

PHOTOISOMERIZATION OF 2,3,6,7-TETRAPHENYL-1,2,3-TRIAZOLO[1,2-*b*]-1,2,3-TRIAZOLE

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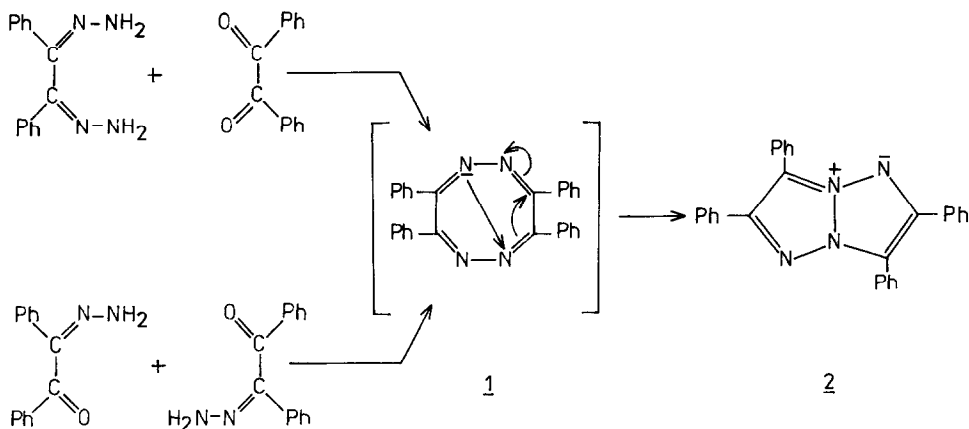
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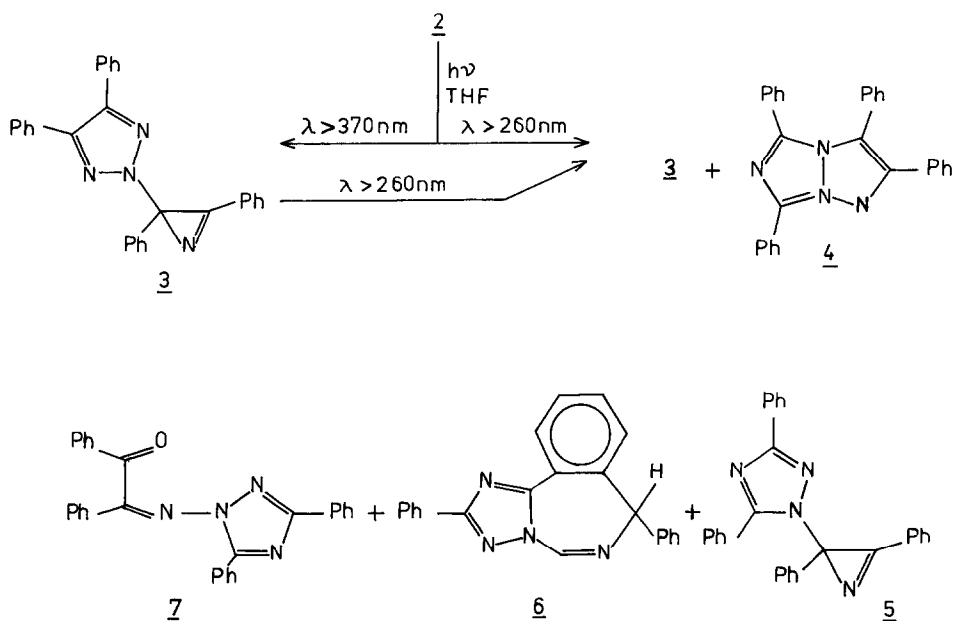
**Summary:** Irradiation of the title compound brings about consecutive photoisomerizations *via* derivatives of 1,2,3-triazolyl-2H-azirine, 1,2,3-triazolo[1,2-*a*]-1,2,4-triazole and 1,2,4-triazolyl-2H-azirine, leading finally to a dihydrotetraazabenz[*e*]azulene.

