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Reactions of Aroylhydrazones. II.[1] Oxidative Cyclization of Benzil Bis(aroylhydrazones) to Substituted 1,2,3-Triazoles

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Benzil bis(aroylhydrazones) were oxidized with iodine and yellow mercury(II) oxide to 1-(1-α-aroyloxyarylideneamino)-4,5-diphenyl-1,2,3-triazoles. The structure of the prepared compounds was determined by studying their chemical and spectral properties.

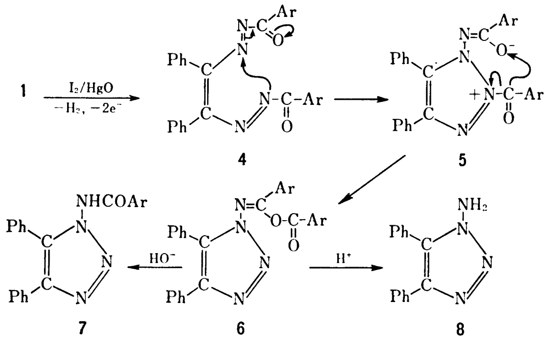
Bis(aroylhydrazones) of 1,2-dicarbonyl compounds have been known to undergo oxidation to give different products[2–5] depending upon the parent 1,2-dicarbonyl compound[2,5] and the oxidizing agent used.[2,6] Oxidation of these compounds with alkaline potassium hexacyanoferrate(III) or iodine and yellow mercuric oxide was first reported by Stolle[6] to give products which ascribed, at that time, 1,2,3,4-dihydrotetrazine structures.[6,8] However, the structure of the oxidation products was reassigned to be substituted 1-amino-1,2,3-triazoles on the basis of their infrared,[2] nuclear magnetic resonance,[2] and X-ray analyses.[9]

Continuing our studies on the reactions of hydrazones,[4,5,10–12] we report now the preparation and oxidative cyclization, with iodine and yellow mercuric oxide, of benzil bis(aroylhydrazones) (**1**) to 1-(α-aroyloxyarylideneamino)-4,5-diphenyl-1,2,3-triazoles (**6**) with emphasis on their spectral and some of their chemical properties.

Results and Discussion

Benzil bis(aroylhydrazones) **1** were prepared in 70—85% yield by condensing benzil with two equivalents of the required aroylhydrazine in ethanol. The infrared spectra of the bis-hydrazones showed the amide I bands of the aroylhydrazone residues at 1680—1670 cm^{-1} in addition to strong C=N absorption at 1650 cm^{-1} and NH bands at 3250—3200 cm^{-1}. Unlike benzil bis(arylhydrazones) which are orange to brown in color, the bis(aroylhydrazones) are colorless. This is attributed to the different types of tautomerism exhibited by these compounds. Thus, whereas the bis(arylhydrazones) were shown to exhibit arylhydrazono-arylazo tautomerism,[13] benzil bis(aroylhydrazones) exhibit a keto-enol tautomerism (**1**⇌**2**) as evidenced by giving pale yellow colors with sodium methoxide, greenish brown colors with neutral ferric chloride solution, as well as by forming stable cupric complexes.[14] Preliminary studies indicated that the stability of these complexes is due to the formation of tetradentate ligands (**3**) similar to those of osulose bis-(thiosemicarbazones).[15,16] The NMR spectrum of benzil bis(benzoylhydrazone) (**1a**) showed the four phenyl groups as a twenty-proton multiplet at δ 7.53 and the two hydrazono protons as a two-proton singlet at δ 12.85.

Oxidation of the bis-hydrazones **1** with iodine and yellow mercuric oxide in absolute ether afforded crystalline products having two hydrogens less than the parent bis-hydrazone and have no amide or NH absorptions in their infrared spectra. The oxidation products, however, showed strong ester absorption at 1760—1740 cm^{-1} in addition to the C=N absorption at 1640 cm^{-1}. The NMR spectrum of the oxidation product of benzil bis(benzoylhydrazone) revealed the absence of the two hydrazono protons of the parent compound and showed only a twenty-proton multiplet (four phenyl groups) at δ 7.50. The oxidation products were thus assigned the structure of 1-(α-aroyloxyarylideneamino)-4,5-diphenyl-1,2,3-triazoles (**6**). This assignment is in agreement with our[1,4,5] as well as with others[2,3,9] findings. The oxidation products are formed (see Scheme 1) first by abstraction of the two hydrazono hydrogens of **1** to give the bis(aroylazoene) (**4**) which cyclizes to the triazole derivative (**5**) followed by migration of the acylonium ion detached from N-2 of the triazole ring to the nucleophilic oxygen of the polarized acylamino group on N-1 to give **6**.



