Pyrolysis and Photolysis of 1-Aroylamino-4,5-diaryl-1,2,3-triazoles: Generation and Thermal Transformations of 4,5-Diaryl-1,2,3-triazolyl Radicals

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The pyrolysis of 1-aroylamino-4,5-diphenyl-1,2,3-triazoles **1** yields, pressumably *via* the 4,5-diphenyl-1,2,3-triazolyl radical (**2a**), 2,3-diphenyl-2*H*-azirine (**11a**) and 2-aryl-4,5-diphenylimidazoles **14** as the major products. Upon irradiation 1-benzoylamino-4,5-diphenyl-1,2,3-triazole (**1a**) gives 4,5-diphenyl-1(2)*H*-1,2,3-triazole (**4a**) *via* the 1,2,3-triazolyl radical **2a**, together with benzamide (**5a**) and 1,2-bisbenzoylhydrazine (**6a**). Products **5a** and **6a** result from the benzoylamino radical **3a** by hydrogen atom abstraction and dimerization respectively.

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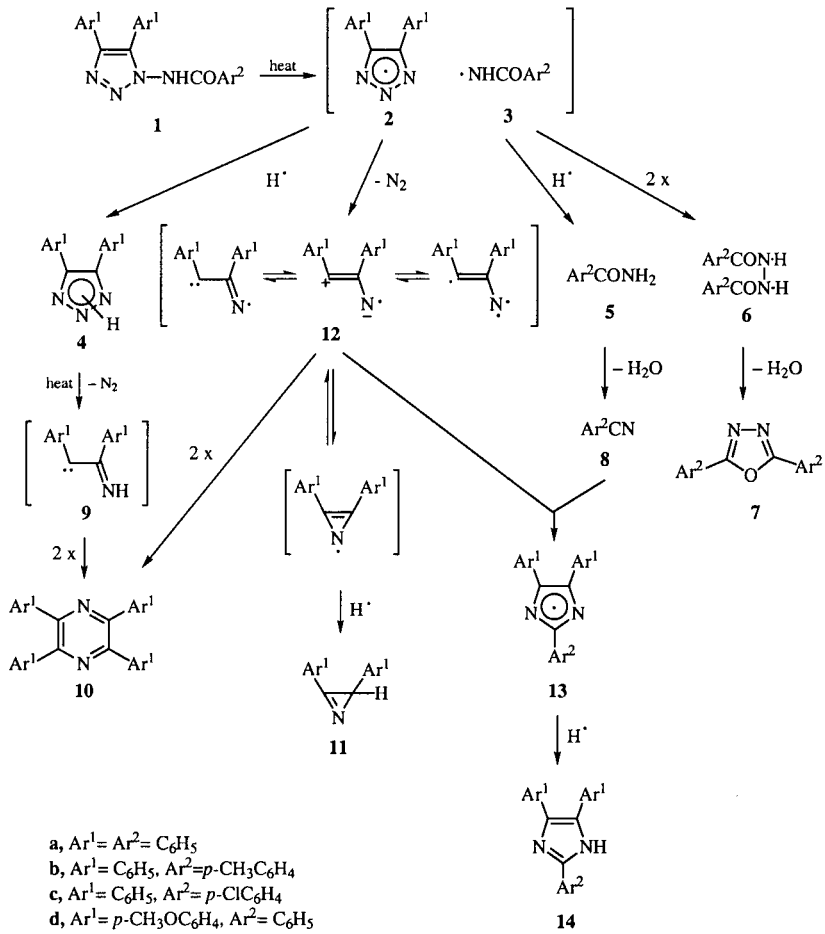
One of the most characteristic general reactions of the 1,2,3-triazoles, under either forced thermal conditions or photolytic such, is the extrusion of nitrogen [1,2]. However, in certain instances when the particular 1,2,3-triazole derivative contained an exocyclic N-N bond, as it was the case with the 1-(*N,N*-bisacyl)amino-1,2,3-triazoles, **17**, it was shown that cleavage of this weak bond was the primary photochemical process [3].

