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THERMAL AND PHOTOCHEMICAL DECOMPOSITIONS OF 1,4-BIS(AZIDOMETHYL)-1,4-DIPHENYLAZINEMETHYLENE[1)]

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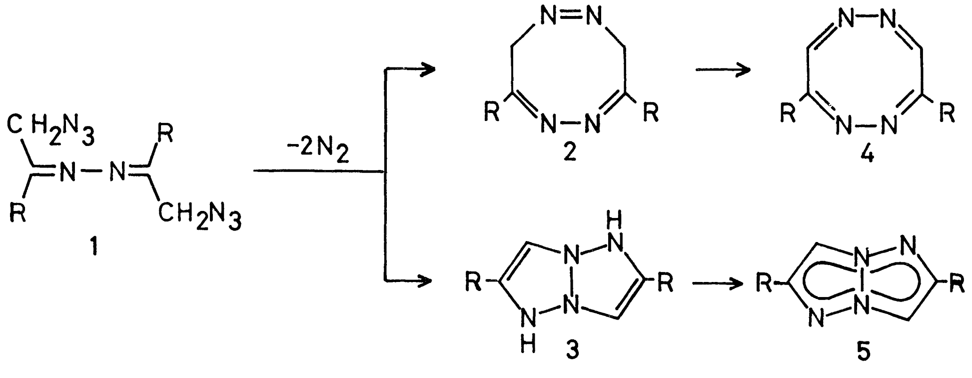
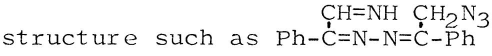
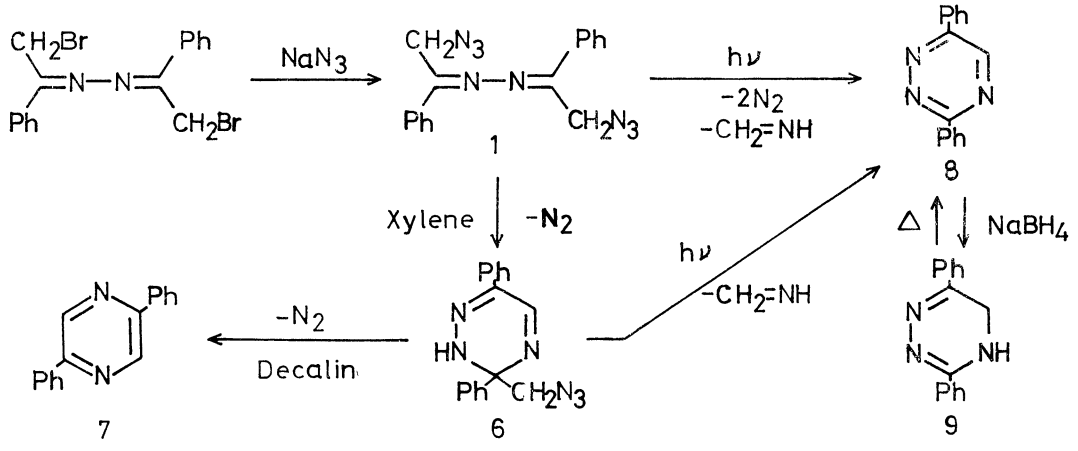
Thermal decomposition of bisazide 1 in refluxing xylene afforded monoazide 6, which on heating in decaline under reflux converted into pyrazine 7. On the other hand, irradiation of 1 gave 1,2,4-triazine 8, which was obtained in excellent yield from photolysis of monoazide 6. The pathways for the formation of products are also suggested.

Hitherto numerous investigations have been reported on thermal and photochemical decompositions of azides of various types.[2)] Decomposition of a new bisazide, 1,4-disubstituted 1,4-bis(azidomethyl)azinemethylene (1), might lead to the formation of dihydro-1,2,5,6-tetraazacyclooctatetraene 2 or 1,2,3-triazolo[3,2-b]-1,2,3-triazole 3, which would be a presursor of tetraazacyclooctateraene 4 or tetraazapentalene 5, [3,4)] respectively. In this paper we wish to report on the preparation of bisazide 1 (R=Ph), and its thermal and photochemical decompositions.



