

DYE-SENSITIZED PHOTOOXYGENATION OF AZIRIDINES

V. Bhat and M. V. George*

Department of Chemistry
Indian Institute of Technology, Kanpur
Kanpur 208016, India

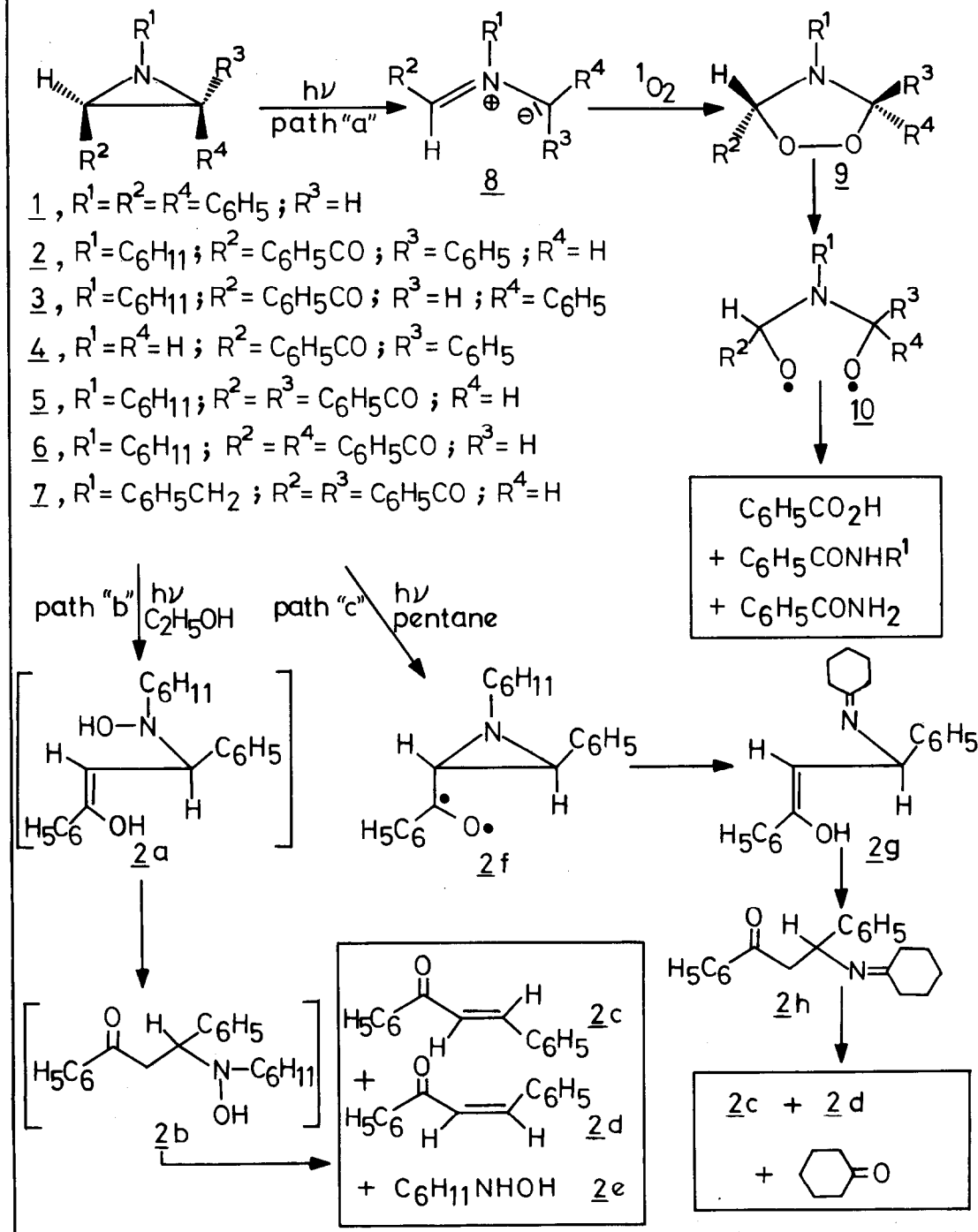
(Received in UK 8 September 1977; accepted for publication 6 October 1977)

Aziridines are known to undergo different modes of ring-opening reactions, under photochemical conditions, depending on the nature of the substituents present in the aziridine ring. Huisgen and coworkers,¹ for example, have shown that a prominent mode of ring-opening of aziridines is through a symmetry allowed [$\omega^2_s + \sigma^2_s$] type of disrotatory cleavage leading to azomethine ylides as intermediates (path "a", Scheme 1). The cis-trans isomerization of several aziridine derivatives and the cycloaddition reactions of aziridines with different dipolarophiles have been rationalized in terms of such a ring-opening process.¹ A similar ring-opening reaction has been postulated in the photochemical transformation of triphenylaziridine (1) in different, polar, protic solvents like alcohols to give a variety of products.²

It has been reported that acyl substituted aziridines undergo a different mode of ring-opening reaction. The photolysis of trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine (2) in 95% ethanol, for example, gave a mixture of products consisting of trans- and cis-benzalacetophenone (2c and 2d) and N-cyclohexylhydroxylamine (2e). The same photolysis, when carried out in pentane solution and using a pyrex filter gave a mixture of products consisting of N-1(2-benzoyl-1-phenylethyl)cyclohexanimine (2h), cyclohexanone and trans- and cis-benzalacetophenone (2c and 2d). The formation of these products have been rationalized in terms of a C-N bond fission of the aziridine ring and proceeding through either path "b" or path "c" as shown in Scheme 1. The photolysis of cis-1-cyclohexyl-2-phenyl-3-benzoylaziridine (3) in aqueous ethanol, on

* To whom enquiries should be addressed.