In view of this most interesting deviation from the general mode of 1,2,3-triazole reactivity we decided to expand our studies to the analogous 1-aroylamino-4,5-diaryl-1,2,3-triazole system **1**, which, indicentally, is easilly obtained from the appropriate bisaroylhydrazones by oxidative cyclization and subsequent hydrolysis of the resulting primary product (isoimide) [4,5].

Pyrolysis of 1-Aroylamino-4,5-diaryl-1,2,3-triazoles.

We found that when 1-aroylamino-4,5-diphenyl-1,2,3-triazoles **1a-d** were heated in the molten state at temperatures between 220 and 250°, untill all, or almost all, the starting

Scheme 1



material was consumed, the crude pyrolysate contained several products. Thin layer chromatography proved to be a satisfactory method of following-up the pyrolysis and of monitoring the ensuing column chromatographic separation.

The specimens obtained by column chromatography were further purified when needed, by recrystallization and identified by comparison of their spectra and melting points with those of authentic specimens.

It was found that, with the exception of 1-benzoylamino-4,5-di-4-methoxyphenyl-1,2,3-triazole (**1d**) which upon pyrolysis gave 4,4'-dimethoxydiphenylacetylene (**15**) and 2-phenyl-4,5-di-4-methoxyphenylimidazole (**14d**), all other 1-aroylamino-4,5-diaryl-1,2,3-triazoles **1a-c** yielded upon heating 2,3-diphenyl-2*H*-azirine (**11a**) and 2-aryl-4,5-diphenylimidazoles **14a-c** as the major products (Scheme 1 and Table).

Both the azirine **11a** and the imidazoles **14a-d** are believed to be primary products derived from the same intermediate **12**.

With respect to the mechanism in general we believe that heating of the triazoles **1** leads to the homolytic cleavage of the weak exocyclic N-N bond (38 Kcal mol^{-1}) [6] with the concomitant formation of the 1,2,3-triazolyl radical **2** and the aroylamino radical **3** (Scheme 1).

The isolation from the pyrolysis mixture of 4,5-diphenyl-1(2*H*)-1,2,3-triazole (**4a**) and benzamide (**5a**) supports this hypothesis since both the triazolyl **2** [3] and the aroylamino **3** [7] radicals are expected to be good hydrogen atom abstractors. Furthermore the isolation in at least one occasion of small amounts (14%) of 2,5-diphenyl-1,3,4-oxadiazole (**7a**) indicates the intermediate formation of bisbenzoylhydrazine (**6a**) from which **7a** is known to result in by dehydration [8]. The presumed formation of bisaroylhydrazine (**6a**) verifies in turn the intermediacy of the benzoylamino radical (**3a**) and therefore the homolytic N-N bond cleavage.

Under the rather forced thermal conditions of the experiments both products **4** and **5** are further transformed and, while the amides **5** upon dehydration yield the nitriles **8**, the 4,5-diphenyl-1(2)*H*-1,2,3-triazoles **4** are expected to produce, after nitrogen loss, presumably *via* the iminocarbenes **9**, the tetrarylpyrazines **10** [9].

In order to exclude the intermediacy of 4,5-diphenyl-1(2)*H*-1,2,3-triazole (**4a**) in the formation of 2,3-diphenyl-2*H*-azirine (**11a**) we pyrolyzed the former at 240°. In accord with the published results for the pyrolysis of this compound at 290° [9], tetraphenylazine (**10a**) was the sole product.

To rationalize then the reasonable yields of the azirine **11a** one has to assume an intermediate such as **12** which results by nitrogen loss from the triazolyl radical **2** before hydrogen atom abstraction takes place. This same intermediate **12** when captured by the nitrile **8**, leads to the imidazolyl radical **13** which after hydrogen atom abstraction produces the isolated triarylimidazoles **14**.

