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Thermal and Photochemical Decompositions of 4,5,6,7-Tetrahydro-1,2,3-benzotriazole Analogues

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In our previous paper[1] we reported that the photolysis of various benzotriazoles gave products different from those of the thermal decompositions. Burgess and his co-workers have observed that both the thermal and photochemical decompositions of monocyclic 1,2,3-triazoles give 1,3-biradical intermediates which undergo the Wolff rearrangement to give the same ketenimine.[2] We wish now to report that the thermolysis and photolysis of 4,5,6,7-tetrahydro-1,2,3-benzotriazole analogues give the cyclized and the ring-contracted products in different ratios.

Results and Discussion

In the thermolysis of 1-phenyl-4,5,6,7-tetrahydrobenzotriazole (I), a preparative flash thermolysis apparatus was used at a pressure below 0.01 mmHg; the vapor of I was passed through a quatrz tube (10 mm diam.) at 590—630 °C. The thermolyzed mixture collected in a trap cooled by liquid nitrogen was column-chromatographed on silica gel to give 1,2,3,4-tetrahydrocarbazole (II) and cyclopentanecarboxanilide (III) in yields of 17 and 20% respectively.

The ring-contracted product (III) must be formed through a ketenimine (IV), followed by the addition of water in the course of separation. When the reaction was carried out in an atmosphere of dry nitrogen, the reaction mixture showed an IR absorption[3] at 2020 cm^{-1}. The intensity of the absorption decreased when the mixture was allowed to stand in the air for several minutes. This fact suggests that the ketenimine (IV) must be present as an intermediate.

Similarly, the thermolysis of 1-phenyl-4,5,6,7-tetrahydrocyclohepta[*d*]-1,2,3-triazole (V) gave an indole

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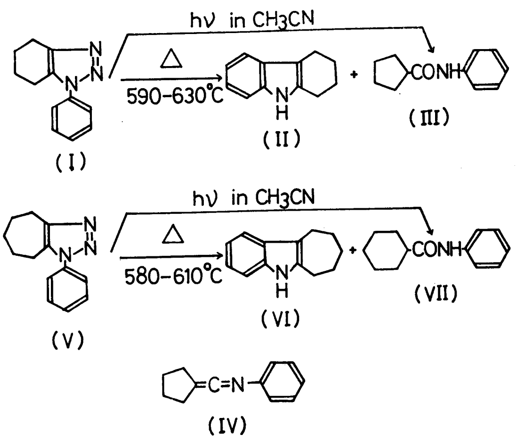
[1] K. Tsujimoto, M. Ohashi, and T. Yonezawa, This Bulletin, **45**, 515 (1972).

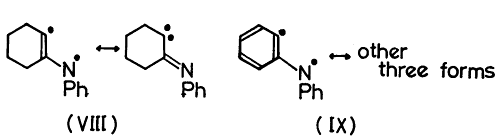
[2] E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, **90**, 1923 (1968).

[3] C. L. Stevens and L. C. French, *ibid.*, **75**, 657 (1953).

derivative (VI) and cyclohexanecarboxanilide (VII) in yields of 25 and 29% respectively. Again, the strong absorption at 2000 cm^{-1} in the IR spectrum of the reaction mixture suggested the presence of the ketenimine intermediate.



On the other hand, the photolysis of I in acetonitrile by means of a low-pressure mercury arc gave III as the major product (62% yield), along with a trace amount of II (less than 5%). The irradiation of a solution of I in benzene also gave III in a 25% yield, but no cyclized product was obtained. Similarly, the irradiation of V in acetonitrile afforded VII as the major product. From these results it became clear that the photolyses of 4,5,6,7-tetrahydro-1,2,3-benzotriazole analogues produce mainly their corresponding ring-contracted products, while their thermolyses give both the cyclized and the ring-contracted products in nearly the same yield. These results imply that the thermally- and the photochemically-generated intermediates have either (i) a different electronic configuration from each other or (ii) the same configuration giving different products in the succeeding dark reactions depending on the reaction environment. Such a behavior as (ii) is frequently observed in the photo-induced decarbonylation of carbonyl compounds.[4] Since, as was demonstrated in our previous paper,[1] the electronic configuration of a 1,3-biradical intermediate such as IX is sensitive to the environment, at this stage we can not judge which one of these two cases has actually occurred in the reactions.



The thermolysis[5] and the photolysis[2] of 1-phenyl-1,2,3-benzotriazole give the same cyclized product quantitatively. The difference in the behavior of the intermediates, VIII and IX, can be explained in terms of the reactivity of the carbene-like character for the Wolff rearrangement;[6] the reactivity of IX is smaller because of the delocalization of the unpaired π-electron on the nitrogen.

Experimental

All the melting points were determined on a micro hot stage and are not corrected. The IR and mass spectra were measured using a Hitachi Model 215 grating spectometer and a double-focussing mass spectrometer (Model JMS-01SG) respectively. The NMR spectra were obtained on a Varian HR-220 spectrometer, using TMS as the internal standard. The starting materials, I and V, were prepared by means of Fusco's method.[7] The pure samples of both I and V were obtained by crystallization from ligroin. A quartz tube (10 mm diam.) was used for the preparative flash vacuum thermolysis at a pressure below 0.01 mmHg and at a temperature of about 600 °C.

