BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (9), 2505—2506 (1977)

Photochemical Dimroth Rearrangement of 1,4-Diphenyl-5-amino- and 4-Phenyl-5-anilino-1,2,3-triazoles[1)]

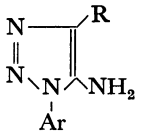
Yoshiro OGATA, Katsuhiko TAKAGI, and Eiji HAYASHI

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464

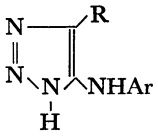
(Received May 14, 1977)

Synopsis. Irradiation of 1,4-diphenyl-5-amino-1,2,3-triazole (**1a**) gives 4-phenyl-5-anilino-1,2,3-triazole (**2a**) and the reverse photochemical reaction is possible. Hence, the reaction is reversible, the ratio of **1a** : **2a** in equibrium being 1.2—1.7, which is different from the ratio 0.33 in the thermal reaction (Dimroth rearrangement). The mechanism is discussed on the basis of spectral data and analogous reactions.

Dimroth discovered a rearrangement of 1-aryl-5-amino-1,2,3-triazoles(**1**) to 5-anilino-1,2,3-triazoles(**2**) in boiling pyridine or in boiling ethanolic sodium ethoxide.[2)] The rearrangement is essentially complete in the above solvent,[3)] but in some other solvents or in melts, **1** gives an equilibrium mixture of **1** and **2** in which the acidic isomer(**2**) usually predominates.[4,5)] The reverse thermal reaction of **2** to **1** (retro-Dimroth rearrangement) leading to the equilibrium state was also reported.[6)]



(**1**)



(**2**)

We wish to report here a photo-equilibrium between the amino(basic) isomer(**1**) and the anilino (acidic) isomer(**2**).

Results and Discussion

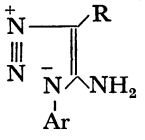
1,4-Diphenyl-5-amino-1,2,3-triazole(**1a**)[7)] (2.0 g) in absolute ethanol(250 ml) was irradiated with a 100-W high-pressure mercury lamp for 40 h under N_2. The irradiated products were separated by TLC, and the rearrangement product(**2a**) (34.9%), unreacted **1a** (53.5%) and unidentified products(12.1 wt%) were obtained.

On the other hand, the irradiation of **2a** (1.9 g) under N_2 in absolute ethanol (200 ml) for 40 h gave a mixture of **1a** (36.6%), unreacted **2a** (30.7%) and unidentified products (32.7 wt%). The longer irradiation, which is sufficient for establishment of the equilibrium, afforded an equilibrium mixture containing **1a** and **2a** in a mole ratio of 1.53 by means of preparative TLC. Whereas, the irradiation of **2a** gave an equilibrium mixture of isolated **1a** and **2a** in the ratio of 1.20. The slight difference in the ratio may be due to the difference of extent of side reactions from **1a** and **2a**.

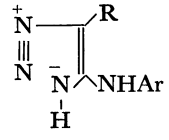
The amount of acidic isomer(**2a**) was determined by acidimetry with aq KOH at appropriate time intervals. As a result, the ratio of **1a** : **2a** became constant approaching to 1.70. This ratio is close to that obtained above by TLC analysis.

Generally, **1a** is favored in the photo-equilibrium of **1a** : **2a**. It is in contrast to the thermal reaction in which the equilibrium mixture consists of a larger amount of **2** than that of **1**, *i.e.*, the reported equilibrium ratio of 0.33 in melts,[6)] while the ratio for photolysis in ethanol is 1.2—1.7, and suggests the difference in mechanism between thermal and photochemical reactions.

The thermal Dimroth rearrangement was postulated to involve a diazonium intermediates(**3** or **4**).[5)] In the case of photolysis, this mechanism is not suitable, because the diazonium intermediate(**3** or **4**) is expected to react



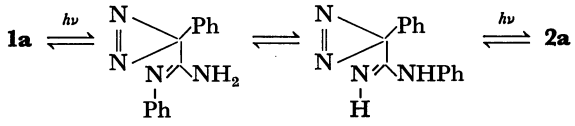
(**3**)



(**4**)

with the solvent.[8)] In our attempt for spectral detection of the intermediates (**3** and **4**), the UV peak around 400 nm[9)] and IR absorption in a range of 2150—2170 cm^{-1},[9)] which are characteristic to diazonium group (C–N_2^+; *e.g.*, a diazonium ketone has UV peaks at 410 and 417 nm[10)] and IR peak at 2137 cm^{-1} [10)]), could not be detected at room temperature. These facts also disfavor the intermediacy of **3** and **4** possessing a diazonium group. But the possibility cannot completely be precluded at present, since the diazonium intermediate should be diluted and short-lived.