In addition to the above, the following results gathered from control experiments support the proposed mechanism for imidazole formation (Table). a. When 1-benzoylamino-4,5-diphenyl-1,2,3-triazole (**1a**) was pyrolyzed in the presence of *p*-tolylnitrile, in addition to 2,4,5-triphenylimidazole (**14a**), 2-*p*-tolyl-4,5-diphenylimidazole (**14b**) was isolated. b. Pyrolysis of 1-*p*-tolyl-4,5-diphenyl-1,2,3-triazole (**1b**) with benzamide gave besides 2-*p*-tolyl-4,5-diphenylimidazole (**14b**) and 2,4,5-triphenylimidazole (**14a**). and, c. Pyrolysis of 2,3-diphenyl-2*H*-azirine (**11a**) in the presence of *p*-tolylnitrile at 240° did not yield any 2-*p*-tolyl-4,5-diphenylimidazole (**14b**).

Table

Products from the Pyrolysis of 1-Aroylamino-4,5-diaryl-1,2,3-triazoles **1** at 220-250°

Entry	Substrate	Pyrolysis time (h)	Products (Isolated yields%)							
			4	**5**	**7**	**8**	**10**	**11**	**14**	**15**
1	**1a**	0.5	3	10	14	-	10	13	16	-
2	**1b**	0.75	-	-	-	17	-	20	28	-
3	**1c**	2.0	-	-	17	-	-	-	11	-
4	**1d**	1.0	-	-	-	-	-	-	6	3
5	**1a** [a]	2.0	-	-	-	-	-	32	27[b]	-
6	**1b** [c]	0.5	-	-	-	-	-	-	15 [d]	-

[a] In the presence of *p*-$CH_3C_6H_4CN$. [b] Total yield of **14a** and **14b** (~ 1:1). [c] In the presence of $C_6H_5CONH_2$. [d] Total yield of **14a** and **14b** (~ 1:1).

Photolysis of 1-Aroylamino-4,5-diaryl-1,2,3-triazoles.

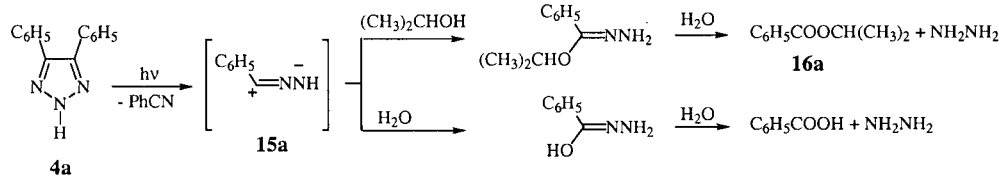
In the photolysis experiments light from a medium pressure mercury arc filtered through quartz (>220 nm) was employed. Isopropyl alcochol was used as the solvent by virtue of its capacity to easily provide hydrogen atoms to the incipient radicals **2** and **3**.

Product analysis revealed a similar yet simpler fragmentation pattern than that realized in the pyrolysis experiments (Scheme 2). The formation of 2,4-diphenyl-1(2)*H*-1,2,3-triazole (**4a**, 9%), benzamide (**5a**, 46%) and dibenzoylhydrazine (**6a**, 16%) clearly supports the photoinduced-elimination of the triazole group in the form of the 1,2,3-triazolyl radical **2**.

This is in accord with previous studies involving the analogous 1-(*N,N*-bisaryl)amino-1,2,3-triazole system (Structure **17**) [3] and it is due to the presence of the weak N-N bond in the vicinity (β-position) of the excited carbonyl chromophore. The isolation of traces of 2,3,5,6-tetraphenylpyrazine (**10a**, <1%) indicates the dimerization of an intermediate such as **9a** or **12a**.

