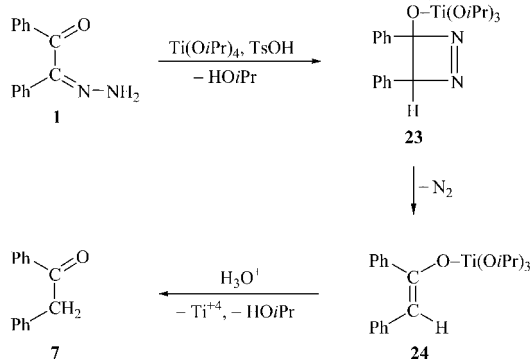
To circumvent such reversible dehydration–rehydration in the dimerization of benzil monohydrazone (**1**), we have treated **1** at room temperature in toluene solution with 0.5 equiv. of titanium(IV) isopropoxide (**21**) and catalytic amounts of *p*-toluenesulfonic acid. Subsequent hydrolysis showed that 59% of **1** had been consumed and that 31% of **7** and 28% of **13** had been formed. One straightforward interpretation of this outcome would be that intermediate **19** would have undergone irreversible dehydration with **21** to form **3**. Because of the ring strain and antiaromaticity of such a planar ring, **3** would rapidly undergo ring closure to fused ring **22**, just as cyclooctatetraene has been shown to do. However, **22** then would undergo facile loss of N₂ with the generation of azaaromatic **13** (Scheme 4).^[11]



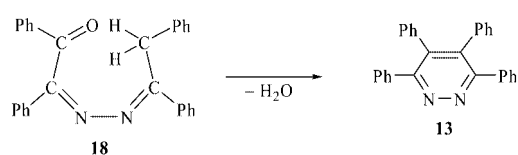
Scheme 4.

In an analogous manner, Wolff–Kishner product **7** could arise from the cyclizing action of Ti(O*i*Pr)₄ and acid catalyst on monomer **1** to form titanate ester **23**, which would readily lose N₂ to yield **24**. Hydrolysis would produce benzil phenyl ketone (**7**) (Scheme 5).

A plausible alternative route to **13** might be that **1** and **7** would react according to Equation (5) to form **18**, which could then undergo intramolecular dehydration to produce **13** [Equation (7)]. But opposing this alternative path to **13** are two observations: (1) none of proposed intermediate **18** was detectable from the reaction of **1** with Ti(O*i*Pr)₄ at room temperature; and (2) prolonged heating of **18** at 180 °C leads only slowly to **13**. Further research will explore the implications of our findings for the synthesis of labile cyclic imines.



Scheme 5.



(7)

Conclusions

A thorough reinvestigation of the claims that the thermolyses of benzil monohydrazone (**1**) and of benzil dihydrazone (**2a**) in moist air lead to 3,4,7,8-tetraphenyl-1,2,5,6-tetraazocine (**3**) has shown that neither this tetraazocine nor the isomeric tetraphenyl-1,3a,4,6a-tetraazapentalene is formed in these reactions. In both thermolyses, the purported **3** has been unambiguously identified as 2,4,5-triphenylimidazole (**17**). The origin of **17** was established by identifying C–C and N–N bond cleavage side products, such as, benzil, benzaldehyde, and benzamide, a source of ammonia. In the classic Radziszewski reaction such components readily combine to form **17**.

Preliminary results support the hope that thermally cyclic imines may be procured by irreversible dehydrations of carbonyl adducts of amines or hydrazines with Ti(O*i*Pr)₄ at lower temperatures, where such undesired cleavages occur less readily.

Experimental Section

Instrumentation and Analysis: Some reactions were carried out under a positive pressure of anhydrous, oxygen-free argon.^[12] Other reactions were carried out in a flask equipped with an air- or water-cooled condenser open to the surrounding moisture (“Metz conditions”). The IR spectra were recorded with a Perkin–Elmer instrument (model 457) and samples were measured either as mineral oil mulls or as KBr films. The NMR spectra (¹H and ¹³C) were recorded with a Bruker spectrometer (model EM-360) and tetramethylsilane (Me₄Si) was used as the internal standard. The chemical shifts reported are expressed on the δ scale in parts per million (ppm) from the Me₄Si reference signal. All ¹H and ¹³C NMR spectra were recorded at 360 MHz and in CDCl₃. The *J* values are not given when they fall in the customary 2–7 Hz range, and the multiplicity of a signal is only indicated when there is baseline separation from other signals; otherwise, the multiplicity is given as

"m". The GC–MS measurements and analyses were performed with a Hewlett–Packard GC 5890/Hewlett–Packard 5970 mass-selective-detector instrument. The gas chromatographic analyses were performed with a Hewlett–Packard instrument (model 5880) provided with a 2-m Ov-101 packed column or with a Hewlett–Packard instrument (model 4890) having a 30-m SE-330 capillary column. Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected.