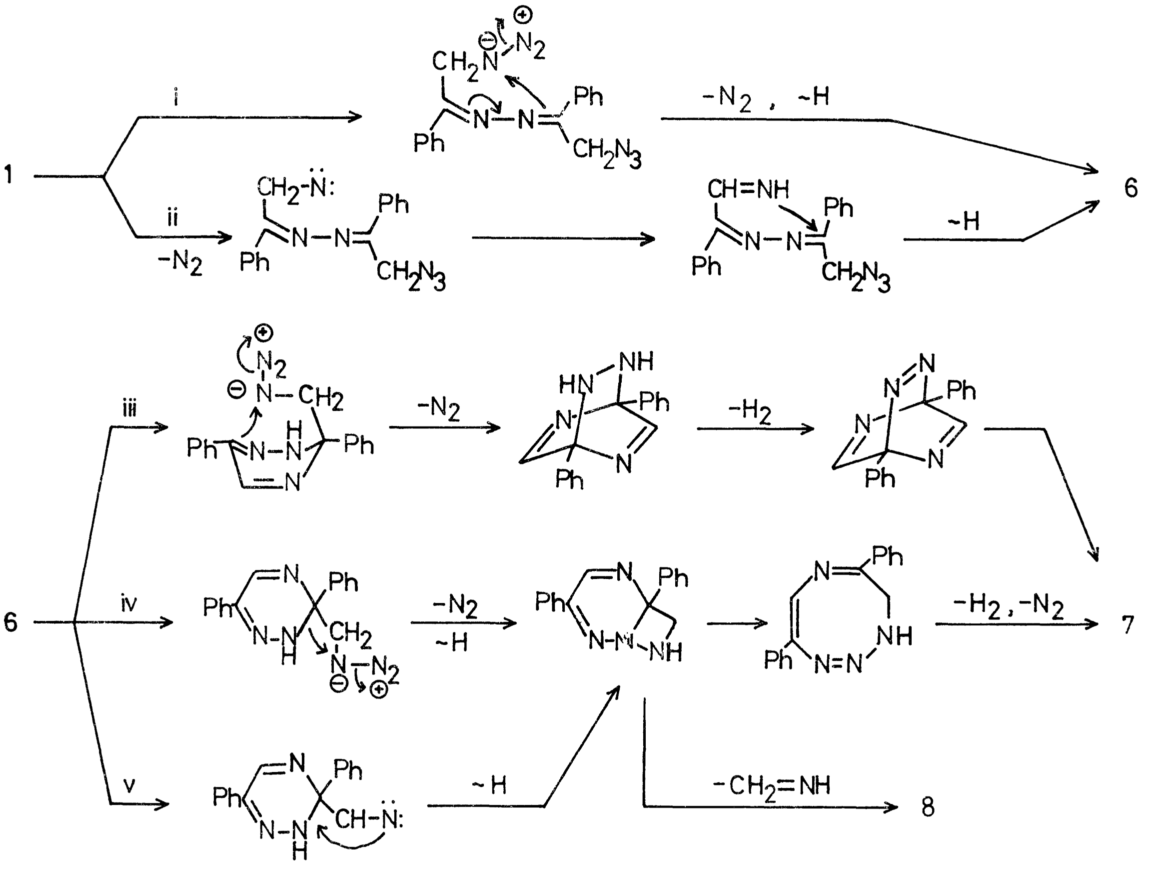
The reaction of 1,4-bis(bromomethyl)-1,4-diphenylazinemethylene[5)] with sodium azide in refluxing methanol for 30 min afforded bisazide 1,[6] as orange yellow prisms in 93% yield. The structure of 1 was established on the basis of spectral data. IR(KBr) $\mathrm{cm^{-1}}$: $\nu_{N_3(asym)}$ 2190, 2160, 2120; $\nu_{N_3(sym)}$ 1275. Bisazide 1 was fairly stable, and its mass spectrum showed a trace abundant parent ion (M^+) at m/e 318, together with major fragment peaks at m/e 290 ($M^+ - N_2$), 262 ($290^+ - N_2$), 247, 234 ($262^+ - N_2$), 117 ($[\mathrm{Ph}\triangle\mathrm{NH}]^{+\cdot}$), 104 ($\mathrm{PhC{\equiv}\overset{+}{N}H}$) and 103 ($[\mathrm{PhCN}]^{+\cdot}$).