Scheme 1.

Compatible with the assigned structure **6**, is the splitting of their enol ester groups on alkali hydrolysis with methanolic ammonia at room temperature yielding the expected 1-aroylamino-4,5,-diphenyl-1,2,3-triazoles (**7**) and one equivalent of the corresponding benzoic acid. Infrared spectra of **7** revealed the absence of the ester absorption bands of their precursors with concomitant absorption at 1700—1660 (amide I) and 3250—3200 cm (NH) due to the newly formed amide function. Acid hydrolysis, with aqueous hydrochloric acid, of **6** or **7** split off two or one equivalent respectively of the corresponding benzoic acid and gave one and the same product from the differently substituted **6** and **7** namely: 1-amino-4,5-diphenyl-1,2,3-triazole (**8**).

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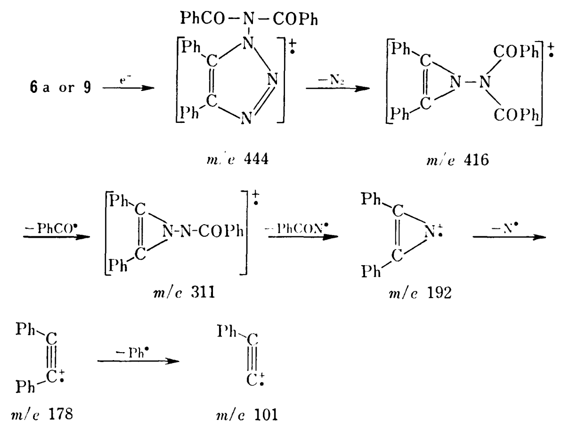
Table 1.

Compound	Mp °C	Yield %	Found % C	Found % H	Found % N	Formula	Calcd % C	Calcd % H	Calcd % N	IR: ν_{max}^{KBr}		
						Benzil bis(aroylhydrazones) (1)				C=N	CONH	NH
1a	207[17]	75	75.2	4.9	12.3	$C_{28}H_{22}N_4O_2$	75.3	5.0	12.5	1650	1670	3200
1b	180	70	75.5	5.2	12.2	$C_{30}H_{26}N_4O_2$	75.9	5.5	11.8	1650	1670	3200
1c	195	80	75.6	5.3	11.4	$C_{30}H_{26}N_4O_2$	75.9	5.5	11.8	1650	1680	3250
1d	220	75	70.9	5.3	10.9	$C_{30}H_{26}N_4O_4$	71.1	5.2	11.1	1650	1670	3250
1e	240	75	64.6	4.1	10.7	$C_{28}H_{20}Cl_2N_4O_2$	64.2	3.9	10.7	1650	1680	3250
1f	275	85	64.4	4.1	10.6	$C_{28}H_{20}Cl_2N_4O_2$	64.2	3.9	10.7	1650	1680	3250
						1-(α-Aroyloxyarylideneamino)-4,5-diphenyl-1,2,3-triazoles (6)				C=N	CONH	
6a	190[2]	40	75.4	4.4	12.7	$C_{28}H_{20}N_4O_2$	75.7	4.5	12.6	1640	1760	
6b	260	35	76.3	4.9	12.0	$C_{30}H_{24}N_4O_2$	76.3	5.1	11.9	1640	1750	
6c	170	40	76.6	5.0	11.6	$C_{30}H_{24}N_4O_2$	76.3	5.1	11.9	1640	1750	
6d	180	40	71.1	4.6	11.2	$C_{30}H_{24}N_4O_4$	71.4	4.8	11.1	1640	1740	
6e	240	45	65.3	3.5	10.6	$C_{28}H_{18}Cl_2N_4O_2$	65.5	3.5	10.9	1640	1750	
6f	192	50	65.3	3.5	10.6	$C_{28}H_{18}Cl_2N_4O_2$	65.5	3.5	10.9	1640	1750	
						1-Aroylamino-4,5-diphenyl-1,2,3-triazoles (7)					CONH	NH
7a	266	70	73.9	5.0	16.3	$C_{21}H_{16}N_4O$	74.1	4.7	16.5		1670	3200
7b	265	60	74.4	4.8	15.4	$C_{22}H_{18}N_4O$	74.6	5.1	15.8		1675	3200
7c	245	70	74.7	4.7	15.4	$C_{22}H_{18}N_4O$	74.6	5.1	15.8		1700	3250
7d	185	70	71.7	4.6	15.3	$C_{22}H_{18}N_4O_2$	71.3	4.9	15.3		1665	3350
7f	225	80	69.3	4.5	15.6	$C_{21}H_{15}ClN_4O$	69.2	4.1	15.4		1665	3350