Starting Reagents and Reaction Products: The following compounds employed in this study, benzil monohydrazone (**1**), benzil dihydrazone (**2b**), benzyl phenyl ketone (**7**), benzil (**2a**), ethyl benzoate (**9**), *trans,trans*-benzaldehyde azine (**12**), benzaldehyde (**15**), benzamide (**16**), and 2,4,5-triphenylimidazole (**17**) were commercially available in at least 98% purity. Benzil bis(ketazine) (**8**), a previously characterized compound, was prepared according to a literature reference.^[9] The previously reported 3,4,5,6-tetraphenylpyridazine (**13**) was synthesized by heating an equimolar mixture of **1** and **7** at 180 °C for 8 h. Column chromatography on silica gel yielded 13% of **13** (m.p. 191–193 °C) with MS (electrospray with NaI) 384.1616 (with Na⁺); calcd. 384.1614; and correct ¹H and ¹³C NMR spectra. The other product, 87%, was the cross-ketazine from **1** and benzyl phenyl hydrazine. Finally, the cross-ketazine from **1** and **11**, namely, **14**, was prepared in 5 mL of 95% ethanol by mixing 250 mg (1.11 mmol) of **1** with 3.0 mL (an excess) of **15**. Storing the solution at 0 °C deposited 340 mg (70%) of yellow **14**, m.p. 139–141 °C.

Analysis and Identification of Reaction Products: From the foregoing known samples, their respective melting points, their ¹H and ¹³C NMR spectra, and their behavior upon thin-layer chromatography were available criteria for the identification and quantification of the various reaction products.

The ¹H and ¹³C NMR spectra of most of the known products are conveniently available from compilations of the Aldrich Chemical Company.^[13] Where such spectra are not readily procurable, the relevant ¹H and ¹³C NMR spectroscopic data are given here in the individual experimental procedures.

Experimental Procedures for the Reactions (seriatim as given in the Results)

Benzil Monohydrazone (1) in Refluxing Ethanol: A solution of **1** (1.00 g, 4.46 mmol) in 95% ethanol (20 mL) was heated at reflux (bath: 110 °C) for 17 h. Dilution with water and extraction with ether gave an organic layer, which was separated and dried with anhydrous Na₂SO₄. Solvent evaporation gave 0.70 g of residue that was directly analyzed by ¹H and ¹³C NMR spectroscopy to yield the composition of 24% of benzyl phenyl ketone (**7**), 25% of benzil bis(ketazine) (**8**), 7% of benzil (**2a**), 15% of ethyl benzoate (**9**), and 4% of *trans,trans*-benzaldehyde azine (**12**).

Benzil Bis(ketazine) (8): M.p. 202–204 °C. ¹H NMR: δ = 7.97–7.94 (d, 2 H), 7.61–7.58 (d, 2 H), 7.53–7.48 (m), 7.38–7.34 (m), 7.27–7.23 (m) ppm. ¹³C NMR: δ = 197.4, 167.0, 135.5, 134.1, 132.2, 131.7, 129.2, 129.0, 128.7, 128.1 ppm.

Thermal Decomposition of Benzil Monohydrazone (1) at 180 °C in Moist Air: A dry sample of **1** (1.00 g, 4.46 mmol) in an open flask was heated at 180 °C (bath) for 8 h. The brown residue (0.95 g) was dissolved directly in CDCl₃ and analyzed by ¹H and ¹³C NMR spectroscopy. Spectral analysis led to a composition of 10% of benzil (**2a**), 19% of benzyl phenyl ketone (**7**), 8% of benzil bis(ketazine) (**8**), 9% of 3,4,5,6-tetraphenylpyridazine (**13**), 10% of benzaldehyde benzil azine (**14**), 22% of benzamide (**16**), and 19% of benzaldehyde (**15**). It should be noted that minor amounts of benzoic acid

could be isolated from the aqueous extract; the acid could arise by oxidation of **15** or hydrolysis of **16** during the pyrolysis.

