Photochemical Generation of 1,4-Diphenylbutane-1,4-diyl

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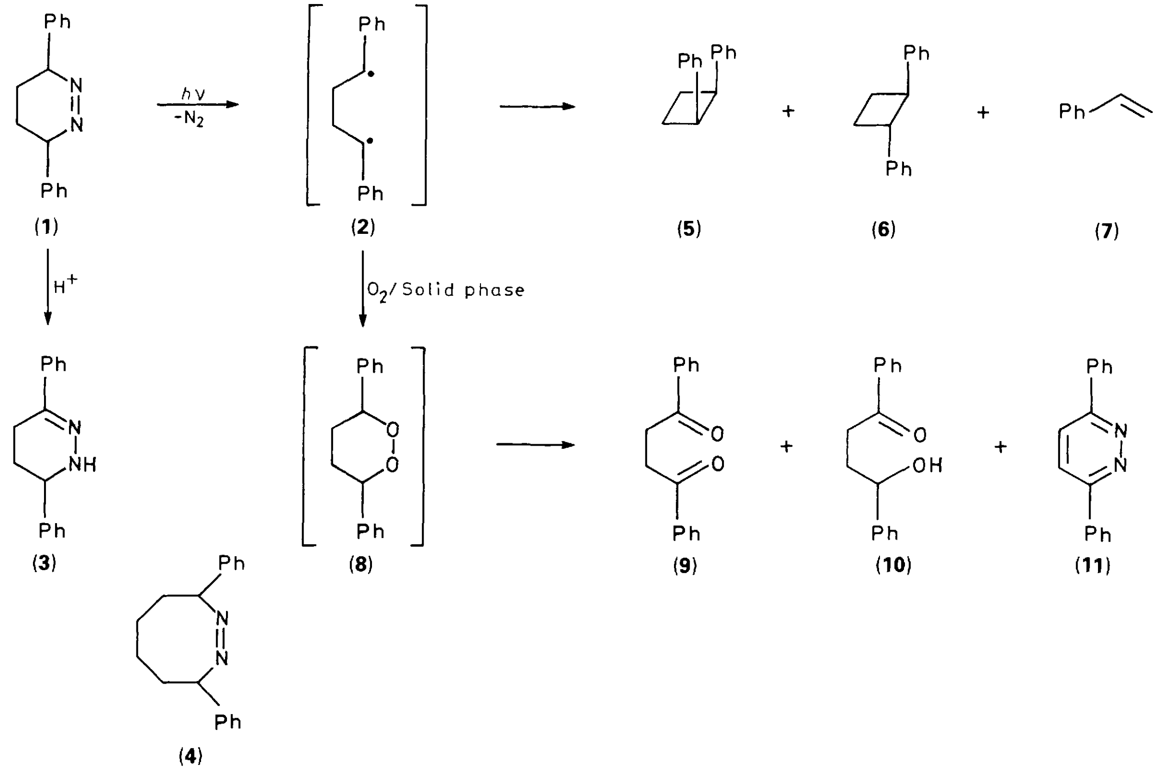
Photochemical deazetation of 3,6-diphenyl-3,4,5,6-tetrahydropyrazine (**1**) was re-examined; evidence was obtained for trapping of a diradical intermediate (**2**) by oxygen when (**1**) was photolysed in the absence of solvent.

Recent reports[1] on the stability of cycloalkanediyl triplet diradicals generated by the photolysis of corresponding azoalkanes showed that substitutions with phenyl groups at the radical sites caused a drastic increase of their lifetimes. This observation imposes the question concerning the stability of analogous phenyl substituted linear alkanediyls. A literature survey reveals that phenyl substituted linear alkanediyls have not been well explored except for those generated by photochemical carbonyl extrusion from cyclic ketones.[2] 1,4-Diphenylbutane-1,4-diyl (**2**), a potential candidate linear



alkanediyl, was once studied but only by the thermolysis of (**1**).[3—6] According to a previous report,[3] the generation of (**2**) by the photochemical decomposition of (**1**) was unsuccessful due to an isomerization to hydrazone (**3**), though a similar cyclic azoalkane (**4**) generated the corresponding diradical by photolysis.[6] As the azoalkane in question is known to be quite sensitive to acids, we re-investigated the photolysis of (**1**) in basic media and revealed that (**2**) could also be generated photochemically. Here we comment on the photolysis of acid-sensitive azocompounds.

