

THE PHOTOCHEMICAL BEHAVIOUR OF BIS ARYL-1,3 TRIAZENES

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SUMMARY

The photolysis of bis aryl-1,3 triazenes carried out in non-aromatic solvents gives products whose structures are consistent with a cage recombination process of homolytically formed radicals and the subsequent abstraction of hydrogen from the solvent molecules by these aryl-amino radicals.

In aromatic solvents, a free-radical chain process leads to the formation of products resulting from the homolytic substitution on the solvent.

Previous attempts to observe a reversible cis-trans photoisomerisation on the N=N double bonds of triazenes as in azobenzenes have been unsuccessful¹.

However, such a photoisomerisation seems to occur in another case as reported on the basis of spectroscopic data².

In all cases it was assumed that the photolysis of triazenes proceeds through a radical species³. However, since identical photoproducts are obtained from the aryldiazonium salt photolysis, also polar intermediates were proposed⁴.

In order to obtain further information on the nature of the reactive species, we have studied the photochemical behaviour of four triazenes (diazoaminobenzene (1), bis(pirydyl-3)-1-3 triazene (2), bis-(4-carboxyethyl phenyl)-1,3 triazene (3) and bis(2,4-dichloro phenyl)-1,3 triazene (4) in methanol and benzene.

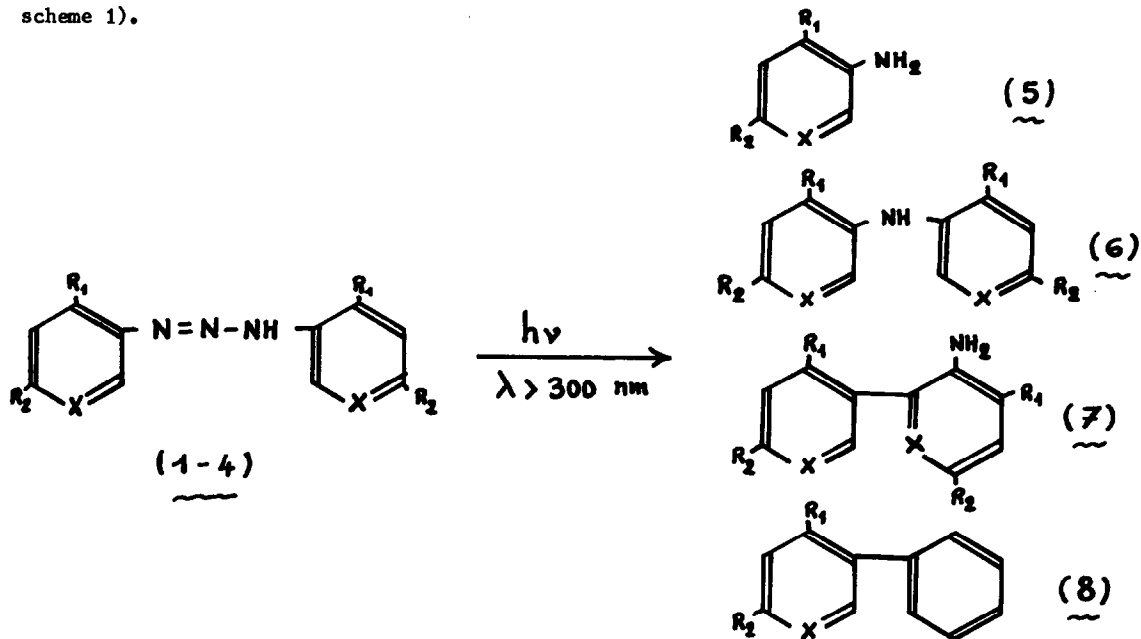
These compounds were chosen as representative triazenes since they are easily obtained and manipulated (long term stability except for diazoaminobenzene).

The triazenes were prepared from the corresponding aromatic amines by mixing at 0-5°C, one part of the amine with two parts of isoamyl nitrite in an inert solvent (hexane for (1), mp : 98°C ;

acetic acid 1/heptane 1,5 for (2), mp : 178°C ; hexane 1/benzene 1 for (3), mp : 156-158°C ; hexane for (4), mp : 132°C).

Experiments were performed by irradiation, through a pyrex filter, under a stream of nitrogen, of a $1,2 \times 10^{-3}$ M solution of triazene using a Mazda 400 W U.V. lamp until 70% of the starting material was consumed.

The photolysis of the four triazenes leads to products whose structure was assigned on the basis of satisfactory analytical (melting points ; C, H, N analysis) and spectral (NMR, MS) data (see scheme 1).