Scheme 1



the other hand, gave a mixture of N-cyclohexylbenzalimine and acetophenone along with a number of minor products.³ The formation of these products have been rationalized in terms of a C-C cleavage of the aziridine ring, initiated by diradical intermediates, generated under photochemical conditions. Similar observations have been made in the photolysis of other aziridine derivatives.⁴

The object of the present investigation has been to examine the photooxygenation of a few substituted aziridines with a view to studying the nature of the products formed in these reactions. The aziridines that we have examined include, 1,2,3-triphenylaziridine (1), trans- and cis-1-cyclohexyl-2-phenyl-3-benzoylaziridines (2 and 3), trans-2-phenyl-3-benzoylaziridine (4), trans- and cis-1-cyclohexyl-2,3-dibenzoylaziridines (5 and 6), and trans-1-benzyl-2,3-dibenzoylaziridine (7). The oxygenation reactions were carried out by irradiation⁵ of a benzene solution (175 ml) of the aziridine containing a small quantity of Rose Bengal solution (15 ml) in either methanol or acetone. Oxygen gas was bubbled through the solution and irradiations were carried out till all the starting material in each case disappeared, as evidenced by tlc tests. The results of our studies are summarized in Table 1.

Table 1: Photooxygenation Products of Aziridines

Starting Aziridine	Solvent	Time (hr)	Products
<u>1</u>	Benzene + acetone	2	$C_6H_5CO_2H$ (41%); $C_6H_5CONHC_6H_5$ (40%)
<u>2</u>	Benzene + acetone	1/2	$C_6H_5CO_2H$ (29%); $C_6H_5CONHC_6H_{11}$ (9%); $C_6H_5CONH_2$ (16%)
<u>2</u>	Benzene + methanol	1/2	$C_6H_5CO_2H$ (43%); $C_6H_5CONHC_6H_{11}$ (7%); $C_6H_5CONH_2$ (10%)
<u>3</u>	Benzene + methanol	3/4	$C_6H_5CO_2H$ (56%); $C_6H_5CONHC_6H_{11}$ (8%); $C_6H_5CONH_2$ (10%)
<u>4</u>	Benzene + acetone	1½	$C_6H_5CO_2H$ (54%); $C_6H_5CONH_2$ (29%)
<u>5</u>	Benzene + acetone	1/2	$C_6H_5CO_2H$ (77%)
<u>6</u>	Benzene + methanol	3/4	$C_6H_5CO_2H$ (63%)
<u>7</u>	Benzene + methanol	1	$C_6H_5CO_2H$ (70%)

Examination of Table 1 reveals that the photooxygenation of 1, for example, leads to a mixture of products consisting of benzoic acid (41%) and benzanilide (40%). The formation of these products can be rationalized in terms of the reaction pathway "a" shown in Scheme 1. In this scheme, we assume that the azomethine ylide 8, formed from 1 undergoes addition reaction with singlet oxygen to give the cyclic product 9, which subsequently gives rise to the diradical intermediate 11. Further reorganization of 11 will lead to benzoic acid and benzanilide. Similar cycloadditions of singlet oxygen with 1,3-dipolar substrates like diazomethane⁶ and nitrones⁷ are reported in the literature.

It is interesting to note that the irradiations of both the trans- and cis-aziridines 2 and 3, respectively gave the same mixture of products consisting of benzoic acid, N-cyclohexylbenzamide and benzamide. Further, it has been observed that the irradiation of 2 in presence of either acetone or methanol gave the same mixture of products, indicating thereby that the solvent effects are not very appreciable in these cases. The formation of benzamide in these reactions may be attributed to further fragmentation of N-cyclohexylbenzamide, under the photolytic conditions. The photolysis of 4, on the other hand, gave only a mixture of benzoic acid and benzamide as expected. Similarly, the photooxygenation of the dibenzoylaziridines, 5, 6 and 7, gave in each case benzoic acid as the major product. The results of our studies indicate that both aryl and aroyl substituted aziridines undergo photooxygenation reactions and that the initial ring-opening in all these cases appear to be through path "a" and not through either path "b" or "c", as shown in Scheme 1.

References

1. R. Huisgen, W. Scheer and H. Huber, J. Amer. Chem. Soc., 89, 1753 (1967).
2. H. Nozaki, S. Fujita and R. Noyori, Tetrahedron, 24, 2193 (1968).
3. A. Padwa and L. Hamilton, J. Amer. Chem. Soc., 89, 102 (1967).
4. A. Padwa and W. Eisenhardt, J. Amer. Chem. Soc., 90, 2442 (1968).
5. All irradiation experiments were carried out using a Hanovia, 450 W, Medium Pressure Mercury Lamp in a quartz-jacketed immersion well.
6. D. P. Highley and R. W. Murray, J. Amer. Chem. Soc., 96, 3330 (1974).
7. T.-Y. Ching and C. S. Foote, Tetrahedron Lett., 3771 (1975).