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COMPETING PATHWAYS IN THE PHOTODENITROGENATION OF A 3,5-DIHYDRO-4*H*-1,2,3-TRIAZOL-4-ONE. A NOVEL ROUTE TO AZIRIDINONES [1]

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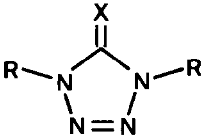
SUMMARY: The photodenitrogenation of the 3,5-dihydro-4*H*-1,2,3,-triazol-4-one **6**, obtained from 1-azidoadamantane (**5**) and the lithium enolate of methyl isobutyrate, produced acetone, the isocyanide **10** and the aziridinone **7**, which was solvolysed to the α-methoxy amide **8** during photolysis in [D_4]methanol.

The photoextrusion of nitrogen from the dihydrotetrazole derivatives **1a** - **c** [2] and the dihydropyrazoles **2b** - **d** [3] afforded heteromethylenecyclopropanes. On photolysis of **1b** in a matrix at 77 K triplet trisiminomethane diradicals have been identified by ESR spectroscopy [4]. Therefore, it seemed highly desirable to study the photochemistry of similar dihydro-1,2,3,-triazoles **3** which may be regarded as a formal interstice between the dihydrotetrazoles **1** and dihydropyrazoles **2**. Here we report the results of the photolysis of the 3,5-dihydro-4*H*-1,2,3-triazol-4-one **6**.



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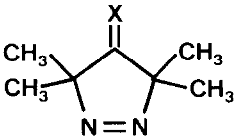

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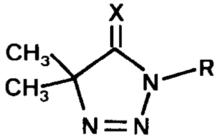

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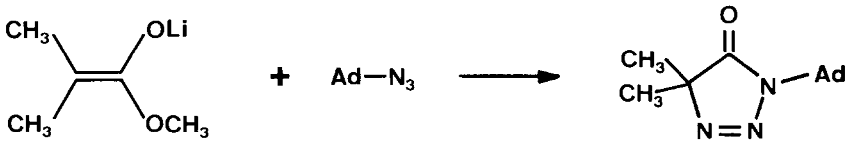
1a - **3a**: X = CR_2; **1b** - **3b**: X = NR; **1c** - **3c**: X = O; **1d** - **3d**: X = S. R = alkyl.

The 3,5-dihydro-4*H*-1,2,3-triazol-4-one system is known since 1958 [5]. Its 5,5-diphenyl derivative has been utilized for the formation of poly-α,α-diphenylglycine [6]. Recently this system was rediscovered by Trost and Pearson, who prepared a new example from the lithium enolate of methyl isobutyrate (**4**) and azidomethyl phenyl sulfide [7]. Since enolates of ketones react smoothly with relatively unreactive alkyl azides, e. g. methyl and benzyl azide, to yield 3,5,-dihydro-4*H*-1,2,3,-triazoles [8], formation of **6** in the reaction between the lithium enolate **4** and 1-azidoadamantane (**5**) [9, 10] could be anticipated.



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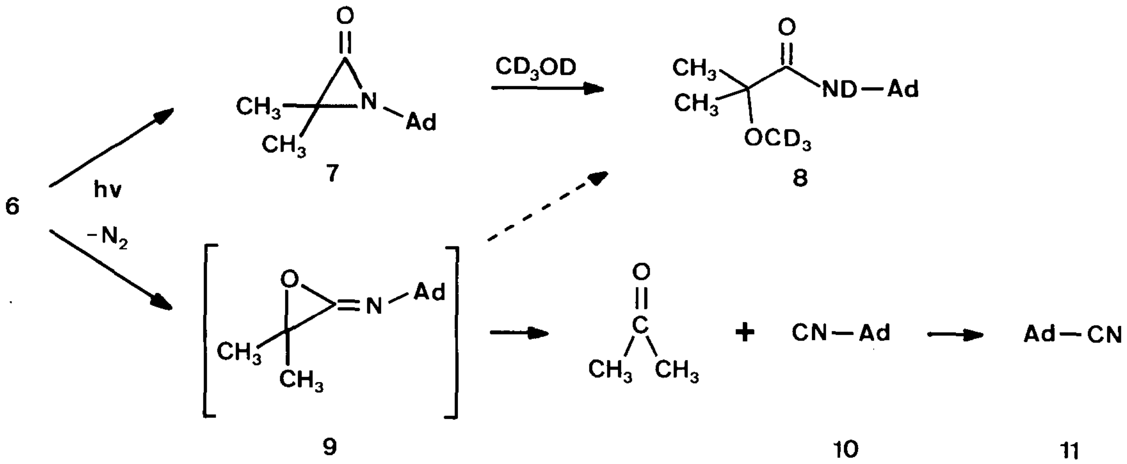
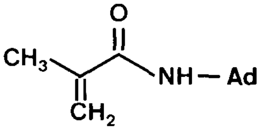
Thus, when a solution of **5** in tetrahydrofuran was added at -78 °C to a suspension of 1.05 moles of **4** in hexane (prepared from lithium diisopropylamide and methyl isobutyrate), after 3 h at room temperature the usual work-up including sublimation and recrystallization from pentane at -20 °C yielded 70 % of **6** as colorless crystals melting at 74 °C with decomposition. The structure **6** was based on elemental analysis and spectra: MS (70 eV): *m/e* = 219 (6 %, M-N_2), 204 (1, M-N_2, -CH_3), 191 (2, M-N_2, -CO), 162 (12), 135 (100, $C_{10}H_{15}$). IR (CCl_4): 1730 cm^{-1} (C=O). UV (hexane): λ_{max} (lg ϵ) = 251 (3.663), 309 (2.492). ^1H NMR (C_6D_6): δ = 1.18 (s, 2 CH_3), 1.4 - 1.6, 1.8 - 2.1, 2.2 - 2.4 (m, adamantyl). ^{13}C NMR: Table 1. In the dark, a benzene solution of **6** is perfectly stable at room temperature; however, in [D_4]methanol solution, 7 % of **6** had been decomposed at 22 °C after 18 h.