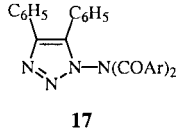
The formation in significant amounts of isopropyl benzoate (**16a**, 13%) and also of benzoic acid (35%) could be explained in terms of the reactions depicted in Scheme 3. Irradiation of 4,5-diphenyl-1(2)*H*-1,2,3-triazole (**4a**) in its 2*H*-tautomeric form leads, after elimination of benzonitrile, to the benzonitrilimine (**15a**). The latter, after nucleophilic capturing by isopropyl alcohol or water and subsequent hydrolysis, gives isopropyl benzoate (**16a**) and benzoic acid respectively.

Scheme 3



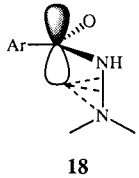
2*H*-1,2,3-Triazoles are known to eliminate nitriles under both electron impact [10] and photolysis [11]. Furthermore, in the latter case the resulting nitrilimine was trapped by cyclopentene. It is worth mentioning that the formation of methyl benzoate during the related irradiation of 4,5-diphenyl-1(2)*H*-1,2,3-triazole (**4a**) in methanol was reported albeit without any mechanistic explanation [9].

Even though both the multiplicity of the excited state (singlet or triplet) and the character of it (n,π* or π,π*) are unknown yet, it is reasonable to assume that the coupling of the carbonyl π* orbital with the exocyclic N-N σ* orbital stabilizes the reactive state. This coupling, which weakens the N-N, would require it to be perpendicular to the carbonyl [12] (structure **18**) thus assuming conformations that can be easily attained in the title compounds as the study of the models reveals.



17

Structure 17



18

Structure 18

EXPERIMENTAL

Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded for Nujol mulls on a Perkin-Elmer 297 or 257 spectrometer calibrated with the 1602 cm^{-1} absorption of polystyrene. Proton nmr spectra were obtained in deuteriochloroform solution with tetramethylsilane as internal standard, using a Bruker AW 80 or a Bruker AM 300 instrument. The mass spectra were recorded from a VG Tritech TS-250 spectrometer and elemental microanalyses were performed with a Perkin-Elmer 240 B analyzer.

The reactions were monitored by tlc using pre-coated 0.25-mm Merck silica gel 60 F_{254} plates, and the spots were visualized under uv light.

All solvents used were purified according to established procedures [13].

Compounds **1a** [4], **1b-c** [14], **4a** [15], **7a** [8], **10a** [16], **11a** [17], **14a** [18], **14b** [19], **14c** [20] and **14d** [21] were either identified from their reported spectra or synthesized according to the reported procedures and used for the identification of the unknown samples.

Anisil bisbenzoylhydrazone (**19**) was prepared by refluxing the diketone with benzoylhydrazine in ethanol solution [22] and was oxidized in methylene chloride using lead tetraacetate [23] to 1-(-aroyloxybenzilideneamino)-4,5-bis(4-methoxyphenyl)-1,2,3-triazole (**20**). Hydrolysis of **20** [5] gave 1-benzoylamino-4,5-bis(4-methoxyphenyl)-1,2,3-triazole (**1d**).

Anisil Bisbenzoylhydrazone (**19**).

The yield of **19** was 57%, colorless crystals, mp 220-222° (methylene chloride-petroleum ether); ir (Nujol): 3160, 1635, 1349, 1245, 1032, 824, 700; ms: m/z (relative intensity) 374 (24), 219 (36), 180 (19), 131 (43), 69 (100).

Anal. Calcd. for $C_{30}H_{26}N_4O_4$ (506.54): C, 71.13; H, 5.17; N, 11.06. Found: C, 71.02; H, 5.05; N, 11.23.

1-(-Aroyloxybenzilideneamino)-4,5-di-4-methoxyphenyl-1,2,3-triazole (**20**).

This compound was obtained as colorless crystals, mp 183-184° (methylene chloride-petroleum ether); ir (Nujol): 1740, 1352, 1248, 1173, 1021, 830, 700; ^1H nmr (deuteriochloroform): 3.79 (s, 3H, CH_3O), 3.89 (s, 3H, CH_3O), 6.79-7.72 (m, 14H, aromatic), 7.95 (d, 2H, aromatic), 8.22 (d, 2H, aromatic); ms: m/z (relative intensity) 476 (M^+-28, 5), 252 (18), 135 (83.6), 105 (92), 77 (100).

