Photolysis of 2-Diazo-2-phenylacetophenone *O*-Benzyloxime and its Subsequent Products

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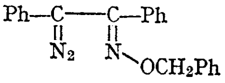
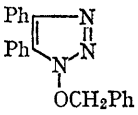
THIS investigation involves photolysis of 2-diazo-2-phenylacetophenone *O*-benzyloxime (I) and its products. This photochemical system is of interest because (a) the major photochemical process occurring with loss of nitrogen results in intramolecular carbon–hydrogen insertion rather than isomerization to diphenylketen *O*-benzyloxime (the product of Wolff rearrangement) or 1-benzyloxy-2,3-diphenylarizine, and (b) the initial product undergoes rapid dehydrogenation, photoisomerization, and photo-oxidation.

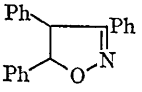
Diazo-compound (I) of probable α-stereochemistry and 1-benzyloxy-4,5-diphenyl-1,2,3-triazole (II; m.p. 137°) are obtained from the *O*-benzyl ether of α-oximinobenzil[1,2] and toluene-*p*-sulphonylhydrazide and decomposition of the resulting toluene-*p*-sulphonylhydrazone (m.p. 173°) with sodium methoxide.

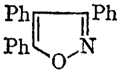
Photolysis of (I) in pentane or diethyl ether at >3000 Å at 15° results in triphenylisoxazolines[3] (III; minor) and triphenylisoxazole (IV; major). Irradiation of (I) thus involves loss of nitrogen and the initial stereochemistry about the alkoximino-group[4] and major carbon–hydrogen insertion to give isoxazolines (III);[5] dehydrogenation of (III) by (I) yields isoxazole (IV)[5] Photolysis of (I) resulting in high-order 1,5-carbon–hydrogen insertion rather than phenyl migration presumably results from a carbenic process having favourable stereochemistry.

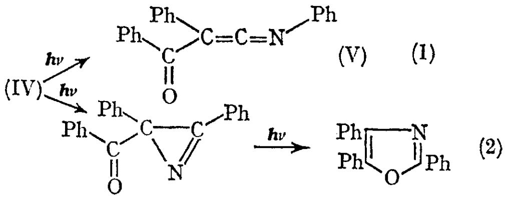
Irradiation of triphenylisoxazole (IV) at 15° in pentane, diethyl ether, or benzene at >3000 Å or at 2537 Å (Equations 1 and 2) results in *N*-phenylbenzoylphenylketenimine[5] (V; ~ 40%), 3-benzoyl-2,3-diphenylazirine (VI),[6] and triphenyloxazole (VII; ~ 40%).[6] Photolysis of (IV) to (V) is a rapid


(I)


(II)


(III)


(IV)



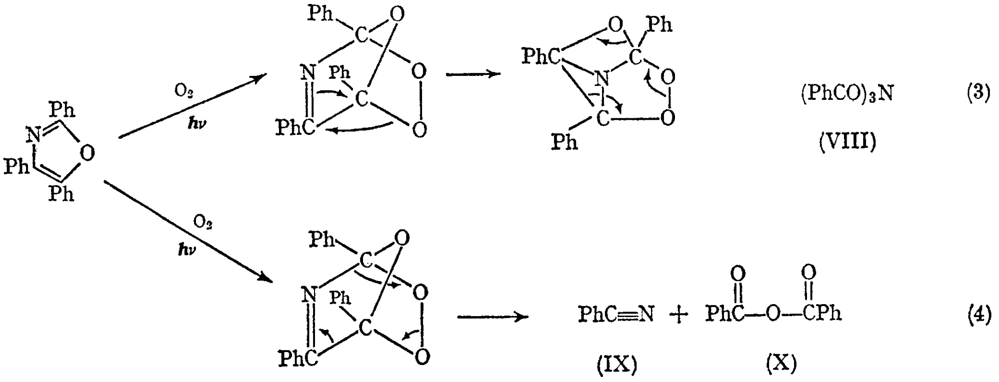
(V) (1)

