Reductive Ring Cleavage of 3,5-Dimethylisoxazole by Irradiation in the Presence of Triethylamine

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Summary Irradiation of 3,5-dimethylisoxazole in acetonitrile in the presence of triethylamine resulted in the reductive cleavage of the isoxazole ring by formation of an encounter complex.

Although transpositions are the most-commonly observed type of reaction in the photochemistry of five-membered heterocyclic compounds, 3,5-dimethylisoxazole (**1**) undergoes a photoinduced solvent attack to give open-chain compounds (**2a**) and (**3**) as the major reaction products. A reaction path through ketenimine (**4**) and azirine (**5**) has been proposed.[1]

We now report a novel photo-induced reductive ring cleavage of (**1**). Irradiation of an acetonitrile solution of (**1**) (1·5 g in 150 ml) containing 2 g of triethylamine (**6**) with a medium-pressure mercury lamp through a quartz vessel gave two compounds (**7**) and (**2b**) in 50% and 7·6% isolated yield, respectively. It was found from the n.m.r. spectrum that the crude reaction mixture prior to distillation contained (**1**), (**7**) and (**2b**) in a ratio of 28:51:21. The structure of each product was deduced from spectroscopic data. [(**7**) *m/e* 99 (*M*)$^{+}$, 84 (base peak) and 42; i.r. and n.m.r. spectra identical with those reported;[2] (**2b**) (above *m/e* 90); *m/e* 170 (*M*$^{+}$), 155, 153, 141, 127 and 98 (base peak); n.m.r.

($CDCl_3$) δ 1·29 (6H, t), 2·06 (3H, s), 2·93 (3H, d), 3·29 (4H, q), 4·80 (1H, s), and 10·30 (1H, b); i.r. (CCl_4) 1612, 1590 and 1520 cm^{-1}].

Compound (**7**) could arise *via* (a) homolytic N-O bond fission of isoxazole and subsequent hydrogen abstraction from solvent by the resulted diracical (**8**), (b) secondary reaction induced by photolysis products of (**6**) and (c) charge-transfer complex formation between (**1**) and (**6**).

TABLE[a]

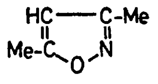
Solvent	Product yield/%					
Acetonitrile in the absence of (**6**)	(**5**)	(14·2)	(**2d**)	(4·6)		
Tetrahydrofuran	(**5**)	(13·7)	(**2d**)	(16·7)		
Methanol-triethylamine ..	(**2a**)	(27·4)	(**3**)	(12·0)	(**2d**)	(19·1)
Propan-2-ol	(**2c**)	(29·4)				

[a] The amount of recovered starting material was not determined.

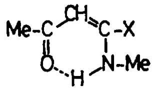
Results obtained using various solvents are summarized in the Table. Identification of the products was done spectroscopically. The fact that no reduction product was detected in the reaction in propan-2-ol or tetrahydrofuran eliminates path (a). As both (**1**) and (**6**) have absorption maxima in nearly the same wavelength region, there might be a possibility that (**6**) undergoes photolysis and the photolysis products (or unstable intermediates) induced the reduction of (**1**) [path (b)]. Therefore, we carried out the irradiation with varying ratios of (**1**) and (**6**). As the (**6**) : (**1**) ratio was increased from 1 to 5 and then to 10, the yield of (**7**) in a limited reaction time decreased from 69% to 16% and then to 6%, as determined by gas chromatography and n.m.r. spectroscopy using bromobenzene as internal reference. This observation indicates that the reaction is initiated by the excitation of (**1**) and thus path (b) is ruled out.

The formation of minor product (**2b**) is considered to involve (**9**) which could be derived from (**4**).

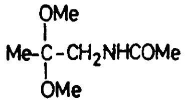
We conclude from our observations (i) that (**4**) and (**5**) are primary products in the conventional photolysis of (**1**), although these products are actually isolable in the solvent-participated forms in most cases, and (ii) that the path leading to (**5**) is replaced by photoreduction through an encounter complex formation,[3] when irradiation was carried out in acetonitrile in the presence of (**6**), but the path leading to (**4**) is left intact under these conditions.



(1)

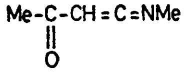


(2)


$\mathrm{Me{-}\overset{\displaystyle OMe}{\underset{\displaystyle OMe}{C}}{-}CH_2NHCOMe}$

(3)

a, X = OMe c, X = OPr^i
b, X = NEt$_2$ d, X = OH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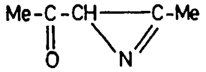
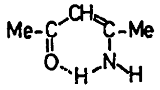
(4)



(5)



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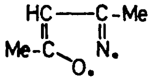
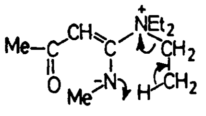


(8)



(9)

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[3] J. A. Barltrop, *Pure Appl. Chem.*, 1973, **33**, 179.