Thermal rearrangement of 1-(α-benzoyloxybenzylideneamino)-4,5-diphenyl-1,2,3-triazole (**6a**), by heating above its melting point, gave 1-dibenzoylamino-4,5-diphenyl-1,2,3-triazole (**9**) through the 1,3-acyl migration of the enol benzoate group. The infrared spectrum of **9** showed only CON absorption band at 1720 cm^{-1} and no ester or NH absorptions. Compound **9** was also obtained when **8** was benzoylated with benzoyl chloride in pyridine. Conversely, **9** was converted to **8** on hydrolysis with aqueous hydrochloric acid. It was interesting to find out that both **6a** and **9** gave exactly the same mass spectrometric fragmentation pattern (see Scheme 2). This is probably due to the thermal isomerization of **6a** to **9** on the probe of the mass spectrometer before it undergoes fragmentation. Thus, both compounds showed the molecular ion peak (M^+) at *m/e* 444 in addition to the fragments at *m/e* 416 (M^+-N_2), *m/e* 311[$M^+-(N_2+PhCO)$]. The latter ion loses an *N*-benzoyl radical to give the diphenylaziridinium ion at *m/e* 192 which successively loses a nitrogen atom to give the diphenylacetylene ion at *m/e* 178 and a phenyl radical to give the phenylacetylene ion at *m/e* 101.



Scheme 2.

Refluxing of either **6a**, **7a**, or **8** with acetic anhydride gave 1-acetamido-4,5-diphenyl-1,2,3-triazole (**10**).

Experimental

Melting points were determined on a Kofler block and are uncorrected. Infrared spectra were recorded, for potassium bromide discs, with a Unicam SP 200 spectrophotometer. Nuclear magnetic resonance spectra were recorded at 60 MHz with a Varian T-60 spectrophotometer and with deuteriodimethylsulfoxide as a solvent containing 1% tetramethylsilane as internal standard. Mass spectral analyses were performed on a Varian M-66 spectrometer. Homogeneity of the prepared compounds were checked by thin layer chromatography on Silica Gel G plates, and the spots were detected by spraying with 20% (v/v) sulfuric acid, followed by heating on a hot plate for a few minutes.

*Benzil Bis(aroylhydrazone) (**1a**—**1f**; Table 1).* A solution of benzil (1 g) in ethanol (30 ml) was treated with the solution of the required aroylhydrazine (2 equivalents) in ethanol (20 ml) and a few drops of glacial acetic acid, and the mixture was heated on a water bath for 45 min. The mixture was kept at room temperature for an overnight, and the bishydrazone which separated was filtered and crystallized from 1 : 1 mixture of methanol-benzene. The bis-hydrazones are soluble in methanol and ethanol and are insoluble in hexanes.

*1-(α-Aroyloxyarylideneamino)-4,5-diphenyl-1,2,3-triazoles (**6a**—**6f**; Table 1).* A suspension of benzil bis(aroylhydrazone)

(1 g) in absolute ether (150 ml) was treated with yellow mercuric oxide (2 g), magnesium oxide (0.2 g) and iodine (2 g) for 96 h at room temperature. The suspension was filtered, and the inorganic residue was washed with chloroform (3 × 100 ml), and the filtrate and washings were combined and successively extracted with potassium iodide and sodium thiosulfate solutions and then with water and dried (sodium sulfate). Evaporation of the solvents gave the products which were crystallized from methanol.

1-Aroylamino-4,5-diphenyl-1,2,3-triazoles (7a—7f; Table 1). A solution of 1-(α-aroyloxyarylideneamino)-4,5-diphenyl-1,2,3-triazole (1 g) in methanol (200 ml) was treated with 20% ammonium hydroxide solution (20 ml) for 24 h at room temperature. The mixture was evaporated under reduced pressure, and the residue was triturated with water and filtered. The products were crystallized from methanol (see Table 1). Acidification of the filtrate gave one equivalent of the corresponding substitute benzoic acid.

1-Amino-4,5-diphenyl-1,2,3-triazole (8). Hydrolysis of compounds **6a**—**6e** or **7a**—**7f** (1 g) was carried out by heating under reflux, with concentrated hydrochloric acid (20 ml) for 24 h after which the reaction mixture was cooled, diluted with ether (200 ml), and the ethereal layer was washed with a saturated solution of sodium hydrogencarbonate and water and then dried (sodium sulfate). Evaporation of the solvent gave **8** (72—81% yield) which crystallized from benzene in plates, mp 136 °C. IR: $\nu_{\max}^{\mathrm{KBr}}$ 3300 cm^{-1} (NH). Found: C, 71.3; H, 5.0; N, 23.5%. Calcd for $C_{14}H_{12}N_4$: C, 71.2; H, 5.1; N, 23.7%. Acidification of the washings gave the corresponding substituted benzoic acid (two equivalents from **6** and one equivalent from **7**).