The condensation product of benzil dihydrazone with benzil<sup>2</sup>, as well as that of two molecules of benzil monohydrazone<sup>3</sup> was found by <sup>1</sup>H-NMR<sup>4</sup> and <sup>13</sup>C-NMR<sup>5</sup> to be 2,3,6,7-tetraphenyl-1,2,3-triazolo[1,2-*b*]-1,2,3-triazole (2) rather than 3,4,7,8-tetraphenyl-1,2,5,6-tetraazacyclo-octa-2,4,6,8-tetraene (1), as previously assumed by Metzger<sup>2</sup> and Schlesinger<sup>3</sup>.



The structure 2 represents a pseudoaromatic, mesoionic compound<sup>6</sup> with a conspicuous photochemical reactivity. Indeed, irradiation of 2 with  $\lambda > 370 \text{ nm}$ <sup>7</sup> leads solely to 1,2-diphenyl-1-(4,5-diphenyl-2H-1,2,3-triazol-2-yl)-2H-azirine (3) in a high yield (80-85%). By contrast, short-wave irradiation of 2 or 3 leads to a mixture of at least eight products, four of which could be isolated by column chromatography in amounts allowing spectral characterization. All the photoproducts 3 - 6 turned out to be isomers of the starting compound ( $M^+$ ,  $C_{28}H_{20}N_4$ ,  $m/z$  412 for 2 - 6). The structure of 3 was confirmed by <sup>13</sup>C-NMR spectra and chemical correlation<sup>8,9</sup>. Reduction of 3 with  $LiAlH_4$  afforded 2,3-diphenylaziridine<sup>10</sup> and 4,5-diphenyl-1,2,3-tri-

azole<sup>11</sup> which, together with <sup>13</sup>C signals of the heterocyclic quaternary carbons (164.48, 136.23 and 57.20) gave conclusive evidence for the connection of the triazole and 2H-azirine rings. Irradiation of 3 gave rise to 2,3,5,7-tetraphenyl-1,2,3-triazolo[1,2- $\alpha$ ]-1,2,4-triazole (4), the structure of which was inferred from the <sup>13</sup>C-NMR (147.69s, 108.71s) and mass spectra [ $m/z$  384, (M-N<sub>2</sub>)<sup>+</sup>]. On standing in tetrahydrofuran solution, 4 was slowly oxidized by air to benzil derivative 7 (M<sup>+</sup>, C<sub>28</sub>H<sub>20</sub>N<sub>4</sub>O,  $m/z$  428)<sup>8</sup>. Further photocleavage of the 1,2,3-triazole ring in 4 led to 1,2-diphenyl-1-(3,5-diphenyl-1H-1,2,4-triazol-1-yl)-2H-azirine (5). The presence of the 1,2,4-triazole and 2H-azirine rings in 5 was inferred from the <sup>13</sup>C-NMR spectra<sup>8</sup> and confirmed by LiAlH<sub>4</sub> reduction which yielded 3,5-diphenyl-1,2,4-triazole<sup>12</sup> and *cis*-2,3-diphenylaziridine<sup>10</sup>. The final, photostable product of the isomerization of 2 was identified by <sup>1</sup>H- and <sup>13</sup>C-NMR spectra<sup>8</sup> as 3a,6-dihydro-2,4,6-triphenyl-1,3,3a,5-tetraazabenz[e]azulene (6).

