THE PHOTOCHEMISTRY OF 1,2,3-TRIPHENYLAZIRIDINE

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Abstract—Photochemical behaviour of 1,2,3-triphenylaziridine has been investigated. Irradiation in alcoholic solvents induces a novel type of alcoholytic cleavage of the aziridine ring to give benzaldehyde acetals and N-benzylaniline. Competitively, fragmentation occurs to give rise to benzalaniline and phenyl-carbene, the latter being trapped with alcohols as alkyl benzyl ethers. Photolysis in cyclohexene affords a 1,3-cycloaddition product, 1,2,3-triphenyloctahydroisoindole as a mixture of two stereoisomers.

CONSIDERABLE attention has been focused on the photochemistry of small ring compounds. Homolytic cleavage of cyclopropane derivatives in nonpolar solvents has been known to cause *cis-trans* isomerization,¹ rearrangement to olefins² and carbene formation.³ In protic solvents, on the other hand, heterolytic addition of the solvents occurs predominantly to afford substituted propanes.⁴ Recent publications have dealt with photochemical reactions of oxiranes^{5,6} and aziridines.⁷ As only acyl aziridines have been subjected to photolysis, the photoreactions of 1,2,3-triphenylaziridine⁸ (I) presented a variety of possible pathways.

First, irradiation was effected on solutions of I (UV_{max} in EtOH 239 mµ (log ε 4.58)) in alcoholic solvents and the results are summarized in Table 1. GLC separation of the photolysates gave benzaldehyde acetals (III), N-benzylaniline (IV), benzalaniline (V) and alkyl benzyl ethers (VI) as major products.

Solvent	Conversion, ^b	Yield, % ^{c.d}			
(ROH)	%	111	IV	v	VI
МеОН	86	33	40	24	5
EtOH	86	18	20	18	3
iso-PrOH	80	7	23	25	2
t-BuOH	75	0	20	49	0

TABLE 1. PHOTOLYSIS OF 1,2,3-TRIPHENYLAZIRIDINE IN ALCOHOLS"

[•] Irradiation was effected on 0-04M solutions placed in quartz tubes $(2 \times 25 \text{ cm})$ with an external 200 W high-pressure Hg arc at a distance of 3 cm under N₂ atmosphere at room temp for 60 hr.

^b Based on the weight of I which was recovered unchanged upon alumina column chromatography of the photolysates.

^c Determined by GLC and based on the consumed I.

⁴ The appearance of a GLC peak of benzaldehyde (<10%) was observed in each case, but the IR spectra of the photolysates clearly showed the absence of benzaldehyde. It was established that the products III \sim VI were stable under the GLC conditions. Benzaldehyde possibly arises during the GLC analysis from thermally labile product(s) unidentified.



The transformation of solvent alcohols into the respective acetals III involves a fission of polar O—H bond rather than homolytically weaker α —C—H bond of alcohols. This suggests that the attacking reagent must be ionic in nature. The reaction would presumably proceed *via* intermediary O,N-acetals II, alcoholysis of which gives III and IV. The formation of IV was observed also in t-butyl alcohol and even in cyclohexane as shown below. This observation might imply that a homolytic reaction is participating to some extent. The isolation of acetone among the reaction products in isopropyl alcohol would support such an assumption. Possible photoreduction of the anil V to IV in isopropyl alcohol⁹ was excluded by separate experiments.

Benzalaniline V is ascribed to another mode of ring-opening of I which gives phenylcarbene as a counterpart. This is formally analogous to the photolysis of an oxirane yielding a carbonyl compound and a carbene.⁵ Phenylcarbene thus generated was trapped by solvent alcohols to afford alkyl benzyl ethers (VI) which were obtained in rather low yields.¹⁰ Photolysis in cyclohexane gave a C—H insertion product, benzylcyclohexane (2% yield) together with IV (32%), V (30%) and bicyclohexyl (trace).