3,4,5,6-Tetraphenylpyridazine (13): M.p. 192–193 °C. ¹H NMR: δ = 7.41–7.31 (m), 7.29–7.20 (m), 7.12–7.03 (m), 6.87–6.84 (d, 2 H) ppm. ¹³C NMR: δ = 158.9, 138.1, 137.4, 135.2, 130.4, 130.1, 128.2, 127.81, 127.80, 127.4 ppm.

Benzaldehyde Benzil Azine (14): M.p. 139–141 °C. ¹H NMR: δ = 8.58 (2 H), 7.97–7.95 (d, 2 H), 7.86–7.84 (d, 2 H), 7.60–7.25 (m) ppm. ¹³C NMR: δ = 197.5, 1617.4, 162.1, 135.4, 133.8, 133.6, 132.6, 131.5, 131.4, 129.2, 128.9, 128.87, 128.85, 128.5, 127.8 ppm.

Subsequent column chromatography of the product on silica gel with hexane as the eluent permitted the isolation of 0.20 mg of colorless solid **17**, which proved to be 2,4,5-triphenylimidazole (m.p. 275–276 °C) by spectral and mixture m.p. criteria.

Thermal Decomposition of Benzil Monohydrazone (1) Under a Dry Argon Atmosphere: When the foregoing heating of a 1.0-gram sample of **1** was repeated under a dry argon atmosphere, some products clearly due to C–C or N–N bond cleavage, namely, **15**, **16**, and **17**, were sharply reduced in amount or not at all detected. One product stemming from the C–C bond cleavage in **1** was increased in relative amount: benzaldehyde benzil azine (**14**) rose from 10 to 31%.

Analysis: benzaldehyde benzil azine (**14**), 31%; benzil (benzyl phenyl ketone) azine (**18**), 23%; benzyl phenyl ketone (**7**), 16%; 3,4,5,6-tetraphenylpyridazine (**13**), 12%; and benzil bis(ketazine) (**8**), 18%.

Benzil (benzyl phenyl ketone) Azine (18): M.p. 106–108 °C. ¹H NMR: δ = 7.91–7.82 (m), 7.55–7.12 (m), 4.54 (s, 2 H) ppm. ¹³C NMR: δ = 198.0, 165.9, 164.8, 137.2, 136.5, 135.4, 133.8, 132.9, 131.2, 130.2, 129.0, 128.8, 128.7, 128.6, 128.1, 127.7, 127.6, 126.2, 33.8 ppm.

Thermal Decomposition of Benzil Dihydrazone (2b) at 200 °C in Moist Air: Benzil dihydrazone (**2b**, 1.00 g, 4.20 mmol) was heated in open air in a flask at 200 ± 10 °C. A yellow solid (0.81 g) remained after loss of volatiles. About 30% of **2b** remained with the formation of 60% of benzyl phenyl ketone (**7**) and 10% of *trans,trans*-benzaldehyde azine (**12**). TLC of the entire reaction product showed the presence of small amounts of 2,4,5-triphenylimidazole (**17**) by its retention time and its bright blue fluorescence with UV light.

When an identical thermolysis of **2b** was done, but in the presence of benzaldehyde (12.6 mmol), similar proportions of **2b**, **7**, and **12** were found. But after extraction of the product with CHCl₃, 35 mg of a white solid remained, m.p. 274–276 °C, which proved to be 2,4,5-triphenylimidazole (mixture m.p. and ¹H and ¹³C NMR and IR spectral comparisons).

Dehydration of Benzil Monohydrazone (1) with Titanium(IV) Isopropoxide at Room Temperature: A solution of dried benzil monohydrazone (**1**, 2.00 g, 8.92 mmol), titanium(IV) isopropoxide (1.33 mL, 4.46 mol), and *p*-toluenesulfonic acid (0.10 g, 0.5 mmol) in dried toluene (100 mL) was stirred for 24 h at room temperature during which time the mixture turned a bright orange color. Addition of H₂O (15 mL) caused the color to change to dark brown and a solid to form. Filtration of the suspension, extraction of the filtrate with ethyl ether (3 × 15 mL), drying the ether extracts with anhydrous Na₂SO₄, and removal of the volatiles gave 1.6 g of brown residue. TLC and ¹H and ¹³C NMR spectral analyses showed that the residue consisted of 31% of benzyl phenyl ketone (**7**), 28% of 3,4,5,6-tetraphenylpyridazine (**13**) and 41% of starting material **1**.