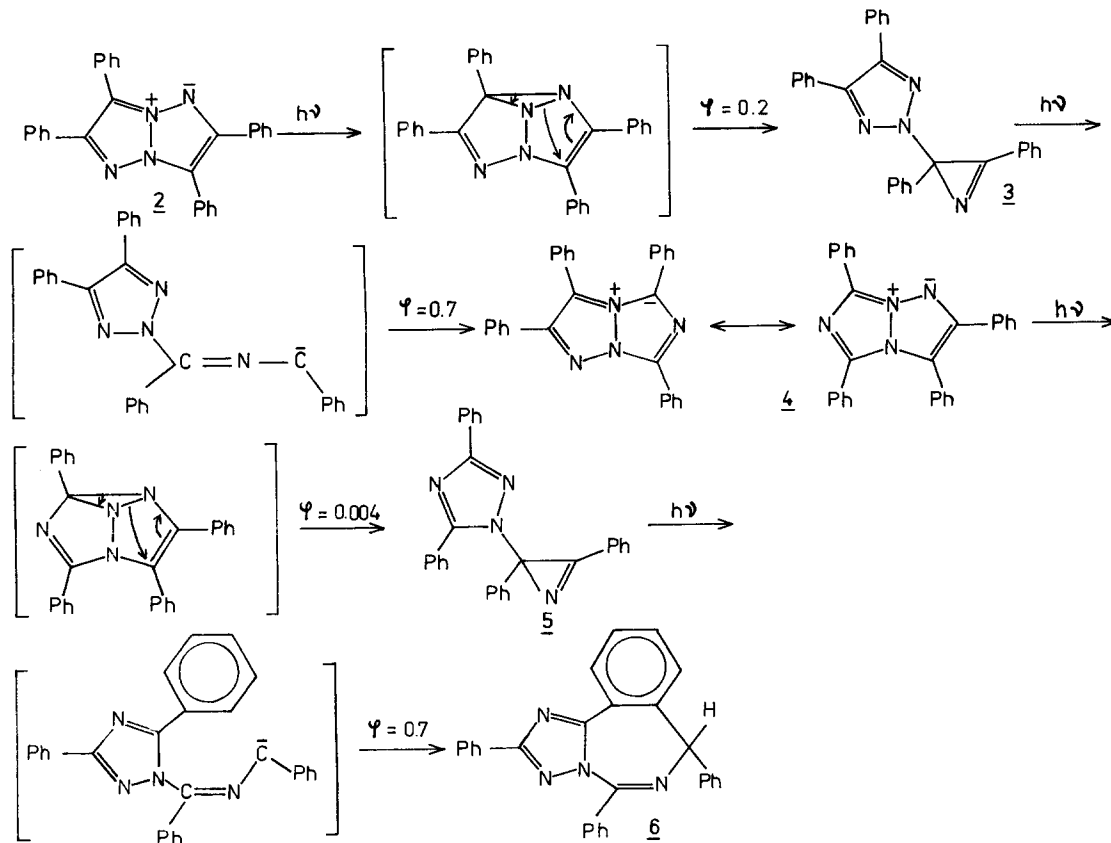


The relative yields of the photoproducts depended on experimental conditions: irradiation with  $\lambda > 270\text{ nm}$  of a clear solution of 2 in THF for 3 hours gave 3, 4, 5 and 6 in 4.5, 7.5, 23 and 30%, respectively. Analogous irradiation of a suspension of 2 in THF led to preferential formation of the intermediate photoproducts (6.3, 23, 27.5 and 7.5% of 3, 4, 5 and 6, respectively).

The reaction course of the photoisomerizations of 2, 3, 4 and 5 was investigated in detail by UV spectroscopy. The changes in transmission at longer wavelengths<sup>13</sup> were monitored in dependence on the irradiation time and wavelength. It appears from these kinetic measurements that the particular photoisomerization steps are very clean, proceeding without apparent side reactions. The tetraazabenz[e]azulene 6 was found to be the final product in all cases. The available spectroscopic parameters ( $\lambda_{\text{max}}$ ,  $\epsilon_{\text{max}}$ ,  $\tau_{\text{fl}}$ ) indicate that the observed transitions are of

the  $S_1(\pi, \pi^*)$  type. This is corroborated by observation that no transient species were found to exist in the nanosecond (fluorescence) or microsecond (absorption) region.

The sequence of the photoproducts, as determined from the kinetic measurements, is shown below, together with the proposed mechanisms depicting the bond reorganization in 2 - 5.