An attempt to capture the transient phenylcarbene with cyclohexene gave the reaction to an unexpected direction. Irradiation of a 0-06M solution of I in cyclohexene gave rise to an adduct (VII) of I and the olefin in a 55% yield and the by-products were found to be 3,3'-bicyclohexenyl, IV and V. Careful search for 7-phenylbicyclo[4.1.0]heptane or benzylcyclohexene proved futile. The adduct VII was separated into two crystalline stereoisomers (VIIa and VIIb in a 2:3 ratio) by fractional recrystallization. Spectral data summarized in Table 2 established the octahydroisoindole structure.* Mass spectra of VIIa and VIIb (Figs 1 and 2) showed a remarkable resemblance and supported the assigned structure, but the stereo-chemical details are not known. This type of cycloaddition proceeded smoothly even in an equimolar mixture of cyclohexene and methanol, IV and V being the by-products. Unexpectedly, photolysis of I in cyclopentene did not give such a cyclo-adduct and the sole isolable products were IV and V.

The formation of VII can be explained by assuming the photochemical transformation of I to a 1,3 dipole or azomethine ylide (VIII) and the subsequent thermal

^{*} Thermal addition of I to electrophilic olefins has been recorded.^{8c}

cycloaddition of olefin.¹¹ The intermediacy of a benzylic diradical IX cannot be excluded.

TABLE 2. PHYSICAL PROPERTIES OF 1,2,3-TRIPHENYLOCTAHYDROISOINDOLE ISOMERS

	VIIa	VIIb		
M.p.	229–230°	154–155°		
UV_{max}^{EOH} mµ (log ε)	252 (4·30), 304 (3·51)	249 (4·23), 296 (3·49)		
NMR (CDCl ₃) δ (TMS)	7.4-6.2 (15H, multiplet, aromatic)	7.7-6.3 (15H, multiplet, aromatic)		
	5.12 (2H, doublet, J 7 c/s, PhCH) 2.4-0.8 (10H, multiplet, cyclohexane ring protons)	4.75 (1H, doublet, J 8 c/s, PhCH), 4.25 (1H, doublet, J 8 c/s, PhCH) 2.3-0.7 (10H, multiplet, cyclohexane ring protons)		
Ph Ph N—Ph VII III + V	$\begin{array}{c} Ph \stackrel{\bullet}{\longrightarrow} CH \stackrel{\bullet}{\longrightarrow} N \stackrel{\bullet}{\longrightarrow} CH \stackrel{\bullet}{\longrightarrow} Ph \stackrel{\bullet}{\longrightarrow} Ph \stackrel{\bullet}{\longrightarrow} Ph \stackrel{\bullet}{\longrightarrow} VIII \qquad \downarrow$	$I = \stackrel{\bullet}{N} \stackrel{\bullet}{\longrightarrow} \stackrel{\bullet}{D} h = Ph - CH \cdots CH - Ph$ $ / / Ph$ Ph $N - Ph$ IX $Y + PhCH:$		

Finally, in order to examine the nature of triplet aziridine, acetophenone-sensitized decomposition was carried out in benzene with light of longer wavelength than 350 mµ. In this run, the incident light was absorbed almost exclusively by acetophenone. Although the formation of complex mixture prevented a detailed analysis of products, IV and V were obtained in 48 and 20% yields, respectively.



FIG. 1 Mass Spectrum of VIIa.



FIG. 2 Mass Spectrum of VIIb.

Throughout these direct and sensitized photolyses the initial cleavage of the C—C bond seems to characterize the photochemical reactions of aziridine I. The intermediate VIII (or less possibly IX) can react with alcohols in two ways to afford either III and IV via II or, alternatively, V and VI. The direction is dependent on the alcohols. There was no sign which indicated the formation of phenylnitrene or the C—N bond cleavage corresponding to the known mode of reactions of oxiranes.⁶ The cis-trans isomerization of I was not detected either.

EXPERIMENTAL

All m.ps are uncorrected. NMR data were obtained on JEOL C-60-H spectrometer. Mass spectra were taken on Hitachi RMU 6D spectrometer at a probe temp of 200°. GLC analyses were performed with cis,trans,trans-1,5,9-cyclododecatriene (CDT) as an internal standard. The column A (5 mm \times 2 m) refers to 17% Apiezon L on 80–100 mesh Neosorb NC coated with KOH, while the column B (5 mm \times 1 m) 30% Silicone DC HV Grease on 80–100 mesh Celite 545.

1,2,3-Triphenylaziridine (I) was prepared by the procedure of Taylor *et al.*⁸⁴ All the solvents used were dried by Na or Mg, stored over Molecular Sieves and redistilled before use. Cyclohexene was further purified by passing through an alumina column.