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When a solution of **6** in dry benzene was irradiated with a Hg or Hg/Xe high pressure lamp [3] (15 °C, Pyrex filter), nitrogen was smoothly evolved. The sample remained clear and colorless up to quantitative conversion (4.5 h), which was followed by IR and ^1H NMR spectroscopy. The photolysis products acetone, isocyanide **10**, and small amounts of the nitrile **11** were readily identified by their IR, ^1H NMR and ^{13}C NMR spectra. A 4 : 1 mixture of the isocyanide **10** [12] and nitrile **11** [13] was isolated in 41 % yield after evaporation of the solvent and sublimation of the residue at 70 °C/20 Torr. A third primary photolysis product, formed in approximately the same amount as acetone, exhibited a strong IR band at 1848 cm^{-1} (characteristic for aziridinones[11]) and a singlet at 1.26 ppm in the proton spectrum together with the adamantane multiplets. This compound was very sensitive towards traces of moisture, affording a product with amide absorption at 1685 cm^{-1}. Therefore, we assign it the aziridinone structure **7**. The aziridinone **7** had previously been obtained by 1,3-dehydrobromination of the corresponding α-bromo amide with potassium *tert*-butoxide in ether [14]. The unsaturated amide **12** [15], prepared from methacrylic acid chloride and 1-aminoadamantane (Table 1), could not be detected among the photolysis products.

In order to confirm the aziridinone structure **7**, the main photolysis product, we photolysed the dihydrotriazolone **6** in [D_4]methanol which affords an α-methoxy amide [11] via solvolysis of an aziridinone under neutral conditions. Besides small amounts of acetone (^1H NMR) and the corresponding amount of the isocyanide **10** (IR, ^{13}C NMR) the α-methoxyamide **8** was indeed obtained as the only other photolysis product. Its structure was based on IR, ^1H NMR and ^{13}C NMR spectra (Table 1). A 17:83 ratio of acetone : α-methoxyamide **8** was determined from the proton spectrum of the irradiated solution.

Aziridinones are photodecarbonylated only upon 254 nm irradiation in quartz equipment thereby producing imines [16]. As expected, **7** was photostable under the conditions of its formation (photoextrusion of nitrogen from **6**). Acetone and the isocyanide **10** most probably arose by [2+1]cycloelimination of the oxiranimine **9**. Such compounds have been invoked as thermally labile intermediates in the thermolysis of aziridinones furnishing isocyanides and carbonyl compounds [11]. Therefore, we irradiated a solution of **6** in [D_8]toluene at -57 °C. However, after 12 h the low temperature proton spectrum showed a quantitative conversion into acetone and the aziridinone **7** (1 : 1), but no signals corresponding to thermally labile intermediates such as **9** were detected.

In order to exclude the possibility of sensitization by benzene, **6** was irradiated in hexane as solvent. Essentially the same results as in benzene solution were obtained, except the aziridinone **7** was only moderately photostable and the isocyanide **10** was rearranged into the nitrile **11** [17]. Furthermore, irradiation of a benzene solution of **6** with the 351 nm line of an argon ion laser [18] neither changed the type of products nor the ratio of acetone vs. aziridinone **7**. The latter experiment also excludes any participation of the acetone formed during the photolysis. Therefore, we conclude that the photoextrusion of nitrogen occurs from the excited singlet state of **6**. We are presently extending our studies to other dihydrotriazolones **3c** and the as yet unknown 3,5-dihydro-4*H*-1,2,3-triazoles **3a**, **3b**, and **3d**.

