THE THERMAL AND PHOTOLYTIC DECOMPOSITION OF 9-ARYL-9-XANTHENYL AZIDES TO 11-ARYLDIBENZO[b,f][1,4] OXAZEPINES

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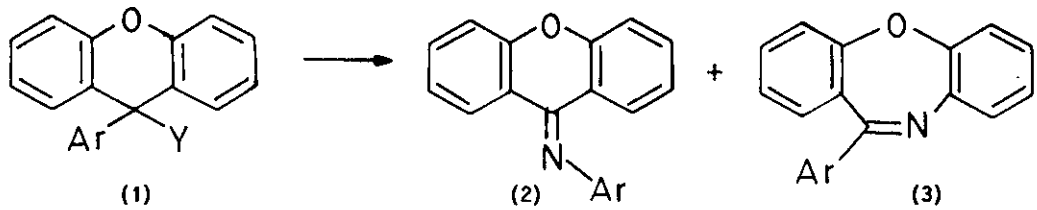
Abstract - In contrast to the different ratios of products obtained in the thermal decomposition of some 9-aryl-9-xanthenyl azides, it was found that photolysis afforded the same product ratio. The mechanism of these reactions is discussed in terms of intermediates as well as conformational and electronic effects in the transition states.

Seven-membered heterocycles are of pharmacological interest[1]. The decomposition reactions of azides are among the methods used to generate azepines. Ring expansions are accomplished either by nitrene insertion into aromatic rings[2] or by Schmidt[3] and Schmidt-type decomposition of azides generated by nucleophilic attack of the azide ion on heterocycles[4,5]. In continuation of our investigations[6,7] on the rearrangement reactions of xanthenyl and related systems, we have extended this study to the azides.

We have confirmed the results of French workers[5] that 9-phenyl-9-xanthenyl azide (1a) rearranged to give the same ratio of the anil (2a) and oxazepine (3a) under both thermal and photolytic conditions. In contrast to this, decomposition of the 9-azido derivatives of 9-phenylthioxanthene, 9-phenylselenoxanthene and 10-oxo-9-phenylanthracene gave different ratios of the respective anils and azepines when decomposed by heat or irradiation[5]. In order to determine the factors which influence the ratio of anil to oxazepine, we have investigated the decomposition of the 9-aryl-9-xanthenyl azides (1a-d).

The 9-aryl-9-xanthenyl azides were synthesised by stirring the appropriate 9-aryl-9-xanthenyl perchlorate (1, Y = ClO_4) in methylene dichloride with sodium azide. The thermal degradations were rapidly accomplished by heating the azides in decalin and the photolyses were slowly effected by irradiating benzene solutions of the azides through quartz with a medium pressure mercury lamp at ambient temperature. The structure of the anils (2) was confirmed by their hydrolyses to xanthone.



a) Ar = C_6H_5, Y = N_3

b) Ar = p-$CH_3OC_6H_4$, Y = N_3

c) Ar = p-$CF_3C_6H_4$, Y = N_3

d) Ar = p-ClC_6H_4, Y = N_3

e) Ar = C_6H_5, Y = OH

f) Ar = C_6H_5, Y = H

Aliquots from the reaction mixtures were withdrawn at intervals and analysed (hplc) using benzophenone as internal and external standards in the thermal and photolytic reactions respectively. The small amounts of xanthone obtained in the various reactions were added to the amounts of respective anils since both arose via 9-aryl migration. This combined amount was used to calculate the amount of 9-aryl substituent migration. The amount of oxazepine (3) produced was due to migration of the aryl group in the xanthene ring. These results were used to determine the relative amounts of 9-aryl substituent migration and ring expansion reaction. The results are given in Table 1.

TABLE 1: Products from the thermal and photochemical degradations of azides (1)

Azide	Reaction			Product yield/%			Ratio Oxazepine (3) / Anil (2) + xanthone
	Condition	Time/h	Conversion/%	Anil (2)	Xanthone	Oxazepine (3)	
1a	Thermal	1	79	23	3	54	2
1b	Thermal	1	84	54	2	44	0.8
1c	Thermal	1	85	17	1	82	4.6
1d	Thermal	1	85	26	2	72	2.6
1a	Irrad.	24	84	30	3	67	2
1b	Irrad.	24	90	34	2	64	1.8
1c	Irrad.	24	85	29	5	67	2
1d	Irrad.	24	90	29	4	67	2

The ratio of oxazepine to anil in all the reactions investigated was independent of the extent of their reaction. A similar result was observed in the thermolysis and photolysis of 9-azido-9-(4-pyridyl)xanthene[8].