1-Phenyl-4,5,6,7-tetrahydrobenzotriazole (I): mp 116.0—116.5 °C (lit: 116 °C)[7].

1-Phenyl-4,5,6,7-tetrahydrocyclohepta[d]*-1,2,3-triazole (V)*: mp 115.8—116.1 °C (lit: 113 °C)[7].

Thermolysis of 1-Phenyl-4,5,6,7-tetrahydrobenzotriazole (I): I (122 mg) was thermolyzed at 590—630 °C (below 0.01 mmHg). The pyrolyte (90 mg) was column-chromatographed on silica gel (20 g, Mallinckrodt, AR-100, 100 mesh). Elution with dichloromethane gave II(17 mg), a tarry material(4 mg), and III(22 mg). II was identified as tetrahydrocarbazole by a comparison of its IR spectrum with that of an authentic specimen. The mixed melting point of these compounds showed no depression. III was a solid which had an mp of 159—160 °C (lit: 159—160 °C)[7]: M$^+$: 189.117 (calculated for $C_{12}H_{15}NO$ 189.115); NMR ($CDCl_3$) δ 1.5—2.0 (8H, m), 2.68 (1H, quintet, $J=1.5$ Hz), 4.84 (1H, br. s) and 7.1—7.6 (5H, m) ppm; IR (KBr) 3200 (ν NH), 1650 (amide ν C=0), 1540 (δ NH) and 750 (phenyl ring) cm^{-1}. Cyclopentanecarboxanilide was prepared from cyclopentanecarboxylic acid chloride and aniline. Its IR spectrum coincided with that of III. The mixed melting point showed no depression.

Thermolysis of 1-Phenyl-4,5,6,7-tetrahydrocyclohepta[d]*-1,2,3-triazole (V)*. V (123 mg) was thermolyzed at 580—610 °C as has been described above. The reaction mixture (90 mg) was column-chromatographed on silica gel, 7 g (Mallinckrodt, AR-100, 100 mesh). Elution with dichloromethane then gave VI(23 mg), VII(32 mg), and 27 mg of a tarry material. VI was identified as 5,6,7,8,9,10-hexahydrocyclohepta[*d*] indole on the basis of the following information: M$^+$: 185.116 (185.120 calculated for $C_{13}H_{15}N$); IR (KBr) 3400 (ν NH), 740 (phenyl ring) cm^{-1}; NMR ($CDCl_3$) δ 1.68—1.93 (6H, m), 2.80 (4H, s), 7.05—7.50 (4H, m) and 7.68 (1H, br. s) ppm. VII had an mp of 145.5—146.3 °C after recrystallization from ligroin. The spectral data are shown below: M$^+$: 203.127 (203.131 calculated for $C_{13}H_{17}NO$); IR (KBr) 3320 (ν NH), 1660 (ν C=O) and 730 (phenyl ring) cm^{-1}. The IR spectrum of VII coincided with that of cyclohexanecarboxanilide, which had been synthesized by the reaction of cyclohexanecarboxylic acid chloride with aniline.

Photolysis of 1-Phenyl-4,5,6,7-tetrahydrobenzotriazole (I) in Acetonitrile. A solution of I (123 mg) in 80 ml of purified acetonitrile was irradiated by means of a 5-W low-pressure

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[4] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, Amsterdam (1965), p. 224.

[5] S. G. P. Plant and J. F. Powell, *J. Chem. Soc.*, **1947**, 937.

[6] M. Jones, Jr. and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968).

[7] R. Fusco, G. Bianchetti, and D. Pocar, *Gazz. Chim. Ital.*, **91**, 849 (1961).

mercury arc lamp for 2 hr. After the removal of the solvent, the reaction mixture was column-chromatographed on silica gel. Elution with dichloromethane gave 17 mg of III, and further elution with ethyl acetate gave 94 mg of the unreacted material. III was identified as cyclopentanecarboxanilide by the method which has been described above.

Photolysis of 1-Phenyl-4,5,6,7-tetrahydrobenzotriazole (I) in Benzene. A solution of I (198 mg) in benzene (80 ml) was irradiated with a 100-W high-pressure mercury arc lamp for 10 hr. After the solvent had then been removed *in vacuo*, the residue was column-chromatographed on silica gel. Elution with dichloromethane gave 22 mg of III. The starting material (100 mg) was recovered by elution with ethyl ether. The tarry materials were not identified. A gas chromatograph of the reaction products did not exhibit the presence of tetrahydrocarbazole.

Photolysis of 1-Phenyl-4,5,6,7-tetrahydrocyclohepta[d]*-1,2,3-triazole (V) in Acetonitrile.* An acetonitrile solution (80 ml) of 122 mg of V was irradiated with a 5-W low-pressure mercury arc lamp for 3 hr under a stream of nitrogen gas. After the solvent had then been removed *in vacuo*, the reaction mixture was column-chromatographed on silica gel. Elution with dichloromethane gave 2 mg of an unidentified material, 22 mg of VII, 54 mg of the starting material, and 38 mg of a tarry product. The VII was identified as cyclohexane carboxanilide by a comparison of its spectrum with that of an authentic specimen which had been prepared by the reaction of cyclohexanecarboxylic acid chloride with aniline.