It is likely that this photo-rearrangement of **1** to **2** involves a valence isomerization which is characteristic to the photolysis of aromatic compound;[11)] *i.e.*, the photolysis may proceed *via* diarines (**5** and **6**), and may



(**5**) (**6**)

involve a process of ring contraction and expansion together with a proton shift of **5** to **6**. A similar mechanism was suggested for five-membered hetero aromatics such as the photo-rearrangement of 3,5-diphenylisoxazole to 2,5-diphenyloxazole *via* a three-membered azirine which was detected spectroscopically.[12)]

Experimental

Materials. 1,4-Diphenyl-5-amino-1,2,3-triazole(**1a**) and 4-phenyl-5-anilino-1,2,3-triazole(**2a**) were prepared by the method of Libers;[7)] **1a**, mp 171—172 °C (lit,[7)] 169—171 °C), λ_{max}(EtOH) 268 nm (log ε 4.18), IR (KBr)(cm^{-1}) 1620(s), 1265(s); NMR (DMSO-d_6, internal TMS) δ 7.95

(m, 3H), 7.72(s, 5H), 7.32(m, 2H), 6.82(s, 2H). **2a**, mp 167—168 °C (lit,[7] 167—169 °C); λ_{max}(EtOH) 238 nm(log ε 4.24), 360 nm(sh); IR(KBr)(cm^{-1}) 1580(s); NMR (DMSO-d_6, internal TMS) δ 8.14(s, 1H), 7.94(m, 2H), 7.50(m, 4H), 7.38(s, 1H), 7.20(d, 3H), 6.90(t, 1H).

*Photolysis of 1,4-Diphenyl-5-amino-1,2,3-triazole(**1a**).* **1a**(2.0 g) in absolute ethanol(250 ml) was irradiated with a 100-W high-pressure mercury lamp for 40 h, and the reaction mixture was evaporated to yield a brown crystalline solid which was separated and analyzed by TLC.

*Photolysis of 4-Phenyl-5-anilino-1,2,3-triazole(**2a**).* **2a** (1.9 g) in absolute ethanol(200 ml) was irradiated similarly, and condensed *in vacuo* to yield brown tarry material which was analyzed by TLC.

TLC Analysis. TLC was carried out on a plate (200×200 mm) uniformly coated with Kieselgel 60PF_{254} (1 mm thickness) by using a mixture of benzene-ethyl acetate (3 : 1) as an eluant. The TLC analysis afforded three substances from the reaction mixture of **1a**(200 mg). The first (R_f=0.52) was unreacted **1a**(107 mg), the second (R_f=0.65) was **2a**(69.8 mg), and the rest (R_f=0.75) was unidentified(20.4 mg). Four substances were obtained from the reaction mixture of **2a**(200 mg). The first (R_f=0.52) and **1a**(73.2 mg), the second (R_f=0.85) (30.0 mg) was unidentified. Identification of the isolated products was done by means of comparison of UV, IR, and NMR spectra with those of authentic specimen.

Actinometry. An ethanol solution (200 ml) of **1a** (503 mg) was irradiated with a 300-W high-pressure mercury lamp, and aliquots (10 ml) were pipetted out at 2 h intervals and titrated by 0.0146 M KOH using phenolphthalein as an indicator. The final aliquot was that of 40 h irradiation.

References

1) Contribution No. 230.
2) O. Dimroth, *Ann.*, **364**, 185 (1904).
3) E. Lieber and T. S. Chao, *J. Org. Chem.*, **22**, 654 (1957).
4) E. Lieber, C. N. R. Rao, and T. S. Chao, *J. Am. Chem. Soc.*, **79**, 5962 (1957).
5) D. R. Sutherland and G. Tennant, *J. Chem. Soc., C*, **1971**, 706.
6) E. R. Brown and D. L. Hammick, *J. Chem. Soc.*, **1953**, 3280.
7) E. Lieber, T. S. Chao, and C. N. Rao, *Org. Synth.*, Coll. Vol. IV, 380 (1963).
8) R. E. Hoover and A. R. Day, *J. Am. Chem. Soc.*, **78**, 5352 (1956).
9) J. F. Ogilive, *J. Mol. Struct.*, **3**, 513 (1969).
10) E. Fahr and L. Neuman, *Ann.*, **715**, 15 (1968).
11) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin Inc., New York (1965), p. 175.
12) E. F. Ullman and S. Singh, *J. Am. Chem. Soc.*, **89**, 6911 (1967).