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PHOTOLYSIS OF A 2-TETRAZENE FROM AN ENEHYDRAZINE

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Abstract: Photolysis of the 2-tetrazene 1 gives the triazole 2 by homolysis of one single N,N-bond. The formation of the other products 4 - 13 can be rationalized by regarding the aza-allyl radical 3 as a common precursor.

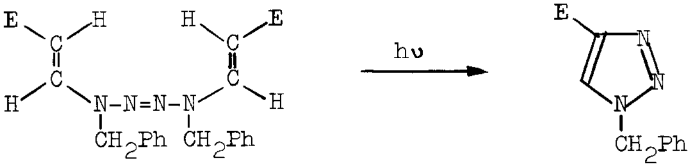
Both, thermolyses[1,2] and photolyses[3] of tetrasubstituted 2-tetrazenes give molecular nitrogen and disubstituted amino radicals. Gowenlock, Jones and Snelling[4] describe the thermolysis of tetramethyl-2-tetrazene as a concerted fragmentation (equ. 1, $R^1 = R^2 = CH_3$):

$$R^1R^2N\text{-}N{=}N\text{-}NR^1R^2 \longrightarrow 2\ R^1R^2N\cdot \ + \ N_2 \qquad (1)$$

$$\searrow \ R^1R^2N\text{-}N{=}N\cdot \ + \ \cdot NR^1R^2 \ \nearrow \qquad (2)$$

Little attention has so far been paid to a possible two-step-mechanism (equ. 2) which Sugiyama e.a. postulate for the photolysis of aromatic 2-tetrazenes, based on the linear dependence of the rate constants upon the viscosity of the reaction medium.[5]

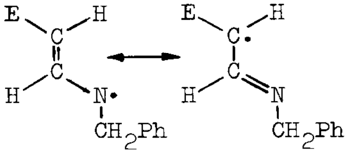
We can now present preparative evidence for the homolysis of a single N,N-bond during photolysis of the 2-tetrazene 1[6] giving methyl 1-benzyl-1,2,3-triazolecarboxylate 2, though in low yield (2%, m.p. 104°C, 5-H s 8.05 ppm), when 1 is irradiated for 6 min in CH_2Cl_2 with

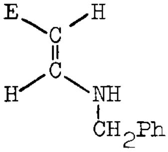


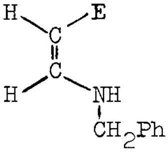
$E = CO_2CH_3$ 1 2

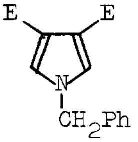
a Philips HPK 125 W lamp. The structure of 2 was independently secured by a cycloaddition between methyl propiolate and benzylazide furnishing also small amounts of the isomeric 5-carboxylate (m.p. 44°C, 4-H s 8.12).

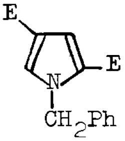
Other products of the photolysis are the diastereomeric enamines 4 and 5[7] (5%, 1:1) resulting from hydrogen abstraction by the primarily formed aza-allyl radical 3, and the







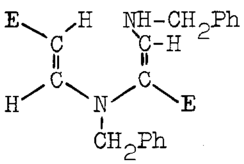




$E = CO_2CH_3$ 3 4 5 6 7

pyrroles 6[8] (1%, rising to 9% upon longer irradiation, m.p. 64-66°C) and 7 (2%, rising to 12% upon longer irradiation, m.p. 99°C, 3,5-H d 7.40, d 7.44 [J = 2 Hz]).

The diastereomeric enamines 8 (10%, oil, vinyl-H d 4.78, d 7.60 [J = 13.5 Hz], d 7.40 [J_{NH} = 5 Hz]) and 9 (11%, oil, vinyl-H d 4.75, d 7.68 [J = 13.5 Hz], d 6.40 [J_{NH} = 14.5 Hz], NH 7.8 - 8.1 ppm) and the enamine 10[9] (4%, m.p. 106-107°C) are no precursors for either 6 or 7, but the bis-enamine 11 (probable configuration 1%, m.p. 168-170°C, vinyl-H 7.59 [J_{NH} = 14 Hz]) may be an intermediate to 6 and to the aminopyrrole derivatives 12 (1%, oil, 5-H 6.89) and 13 (1%, m.p. 109-111°C, N=CH s 8.80, 5-H covered by phenyl).



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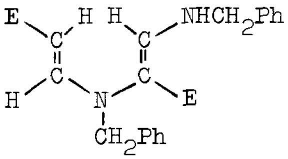

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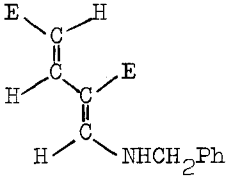

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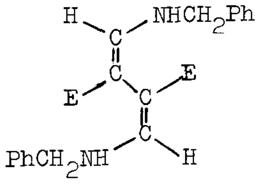

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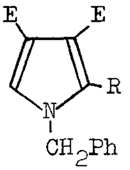

12 R = $NHCH_2Ph$
13 R = N=CHPh

E = CO_2CH_3

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