Photolysis of I in alcohols. After 60 hr irradiation of a 0.04M soln of I in the respective alcohol (50 ml), the photolysate was concentrated in vacuo and subjected directly to GLC (column A, 220°). The results were summarized in Table 1. Preparative GLC (column A) of the mixture obtained in MeOH gave benzaldehyde (rel retention time with reference to CDT 0.3), VIa;¹² (0.3), IIIa¹³ (0.4), V¹⁴ (3.6), m.p. 48°, and IV¹⁵ (4.0). Two unidentified minor components (rel retention times 2.0 and 2.2, resp.) were also produced. Benzaldehyde and IIIa were separated on the column B (120°), the rel retention times being 0.15 and 0.19, respectively. Photolysis in EtOH yielded VIb^{*} (0.4), IIIb¹³ (0.5) together with benzaldehyde, IV and V. Reaction in iso-PrOH gave VIc¹² (0.4) and IIIc¹³ (0.6) besides benzaldehyde, IV and V. A N₂ stream passed through the reaction mixture was passed into alcoholic 2,4-dinitrophenylhydrazine soln. The ppts obtained were found to be 2,4-dinitrophenylhydrazone of acetone, m.p. and mixed m.p. 123–124°. When t-BuOH was used as a solvent, benzaldehyde, IV and V were obtained. All the products were identified

* Authentic sample was obtained by the method of Ref. 2.

by comparison of IR spectra and GLC retention times with the authentic samples. Unchanged I was recovered from chromatography on an alumina column.

Photolysis of I in cyclohexane. A 0-04M soln of I in cyclohexane (50 ml) was irradiated for 60 hr as described above. GLC separation of the reaction mixture (column A, 220°) gave bicyclohexyl¹⁶ (rel retention time with reference to CDT 1-0, 0-1% yield), benzylcyclohexane¹⁷ (1-3, 2%), N (32%) and V (30%). These compounds were identified by comparison with the authentic samples.

Photolysis in cyclohexene. A mixture of I (8.77 g, 32 mmoles) and freshly distilled cyclohexene (500 ml) was irradiated under N₂ with an immersion type 200 W Hg arc for 43 hr. Concentration followed by steam distillation gave a brownish residue, which was subjected to chromatography on an alumina column. Elution with benzene-n-hexane (1:4) gave a 1:1-adduct, 1,2,3-triphenyloctahydroisoindole (VII), as a crystalline solid (6.25 g, 55% yield). Recrystallization from n-hexane yielded an isomer VIIa, m.p. 229–230°. (Found: C, 88·1; H, 7·7; N, 3·8. C₂₆H₂₇N requires: C, 88·3; H, 7·7; N, 40%). The mother liquor was concentrated and recrystallized from EtOH to give another isomer VIIb, m.p. 155–156°. (Found: C, 88·1; H, 7·6; N, 3·9. C₂₆H₂₇N requires: C, 88·3; H, 7·7; N, 40%). IR spectra (KBr) of VIIa and VIIb proved the absence of an N—H bond. Other spectrometric data are summarized in Table 2 and Figs 1 and 2. The product ratio of VIIa and VIIb was found to be 2:3 by NMR spectra.

The steam-distillate was analyzed by GLC (column A at 220°). Preparative separation gave 3,3'-bicyclohexenyl, IV and V, the yields being variable. The products were identified by comparison with the authentic specimens.

Photolysis of I in cyclohexene-methanol mixture. A mixture of I (50 mg, 0.18 mmole), MeOH (3.11 g, 97 mmoles) and cyclohexene (8.41 g, 102 mmoles) was irradiated externally. TLC analysis (Silicagel G, benzene as an eluant and $K_2Cr_2O_7$ -H₂SO₄ mixture as a colouring agent) of the photolysate proved the formation of VII which gave a characteristic wine red spot with an R_f value of 0.7. By-products IV and V were also formed.

Acetophenone-sensitized decomposition of I. A mixture of I (1-01 g, 3.7 mmoles) and acetophenone (1-02 g, 8.5 mmoles) in benzene (70 ml) was placed in a Pyrex tube (2×25 cm) and irradiated through a 9% CuSO₄ aq (15 mm thick) for 48 hr. Chromatography on an alumina column afforded the unchanged I (0-85 g, 84% recovery) and acetophenone (0-53 g, 53% recovery) as isolable products. GLC analysis (column A, 220°) showed the formation of V (20% yield based on the consumed I) and IV (48%).

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