Irradiation of (**1**) with a pyrex filtered high pressure Hg lamp under argon atmosphere in several solvents with *N*,*N*-di-isopropylethylamine (0.01% volume) afforded three products *cis*- and *trans*-1,2-cyclobutanes, (**5**) and (**6**) respectively,† and styrene (**7**). The results are summarized in Table 1. The products obtained were identical with those of thermolysis and no meaningful amount of (**3**) was detected, which suggested that nitrogen elimination had been photoinduced. The quantum yield for the decomposition of (**1**) in EtOAc at 0 °C was 0.03 [potassium ferrioxalate actinometry using a combination of two glass filters: transmittance of 340—390 nm, n – π* absorption of (**1**) in EtOAc: $\lambda_{max.}$ 382 nm, $\varepsilon_{max.}$ 210].

The smaller value for the ratio (**6**)/(**5**) (1.1—1.6) at 20 °C under argon as compared to that of thermolysis (1.8—2.1)[5] is quite reasonable. At the higher temperature, thermodynamically stable anti-diradical (**2**) will be preferred, thus the ratio of *trans* isomer increases. This is well exemplified by the experiment at –70 °C in EtOAc. The ratio (**7**)/[(**5**) + (**6**)], *i.e.* C–C bond cleavage *vs.* C–C bond formation, at 20 °C under argon is in the range 0.9—1.2 except in MeOH, which accords with the thermolysis value at the lower temperature (1.2 at 63 °C; 2.0 at 280 °C).[5] In both respects, therefore, the intermediate diradical (**2**) generated by photolysis is behaving similarly to the one from thermolysis. Dioxygen trapping of diradicals is the most economical and well studied method[7] to investigate whether they have reasonably long triplet lifetimes or not. Though photolysis of (**1**) in either benzene or EtOAc under a continuous stream of oxygen did not give any oxidation product, photolysis of the solid material‡ under air resulted in three new products; the diketone (**9**) (13%), the hydroxyketone (**10**) (19%), and 1,4-diphenylpyridazine (**11**) (11%), in addition to cyclobutanes [13%, ratio (**6**)/(**5**) = 10 : 3]

Table 1. The ratio of the products in photolysis of (**1**).[a]

Solvent	Conditions	Products/%			Product ratio	
		(**5**)	(**6**)	(**7**)	(**6**)/(**5**)	(**7**)/[(**5**) + (**6**)]
Benzene	20 °C/Ar	14	22	37	1.6	1.0
	20 °C/O_2	15	26	54	1.7	1.3
Hexane	20 °C/Ar	15	17	38	1.1	1.2
EtOAc	20 °C/Ar	14	21	33	1.5	0.9
	20 °C/O_2	15	22	58	1.5	1.6
	–70 °C/Ar	17	15	27	0.9	0.8
MeOH	20 °C/Ar	9	10	38	1.1	2.0

[a] After photolysis (2 h) of (**1**) (4.3×10^{-3} M) in the solvents containing 0.01% volume of *N*,*N*-di-isopropyl-ethylamine, the products were analysed by GLC (10% SE30 on Chromosorb GAW).

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† In preparative runs, (**5**) and (**6**) were isolated by preparative HPLC (Si-60 Lichrosorb) and identified by the comparison of their ^1H NMR spectra with those of reported compounds (R. M. Dodson and A. G. Zielske, *J. Org. Chem.*, 1967, **32**, 28).

‡ The reaction vessel was rinsed with aq. sodium carbonate solution and then dried. A solid layer (crystalline deposit) was prepared on the wall of the vessel by evaporating an ether (pre-treated with potassium carbonate) solution of (**1**) while rotating the vessel.

separated by alumina column chromatography. In a separate experiment, formation of styrene (29%) was also observed (GLC). A control experiment showed that (**3**) was inert to photolysis in the solid state under similar conditions. That oxidation products are not derived from (**3**) suggests that they arise from the diyl (**2**), possibly *via* the 1,4-endoperoxide (**8**). Unsuccessful trapping in solution suggests that the triplet lifetime of (**2**) might be quite short compared with similar systems, 1,3-diphenylcyclopentane-1,3-diyl and 1,4-diphenylcyclohexane-1,4-diyl.[1] The efficient trapping of (**2**) in the solid phase might be due to the higher gaseous oxygen concentration or the immobility of the molecular framework which reduces the probability of intersystem crossing to a singlet diradical by spin-orbit coupling as can be anticipated from the Salem rule.[8]

The present findings highlight difficulties associated with the photolysis of sensitive azoalkanes especially to acids and also open a new dimension in diradical dioxygen trapping chemistry.

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