#### References and notes

1. This study has been started some years ago at MPI für Strahlenchemie, Mülheim/Ruhr, FRG. J.K. is grateful to the Max Planck Society for fellowship. The cooperation of the late Dr. H. Partale and valuable advices of Prof. O.E. Polansky at the beginning of this study are gratefully acknowledged.
2. R. Metzke, *Angew. Chem.*, 68 (1956) 581.
3. H. Schlesinger, *Angew. Chem.*, 72 (1960) 563.
4. J. Leitich, MPI f. Strahlenchemie Mülheim/Ruhr (FRG), personal communication.
5.  $^{13}\text{C}$ -NMR (DMSO- $d_6$  + dioxane, 80°C): 131.16s, 128.76, 128.45, 128.40 (> 2C), 127.66, 127.05, 126.27s.
6. This class of compounds has been reviewed: Ch.A. Ramsden, *Tetrahedron*, 33 (1977) 3220.
7. The irradiations were carried out in an immersion photochemical reactor (F. Liška, V. Dědek, J. Kopecký, J. Mostecký and A. Dočkal, *Chem. Listy*, 72 (1978) 637) with a GWV ( $\lambda > 370$  nm) or Solidex ( $\lambda > 260$  nm) filter. Nitrogen was passed through the reaction mixture (15 min.) prior to irradiation with a high-pressure mercury lamp (Tesla RVK 125 W) at 22 to 25°C.

8. 3: m.p. 194-194.5°C; <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 40°C): 164.48s, 144.78s, 136.23s, 134.58d, 130.26d, 130.05s, 129.73d, 128.59d (2C), 128.47d, 128.16d, 127.92d, 125.78d, 121.07s, 57.20s;
  - 4: m.p. 192-193°C, <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 40°C): 147.69s, 131.06s, 130.78d, 128.63d, 128.61d, 128.38d, 128.28d, 128.10d, 127.83d, 127.76d, 127.53d, 127.28d, 127.19s, 127.05s, 126.84s, 126.62s, 124.64d, 108.71s;
  - 5: m.p. 142-143°C; <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 40°C): 164.90s, 160.56s, 156.02s, 137.02s, 134.97d, 130.78s, 130.55d, 130.25d, 129.91d, 129.69d, 128.85d, 128.62d, 128.45d, 128.09d, 127.17s, 126.07d, 124.81d, 120.68s, 53.92s;
  - 6: m.p. 223-224°C; <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 40°C): 171.78s, 160.01s, 152.70s, 139.70s, 135.60s, 133.08s, 131.55d, 131.31d, 130.62s, 130.52d, 129.48d, 129.22d, 129.03d, 128.71d, 128.46d (2C), 128.29d, 128.06d, 127.95d, 125.81d, 73.32d;
  - 7: m.p. 142-143°C; <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 23°C): 193.79s, 157.84s, 157.43s, 152.89s, 135.96s, 133.69d, 132.99s, 131.65d, 130.54d, 130.47d, 129.93s, 129.78d, 129.57d, 129.02d, 128.97d, 128.60d, 128.52d, 128.31d, 128.02d, 126.51d.
9. K. Isomura, H. Taniguchi, M. Mishima, M. Fujio and Y. Tsuno, *Org. Mag. Res.*, 9 (1977) 559.
  10. H.E. Baumgarten and J.M. Petersen, *J. Amer. Chem. Soc.*, 82 (1960) 459-463.
  11. R. Stollé, E. Münch and W. Kind, *J. prakt. Chem.*, 70 (1904) 440.
  12. H. Wolchowe, *Monatsh. Chem.*, 37 (1916) 473.
  13. The kinetic studies were carried out on a Specord UV spectrometer (Carl Zeiss, Jena, GDR) using a high-pressure mercury lamp HBO 101 (Narva, GDR) with a monochromator GM 100-1 (Schoeffel Instrument, U.S.A.) for illumination. The quantum yields were determined using the ferrioxalate actinometer<sup>14</sup>.
  14. C.A. Parker and C.G. Hatchard, *Proc. Roy. Soc., Ser. A* 235 (1956) 518.

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