Anal. Calcd. for $C_{30}H_{24}N_4O_4$ (504.52): C, 71.41; H, 4.80; N, 11.11. Found: C, 71.18; H, 4.65; N, 11.31.

1-Benzoylamino-4,5-di-4-methoxyphenyl-1,2,3-triazole (**1d**).

This compound was obtained as colorless crystals, mp 221-222° (alcohol); ir (Nujol): 3110, 1682, 1243, 1174, 1016, 843, 685; ^1H nmr (deuteriochloroform): 3.76 (s, 3H, CH_3O), 3.77 (s, 3H, CH_3O), 6.73 (d, 2H, aromatic *o*- to CH_3O), 6.85 (d, 2H, aromatic *o*-CH_3O), 7.20-7.52 (m, 6H, aromatic), 7.83 (d, 2H, *o*- to CO), 11.17 (s, 1H, NH); ms: m/z (relative intensity) 400 (M^+, 15), 252 (56), 134 (65), 105 (94), 77 (100).

Anal. Calcd. for $C_{23}H_{20}N_4O_3$ (400.42): C, 68.99; H, 5.03; N, 13.99. Found: C, 68.76, H, 4.89; N, 14.16.

Pyrolysis of 1-Benzoylamino-4,5-diphenyl-1,2,3-triazole (**1a**).

1-Benzoylamino-4,5-diphenyl-1,2,3-triazole (**1a**, 1.352 g, 4.0 mmoles) was pyrolyzed at 240-250° until all gas evolution ceased and tlc analysis showed >80% consumption of the starting material (~ 0.5 hour). The pyrolysate was chromatographed on a silica gel medium pressure column using a mixture of petroleum ether-ethyl acetate of increasing polarity as eluent. The following products were obtained: 2,3-diphenyl-2*H*-azirine (**11a**, 81 mg, 13%), 2,3,5,6-tetraphenylpyrazine (**10a**, traces), 2,5-diphenyl-1,3,4-oxadiazole (**7a**, 52 mg, 14%), 2,4,5-triphenylimidazole (**14a**, 154 mg, 16%), 4,5-diphenyl-1(2*H*)-1,2,3-triazole (**4a**, 16 mg, 3%), 1-benzoylamino-4,5-diphenyl-1,2,3-triazole (**1a**, starting material, 224 mg, 17%) and, benzamide (**5a**, 40 mg, 10%).

According to the general procedure described above all pyrolyses of 1-aroylamino-4,5-diaryl-1,2,3-triazoles **1** were carried out. Pyrolysis conditions and isolated product yields are summarized in the Table.

Photolysis of 1-Benzoylamino-4,5-diphenyl-1,2,3-triazole (**1a**) in Isopropyl Alcohol Solution.

A solution of 1-benzoylamino-4,5-diphenyl-1,2,3-triazole (**1a**, 1.352 g, 4 mmoles) in 600 ml of isopropyl alcohol was irradiated in a quartz vessel at 20° using a 250 W medium pressure mercury arc, until **1a** was largely (>90%) consumed (14 hours). Evaporation of the solvent, and chromatography of the residue on a silica gel medium pressure column using a mixture of petroleum ether-ethyl acetate as eluant, gave the following products: 2,3,5,6-tetraphenylpyrazine (**10a**, traces), isopropyl benzoate (**16a**, 74 mg, 13%), 4,5-diphenyl-1(2*H*)-1,2,3-triazole (**4a**, 71 mg, 9%), benzoic acid (196 mg, 35%), 1-benzoylamino-4,5-diphenyl-1,2,3-triazole (**1a**, starting material, 118 mg, 9%), 1,2-dibenzoylhydrazine (**6a**, 134 mg, 16%) and, benzamide (**5a**, 202 mg, 46%).

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