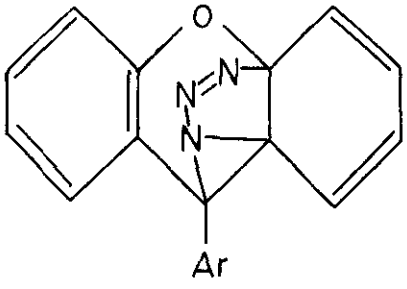
In the thermal reaction, the ratio of oxazepine (3) to anil (2) increased as the electronegativity of the para-substituent on the 9-aryl ring was increased (Table 1). In order for the oxazepines (3) to form, the C_9-N bond would have to be in a pseudo-axial position since only this conformation of the molecule would allow anti-periplanar interaction of the xanthenyl π-electrons with the azide or $^1\Delta$ electronic state of the nitrene. This conformation with the C_9-N bond in the pseudo-axial position could not lead to migration of the 9-aryl substituent to form the anils (2) since peri interaction with the C_1-H and C_8-H would prevent the 9-aryl substituent from attaining the conformation which is required for 9-aryl group migration.

The same ratio of oxazepine to anil in the photolytic reaction was surprising. Irradiation could either effect direct photolysis of the azide or excite the xanthenyl ring system. The ultraviolet spectra of the azide (1a), alcohol (1e) and xanthene (1f) were identical. The weak absorption of the azide group at 285 nm[9] is completely masked by the absorption due to the xanthene ring system. On this basis it is suggested that irradiation excites the xanthenyl chromophore in the photolytic reaction.

If energy transfer from the excited aromatic system to the azide occurs, then in the systems investigated the common xanthenyl chromophore and not the 9-aryl substituent would be expected to be the dominant species in energy transfer to the azide. This would thus lead to the same excited species and would eliminate the complication of reaction through different electronic states since it has been established that singlet and triplet nitrenes[10] react at different positions on the same substrate to produce different products. Direct irradiation of azides in the presence of aromatic hydrocarbons has been proposed to produce singlet nitrenes[11] by singlet energy transfer from the excited aromatic species. The differences in migratory aptitudes of phenyl and pyridyl groups when α,α'-diphenylpyridylazidomethanes[12] were heated and irradiated, have been attributed to the $^1\Delta$ electrophilic state of the nitrene in thermolysis and the $^1\Sigma$ diradical state in photolysis.

The same product ratio obtained for the different 9-aryl substituted 9-xanthenyl azides (1a-d) in the photolytic reactions cannot be due to rearrangements occurring in different conformations of a common nitrene intermediate. If such an energy barrier existed between the different

conformations of a common nitrene intermediate, then a similar or greater energy barrier would be expected between the equatorial and axial azides at ambient temperature. Since the separation of isomeric azides could not be accomplished, it is unlikely that conformational effects control the fixed ratio of products in the photolytic reactions with different 9-aryl substituents. The same product ratio would not be expected to be formed from the different 9-aryl-9-xanthenyl azides in concerted decompositions of the 9-aryl-9-xanthenyl azides since in these substrates the concerted decomposition would also be affected by conformational and steric factors. Hence it is suggested that the excited xanthenyl ring undergoes a 1,3-dipolar addition with the azide to form an intermediate aziridinotriazole (4) which then undergoes a heterolytic decomposition with nitrogen elimination to generate either the anil or the oxazepine by different bond fragmentation of the aziridine ring.



(4)

A similar intermediate has been proposed[14] in the thermal decomposition of azido chromones on the basis of intramolecular addition of azides to olefins[15], β-tetrazolo-trans-benzalazetophenones have been synthesised[16] and triazoline intermediates[17,18] have been postulated in the thermolysis of azidocinnamates containing ortho-cycloalkenyl substituents.

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