When bisazide 1 was heated in xylene under reflux for 1 hr, monoazide 6, mp 133-134°C, was obtained as pale yellow needles in 70.8% yield. Spectral data of 6 are as follows. IR(KBr) $\mathrm{cm^{-1}}$: ν_{NH} 3300; $\nu_{N_3(asym)}$ 2160; $\nu_{N_3(sym)}$ 1300. NMR($CDCl_3$) δ ppm: 3.80 (2H, d, J=3 Hz, CH_2), 7.2-7.7 (11H, m, aromatic protons (10H) and NH), 8.12 (1H, s, N=CH). Mass m/e: 290 (M^+), 262 ($M^+ - N_2$), 234 ($262^+ - N_2$), 206 ($234^+ - CH_2N$), 178 ($[\mathrm{PhC{\equiv}CPh}]^{+\cdot}$), 130, 117, 104, 103. Although acetophenoneketazine and bisazide 1 were easily hydrolyzed with hydrochloric acid in acetic acid at room temperature, to give acetophenone and phenacylazide respectively, 6 was not hydrolyzed under same or more forcing conditions.[7] This fact excludes an open chain azine structure such as  $\mathrm{Ph{-}\overset{CH=NH}{C}{=}N{-}N{=}\overset{CH_2N_3}{C}{-}Ph}$ from the possible structure for 6. On the basis of the above observations and of the results of decomposition of 6 as mentioned below, the structure of 6 was tentatively assigned as 1,6-dihydro-3,6-diphenyl-6-azidomethyl-1,2,5-triazine.



Thermolysis of monoazide 6 in refluxing decalin under an atmosphere of nitrogen for 1 hr afforded 2,5-diphenylpyrazine (7), mp 196-197°C (lit.[8] mp 196°C), as colorless leaflets in 12.5% yield, besides resinous materials. The structure of 7 was confirmed by its spectral data and by comparison with an authentic sample prepared from phenacyl bromide and ammonia.[8] The IR spectrum showed no ν_{NH} absorption, and NMR spectrum(DMSO-d_6) exhibited signals at δ 7.5-7.7 (6H, m), 8.05-8.35 (4H, m) and 9.33 (2H, s).

On the other hand, when a solution of bisazide 1 in diethyl ether was irradiated with 400W high-pressure mercury lamp with a Pyrex filter at room temperature for 5 days, a product 8, mp 157-158°C, was obtained in 21.8% yield, together with large amounts of unreacted bisazide 1.9) The molecular formula of 8 agreed with that of a compound derived from monoazide 6 with the elimination of both nitrogen and methylenimine. Indeed, irradiation of a solution of monoazide 6 in diethyl ether with 100W high-pressure mercury lamp for 2 hr afforded 8 in 93.5% yield. Compound 8 was shown to be 3,6-diphenyl-1,2,4-triazine (lit.10) mp 156-157°C) by spectral data. NMR($CDCl_3$) δ ppm: 7.4-7.7 (6H, m), 8.0-8.3, 8.5-8.7 (each 2H, m), 9.03 (1H, s, N=C$\underline{H}$). Mass m/e: 233 (M^+), 206 (M^+- HCN), 205 (M^+- N_2), 178 (205^+- HCN, 206^+- N_2), 103.11) Treatment of 8 with sodium borohydride in a methanol-diethyl ether mixture gave dihydrotriazine 9, mp 200-201°C (lit.10) mp 195-198°C), in 83% yield. IR(KBr) cm^{-1}: ν_{NH} 3300; $\nu_{C=N}$ 1630. Mass m/e: 235 (M^+), 158 (M^+- Ph),



Scheme 1

131 (158^{+}- HCN), 104, 103. On heating of 9 in acetic anhydride under reflux, 9 converted into 8 quantitatively.

The fact that irradiation of monoazide 6 gave an excellent yield of triazine 8, suggests that photochemical decomposition of bisazide 1 proceeds via monoazide 6. Although exact pathways for thermal and photochemical decompositions of bisazide 1 are not clear, probable pathways for the formation of monoazide 6 from bisazide 1, and of pyrazine 7 and triazine 8 from monoazide 6 may be viewed as depicted in Scheme 1. Particularly, we viewed the photochemical decomposition of bisazide 1 as proceeding via nitrene intermediates as shown in paths ii and v.

Further investigation is in progress and the results will be published in the near future.

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* To whom correspondence should be addressed.

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5) O. Tsuge, M. Tashiro, K. Kamata, and K. Hokama, Org. Prep. Proced. Int., 3, 289 (1971).
6) All compounds in this paper gave satisfactory elemental analyses.
7) Bisazide 1 and monoazide 6 were decomposed with conc. sulfuric acid. The results will be reported in the near future.
8) F. Tutin, J. Chem. Soc., 97, 2495 (1910).
9) Irradiation of a solution of 1 (5.0 g) in 250 ml of ether gave 0.8 g of 8, and 3.7 g of 1 was recovered.
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11) Metastable peaks arising from fragmentations of M^{+}- HCN and M^{+}- N_2 were observed in the mass spectrum.

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