



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-arylamino-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<sup>-1</sup>) [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**)

produce, after nitrogen loss, presumably *via* the iminocarbenes **9**, the tetraarylpyrazines **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*-tolynitrile, 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*-tolynitrile 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%)							
			<b>4</b>	<b>5</b>	<b>7</b>	<b>8</b>	<b>10</b>	<b>11</b>	<b>14</b>	<b>15</b>
1	<b>1a</b>	0.5	3	10	14	-	10	13	16	-
2	<b>1b</b>	0.75	-	-	-	17	-	20	28	-
3	<b>1c</b>	2.0	-	-	17	-	-	-	11	-
4	<b>1d</b>	1.0	-	-	-	-	-	-	6	3
5	<b>1a</b> [a]	2.0	-	-	-	-	-	32	27[b]	-
6	<b>1b</b> [c]	0.5	-	-	-	-	-	-	15 [d]	-

[a] In the presence of *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN. [b] Total yield of **14a** and **14b** (~ 1:1). [c] In the presence of C<sub>6</sub>H<sub>5</sub>CONH<sub>2</sub>. [d] Total yield of **14a** and **14b** (~ 1:1).

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

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 alcohol 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**.



*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-arylamino-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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