Scheme 1

Table I : Yields of photoproducts

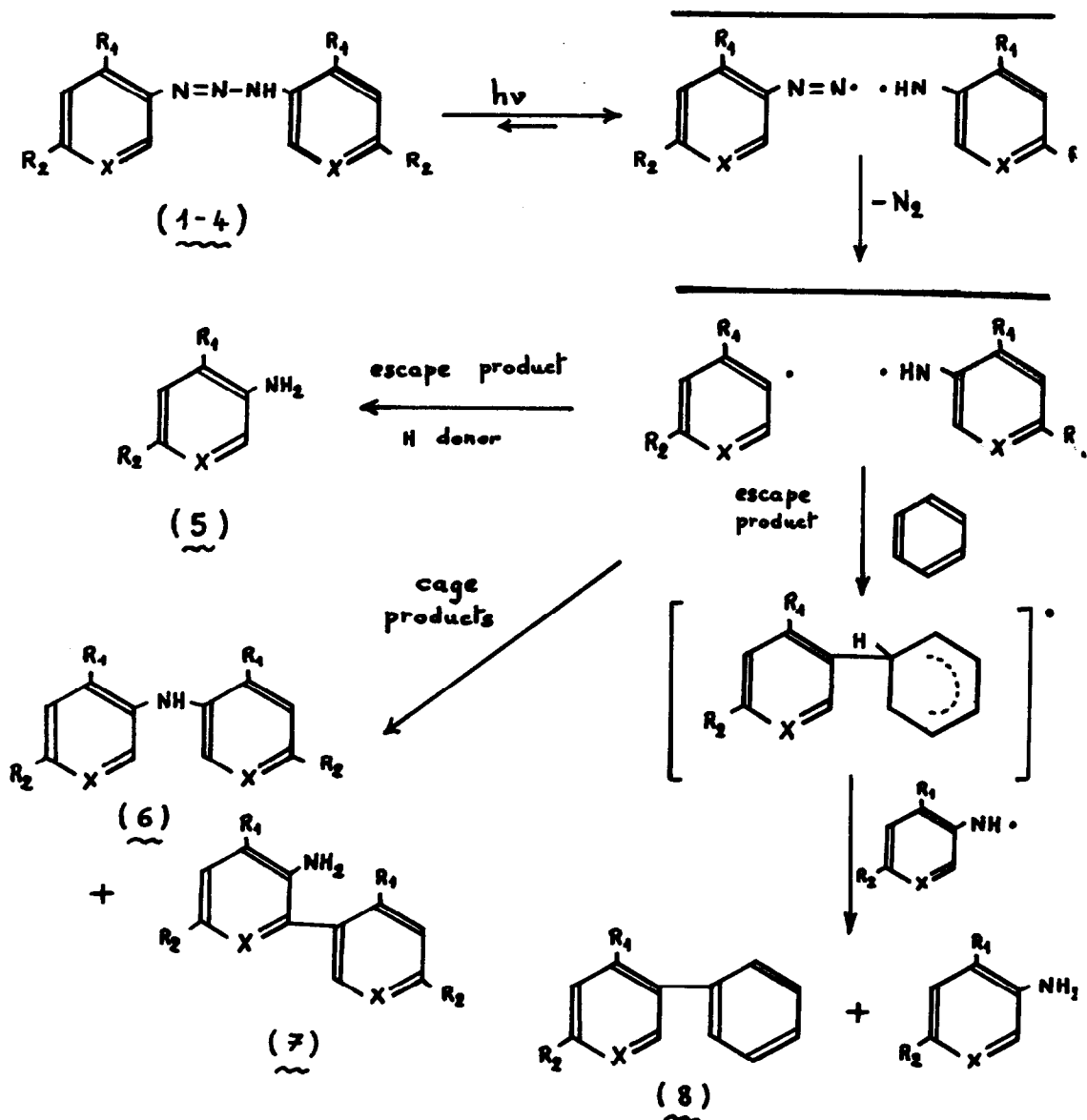
Solvent :	a) methanol	b) benzene				not identified	
		(5)	(6)	(7)	(8)		
** X = CH	R ₁ = R ₂ = H	a	39	5	15,5*	-	21,5
		b	13,5	6,5	19 *	50	11
X = N	R ₁ = R ₂ = H	a		50		-	20
		b	25		50	12	13
X = CH	R ₁ = H R ₂ = COOEt	a	60	30		-	10
		b	35	15		30	20
X = CH	R ₁ = R ₂ = Cl	a	65	15	15	-	5
		b	15	5	30	25	25

* ortho + para isomers

** dibenzopyrrole (carbazole) is formed with 39% yield during the photolysis of diazoaminobenzene in methanol

To account for these results, we propose a process outlined in scheme 2.

The U.V. irradiation of triazenes (1-4) leads to their cleavage with the formation of the corresponding arylamino and aryl radicals, the latter being formed via the phenyldiazanyl radical. The coupling of these two radicals yields an arylamine (6) and/or an aminobiphenyl (7) while the hydrogen abstraction from the solvent by the arylamino radicals which escape from the solvent cage leads to aniline (or pyridine) (5). In aromatic solvents, aryl radicals react with the aromatic ring of the solvent and form a σ complex which is mostly oxidized by the arylamino radicals before dimerisation or disproportionation (See scheme 2).



Scheme 2

The quantum yield (measured with a potassium ferrioxalate actinometer see ref : 5) of triazene disappearance at 360 nm is smaller than 0.1 in methanol and, in three cases, higher than 2 in benzene (see table II).

Table II

solvent/triazenes	Quantum yields			
	(1)	(2)	(3)	(4)
CH ₃ OH	0,11	0,07	0,04	0,06
C ₆ H ₆	2,85	2,65	1,88	2,61

These results suggest that a radical chain process is involved in aromatic solvent.

The nature of the radical which induces the chain reaction is not clear. It would be a triazeny radical formed by a hydrogen abstraction reaction which then decomposes in aryl and arylamino radicals.

The U.V. absorption spectra of the four triazenes do not exhibit the two bands corresponding to cis-trans isomerisation.

It is reasonable to assume from these experimental and spectral data that the photolysis of aryl-1,3 triazenes proceeds through a radical species without any cis-trans photoisomerisation. A detailed discussion of the reaction, the nature of the excited state of the species undergoing this process, and other aspects of the reaction will be the topic of a subsequent publication.

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