(VI) (VII) (2)

and convenient method for preparing a keto-ketenimine.[7] Ketenimine (V) is identified by its keten and imine absorptions at 4·9 μ and 6·2 μ and by its conversion by moisture into 2-benzoyl-2-phenylacetanilide. The structure of azirine (VI) is indicated by its absorptions at 5·6 μ and 5·9 μ for azirine C=N and conjugated carbonyl, by comparison with 3-benzoyl-2-phenyl-1-azirine[6] and by its photolytic conversion into triphenyloxazole (VII). Oxazole (VII) is isolable by chromatography and crystallization.

formally analogous to thermolysis of α-azidostyrene to 2-phenyl-1-azirine and *N*-phenylketenimine.[8] The resistance of azirine (VI) to photoisomerization to isoxazole (IV) does not parallel the specific photolytic conversion of 3-benzoyl-2-phenyl-1-azirine into 3,5-diphenylisoxazole.[6]

Irradiation of triphenyloxazole (VII) in diethyl ether or benzene in oxygen at >3000 Å yields tribenzoylamide (VIII),[5,9] benzonitrile (IX),[5] and benzoic anhydride (X).[5] Photolysis of isoxazole (IV) in oxygen gives (VIII), (IX), and (X) along with ketenimine (V). It is apparent that oxazole (VII) is an intermediate in photo-oxidation of (IV) and there is partitioning of (IV) to (V) under these conditions. Possible sequences for the photo-oxidation of (VII) to (VIII), (IX), and (X) are indicated in Equations 3 and 4. The conversion of (VII) into (IX) and (X) by photo-oxidation of is interest in that (VII) appears to undergo 1,4-photoaddition of oxygen and a reverse Diels–Alder reaction of an intermediate bicyclic peroxide.



$(PhCO)_3N$ (3)

(VIII)

$PhC\equiv N + PhC(=O)-O-C(=O)Ph$ (4)

(IX) (X)

Photolysis of azirine (VI) at ~3000 Å or at 2537 Å yields oxazole (VII). Neither (VI) nor (VII) photoisomerizes to ketenimine (V) or to isoxazole (IV) at these wavelengths. Irradiation of isoxazole (IV) thus involves competitive formation of (V) and of (VI) and (VII). Photolysis of triphenylisoxazole (IV) resulting in phenyl migration to nitrogen to yield a ketenimine (V) is different from that observed for 3,5-diphenylisoxazole.[6] The photolytic behaviour of (IV) is

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[1] K. Auwers and M. Dittrick, *Ber.*, 1889, **22**, 2000.

[2] *O*-Benzil-α-oximinobenzil isomerizes to the β-isomer in hot acidic ethanol; the β-isomer does not form a toluene-*p*-sulphonylhydrazone in refluxing methanol apparently because of steric factors.

[3] Triphenylisoxazolines occur as *cis*- and *trans*-isomers.

[4] It is not known whether *cis, trans*-isomerization about the oximino-group occurs before or after loss of nitrogen during photolysis.

[5] A new reaction.

[6] E. F. Ullman and B. Singh, *J. Amer. Chem. Soc.*, 1966, **88**, 1844, have recently reported that photolysis of 3,5-diphenylisoxazole yields 3-benzoyl-2-phenyl-1-azirine and 2,5-diphenyloxazole.

[7] R. B. Woodward and D. J. Woodman, *J. Amer. Chem. Soc.*, 1966, **88**, 3169, have communicated the first synthesis of keto-ketenimines by reaction of isoxazolium perchlorates with triethylamine.

[8] G. Smolinsky, *J. Org. Chem.*, 1962, **27**, 3557.

[9] Prof. H. H. Wasserman has informed us privately that he and M. B. Floyd have found that triphenyloxazole reacts with oxygen in the presence of Methylene Blue and light to give tribenzoylamide, and this observation will be published shortly.