1-Dibenzoylamino-4,5-diphenyl-1,2,3-triazole (9). *(A) From 6a*: Compound **6a** (0.5 g) was heated at 190 °C in an oil bath for 2 h and then left to cool. The solidified mass was triturated with methanol and filtrered. Crystallization from methanol gave **9** (0.4 g) as plates, mp 155—156 °C. IR: $\nu_{\max}^{\mathrm{KBr}}$ 1720 cm^{-1} (CON). Found: C, 75.5; H, 4.4; N, 12.7%. Calcd for $C_{28}H_{20}N_4O_2$: C, 75.7; H, 4.5; N, 12.6%.

(B) From 8: A solution of **8** (0.5 g) in dry pyridine (5 ml) was treated with benzoyl chloride (2 ml) for 48 h at room temperature. The mixture was poured into ice-water, and the product, which separated, was filtered off and washed with water. Crystallization from methanol gave **9** (0.5 g) as plates, mp 155—157 °C. IR: $\nu_{\max}^{\mathrm{KBr}}$ 1720 cm^{-1} (CON). Found: C, 75.6; H, 4.5; N, 12.8%. Calcd for $C_{28}H_{20}N_4O_2$: C, 75.7; H, 4.5; N, 12.6%.

1-Acetamido-4,5-diphenyl-1,2,3-triazole (10). *(A) From 6a*: Compound **6a** (0.5 g) in acetic anhydride (15 ml) was heated under refluxed for 2 h after which it was poured onto ice and left until the excess acetic anhydride hydrolyzed. The product was filtered, washed with water, and crystallized from methanol to give **10** (0.2 g) as plates, mp 178—180 °C. IR: $\nu_{\max}$ 3300 (NH), 1670 cm^{-1} (COHN). Found: C, 69.3; H, 5.3; N, 20.0%. Calcd for $C_{16}H_{14}N_4O$: C, 69.1; H, 5.1; N, 20.1%.

(B) From 7a: Compound **7a** (0.5 g) was treated in the same way as described above to give **10** (0.3 g), mp 178—180 °C. Found: C, 68.9; H, 5.1; N, 20.0%.

(C) From 8: Compound **8** was refluxed with acetic anhydride as described above to give **10** in 80% yield having the same properties as mentioned.

References

1) Part 1: M. A. E. Shaban, M. A. M. Nassr, and M. A. M. Moustafa, *J. Heterocycl. Chem.*, **12**, 1295 (1975).

2) D. Y. Curtin and N. Y. Alexandrou, *Tetrahedron*, **19**, 1697 (1963).

3) D. Y. Curtin and N. Y. Alexandrou, *Tetrahedron*, **22**, 1309 (1966).

4) H. El Khadem and M. Shaban, *J. Chem. Soc., C*, **1967**, 519.

5) H. El Khadem, M. Shaban, and M. Nassr, *J. Chem. Soc., C*, **1969**, 1416.

6) R. Stolle, *Ber.*, **59**, 1743 (1926).

7) H. von Pechmann and W. Bauer, *Ber.*, **33**, 644 (1900).

8) H. von Pechmann and W. Bauer, *Ber.*, **42**, 659 (1909).

9) H. Bauer, A. J. Boulton, W. Fedeli, A. R. Katritzky, A. Majid-Hamid, F. Mazza, and A. Vaciago, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 662.

10) H. El Khadem, M. Shaban, and M. Nassr, *Carbohydr. Res.*, **23**, 103 (1972).

11) H. El Khadem, M. Nassr, and M. Shaban. *J. Chem. Soc., C*, **1968** 1465.

12) H. El Khadem, M. Shaban, and M. Nassr. *J. Chem. Soc., C*, **1970** 2167.

13) A. J. Fatiadi and H. S. Isbell, *Carbohydr. Res.*, **5**, 302 (1967).

14) M. A. E. Shaban and M. A. Nassr, to be published.

15) G. Henseke and M. Winter, *Chem. Ber.*, **89**, 956 (1956).

16) F. H. H. Carlsson, A. J. Charlson, and E. C. Watton, *Carbohydr. Res.*, **36**, 359 (1974).

17) G. Struve, *J. Prakt. Chem.*, **50**, 295 (1984).