Table 1. ^{13}C NMR data of some 1-substituted adamantanes in [D_6]benzene solution. The assignments are based on single frequency off resonance experiments and the comparison with the carbon-13 spectra of other 1-substituted adamantanes [19].

					1-adamantyl			
	CH_3	C—C=O		other C	α-C	β-CH_2	γ-CH	δ-CH_2
6	21.4	77.3	179.5	–	58.4	40.5	29.7	36.2
10	–	–	–	154.7[a](-NC)	53.8[a]	43.6	28.9	35.4
8[b]	23.5	79.6	176.7	–	52.4	42.5	31.0	37.5
12[c]	19.0	117.5	167.4	142.5(=CH_2)	51.7	41.7	29.9	36.7

[a] (1 : 1 : 1)-Triplet. – [b] In [D_4]methanol solution. – [c] M.p. 96 - 98 °C; IR (CCl_4): 1674 (C=O), 1639 cm^{-1} (C=C).

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REFERENCES AND FOOTNOTES

(1) Photochemical Formation of Methylenecyclopropane Analogues, 7. Paper 6 of this series: Quast, H.; Fuß, A. *Isr. J. Chem.* **1982**, *22*, 31. The results are taken from the prospective dissertation of B. S.

(2) Quast, H.; Bieber, L. *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 428.

(3) Quast, H.; Fuß, A., Heublein, A. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 49. Quast, H., Fuß, A. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 291.

(4) Quast, H.; Bieber, L.; Danen, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1306.

(5) Hohenlohe-Oehringen, K. *Mh. Chem.* **1958**, *89*, 557, 562, 597.

(6) Ikeda, K.; L'abbé, G.; Smets, G.; Delvaux, M. C. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1167. Ikeda, K.; Smets, G.; L'abbé, G. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1177.

(7) Trost, B. M.; Pearson, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 2483.

(8) Olsen, C. E.; Pedersen, C. *Tetrahedron Lett.* **1968**, 3865; *Acta Chem. Scand.* **1973**, *27*, 2271, 2279. Olsen, C. E. *Acta Chem. Scand.* **1973**, *27*, 1987.

(9) Quast, H.; Eckert, P. *Liebigs Ann. Chem.* **1974**, 1727.

(10) For 1,3-dipolar cycloaddition reactions of 1-azidoadamantane to strained or electron deficient alkenes see: Sasaki, T.; Eguchi, S.; Yamaguchi, M.; Esaki, T. *J. Org. Chem.* **1981**, *46*, 1800.

(11) Lengyel, I.; Sheehan, J. C. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 25. Boyd, G. V., in *Supplement B, The Chemistry of Acid Derivatives, Part. I*, Patai, S., ed., Wiley, New York 1979, p. 518.

(12) Sasaki, T.; Eguchi, S.; Katada, T. *J. Org. Chem.* **1974**, *39*, 1239. An authentic sample was kindly provided by Dr. D. Marquarding, Organisch-chemisches Institut der Technischen Universität München, D-8046 Garching.

(13) Owens, P. H.; Gleicher, G. J.; Smith, L. M., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4122.

(14) Stetter, H.; Mayska, P.; Wießner, U. *Neue Synthesen und Reaktionen in der Adamantan-Reihe, Forschungsbericht des Landes Nordrhein-Westfalen Nr. 3095*, Westdeutscher Verlag, Opladen 1982.

(15) Analogous unsaturated amides arose from 3,3-dimethylaziridinones already in refluxing ether [11].

(16) Sheehan, J. C.; Nafissi-V, M. M. *J. Am. Chem. Soc.* **1969**, *91*, 1176. Talaty, E. R.; Dupuy, A. E., Jr.; Golson, T. H. *Chem. Commun.* **1969**, 49.

(17) Maloney, K. M.; Rabinovitch, B. S., in *Isonitrile Chemistry*, Ugi, I., ed., Academic Press, New York 1971, p. 62.

(18) Argon Ion Laser Coherent CR 18 S 6.

(19) Pehk, T.; Lippmaa, E.; Sevostjanova, V. V.; Krayuschkin, M. M.; Tarasova, A. I. *Org. Magn. Reson.* **1971**, *3*, 783. Ajisaka, K.; Kainosho, M. *J. Am. Chem. Soc.* **1975**, *97*, 330. Maciel, G. E.; Dorn, H. C.; Greene, R. L.; Kleschik, W.A.; Peterson, M. R., Jr.; Wahl, G. H., Jr. *Org. Magn. Reson.* **1974**, *6*, 178. Duddeck, H.; Hollowood, F.; Karim, A.; McKervey, M. A. *J. Chem. Soc., Perkin Trans. 2* **1979**, 360.

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