Acknowledgments

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- [1] J. J. Eisch, T. Abraham, *Tetrahedron Lett.* **1976**, 17, 1647–1650.
- [2] Novel conjugated imines are of ongoing importance in our organometallic chemistry both as ligands for subvalent transition-metal complexes (cf. inter alia, J. J. Eisch, X. Ma, K. I. Han, J. N. Gitua, C. Krueger, *Eur. J. Inorg. Chem.* **2001**, 77–88) and as substrates for epimetalation or reductive dimerization (cf., e.g., J. J. Eisch, J. R. Alila, *Organometallics* **2000**, 19, 1211–1213).
- [3] R. Metze, *Angew. Chem.* **1956**, 68, 580–581. Compound **3** was claimed to have been isolated, in low yields ($\approx 10\%$), from: (1) reaction of **1** in formamide at 150 °C as a side product; (2) heating **1** above its m.p.; and (3) heating **1** in ethanol at 170–180 °C in a sealed tube. Compound **3** is said to be a colorless product that crystallizes from benzene as needles melting at 278 °C, which fluoresce a bright blue under UV light.
- [4] H. Schlesinger, *Angew. Chem.* **1960**, 72, 563. Compound **3** was said to have resulted in 12% yield from heating a 1:1 mixture of **2a** and **2b** at 130 °C for 3 h or by heating the identical 1:1 mixture at reflux in ethylene glycol monomethyl ether for 45 h. From benzene, **3** was crystallized (m.p. 285–286 °C). A sample, said to have been prepared according to Metze's method, melted also at 285–286 °C and the mixture m.p. of the two samples was undepressed. Schlesinger accepted Metze's structure for **3** without question and without additional evidence. Schlesinger also let substituted derivatives of **2a** and **2b** react and again simply assumed that the products were the corresponding tetraazocines.
- [5] Metze makes the following statements in ref.^[3] without giving any experimentally determined values or analyses: (1) "Analyse und Molekulargewichtsbestimmung ergaben die Bruttoformular $C_{28}H_{20}N_4$ "; and (2) "Die Substanz..wird erst durch halbkonzentrierte Schwefelsäure bei 210–220 °C unter Druck hydrolytisch in Benzil und Hydrazin aufgespalten im Mol-verhältnis 1:1". Both these statements would require actual experimental values and detail to be considered scientifically credible.
- [6] R. Pflieger, H.-G. Hahn, *Chem. Ber.* **1957**, 90, 2411–2416.
- [7] R. Pflieger, E. Garthe, K. Rauer, *Chem. Ber.* **1963**, 96, 1827.
- [8] M. Brufani, G. Casini, W. Fedeli, F. Mazza, A. Vaciago, *Gazz. Chim. Ital.* **1971**, 101, 322–343.
- [9] H. Staudinger, O. Kupfer, *Ber. Dtsch. Chem. Ges.* **1911**, 44, 22.
- [10] B. Radziszewski, *Ber. Dtsch. Chem. Ges.* **1882**, 15, 1493–1496.
- [11] For initial evidence leading to a postulated equilibrium between cyclooctatetraene and its bicyclo[4.2.0]octatriene isomer and a similar equilibrium between 1,3,5-cyclooctatriene and its bicyclo[4.2.0]octadiene isomer, refer to: E. Müller, *Neuere Anschauungen der Organischen Chemie*, 2nd ed., Springer, Berlin, **1957**, pp. 354–356, and the primary references to the works of Reppe, Cope, and Alder cited therein. It is interesting to note that such reports of the strain and nonplanarity of the eight-membered C_8 -ring appeared before Metze and Schlesinger published their postulated "planar" tetraazocine ring without misgivings.
- [12] Detailed descriptions of useful techniques and procedures for maintaining and working under an anhydrous and inert atmosphere are given in: J. J. Eisch, *Organometallic Syntheses*, Academic, New York, **1981**, vol. 2, pp. 3–52.
- [13] J. C. Pourhert, J. Behnke (Eds.), *Aldrich Library of ^{13}C and 1H FT-NMR Spectra*, Aldrich Chemical Company, Milwaukee, Wisconsin, USA, **1993**, vols. 1,2.

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