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PHOTOCHEMICAL BEHAVIOUR OF CYCLIC IMINO ETHERS: THE N–O BOND FISSION, *syn–anti* ISOMERIZATION AND CYCLOADDITION REACTIONS IN THE C=N–O CHROMOPHORE*

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Summary

Photochemical reactions of 3-aryl-2-isoxazolines and six-, seven- and eight-membered analogues were investigated. 3-Phenyl-dihydro-1,2-oxazine was irradiated to give several products which were derived from the initial N–O bond fission, whereas the seven- and eight-membered analogues were found to be stable to light. Only the *syn–anti* isomerization was observed. In addition, a novel [2 + 2] photocycloaddition reaction of 2-isoxazolines having cyano or methoxycarbonyl groups on the 3-aryl moiety with some aromatic compounds such as benzene, furan, indene and thiophene was discovered. The UV absorption and emission spectra of 3-phenyl-2-isoxazoline and its related heterocyclics are also discussed.

It is well documented that radiationless decay due to twisting around the C=N bond is responsible for the low reactivity of the excited imino compounds [1]. If the Ph–C=N–O chromophore is not constrained in a rigid ring system, a decay process consisting of the *syn–anti* isomerization should be the main photochemical reaction path for the imino ethers. For instance, the excited state of the *O*-methyl ether of acetophenone oxime **1** (Fig. 1) exhibits neither bond fission nor an emission spectrum [2]. Contrary to this, if the Ph–C=N–O chromophore is constrained in a rigid ring, the excited state of imino ethers should show other types of photoreaction because of inhibition of the *syn–anti* isomerization [3]. The photochemistry of 3-phenyl-2-isoxazoline **2** (Fig. 1) shows this case; many studies have been carried out on the 4- and/or 5-substituted derivatives and they disclose that the reactions start usually from N–O bond fission [4 - 6]. This sharp contrast in the photochemical behaviour of the constrained and non-constrained imino ethers prompted us to study the photoreactions of six-, seven- and eight-membered heterocyclics (Fig. 1, 3, 4 and 5) in addition to the five-membered analogue **2**.

For the photochemistry of the 3-phenyl-2-isoxazoline derivatives **2**, the general reaction pattern proposed is shown in Fig. 2 [4, 7]. The reaction starts

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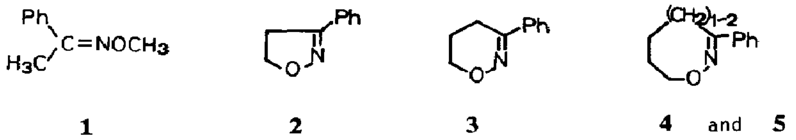

Fig. 1.

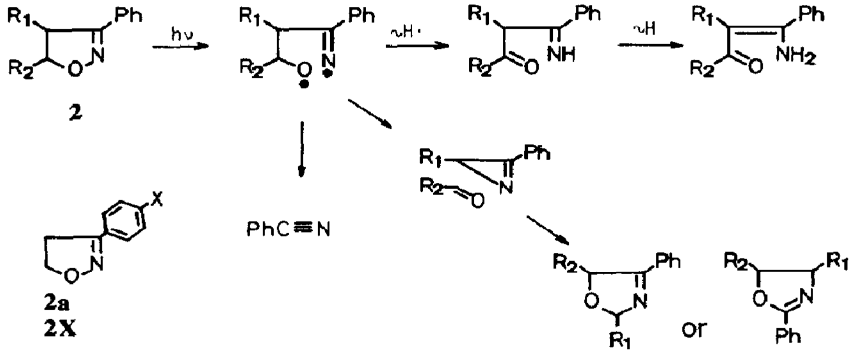

Fig. 2.

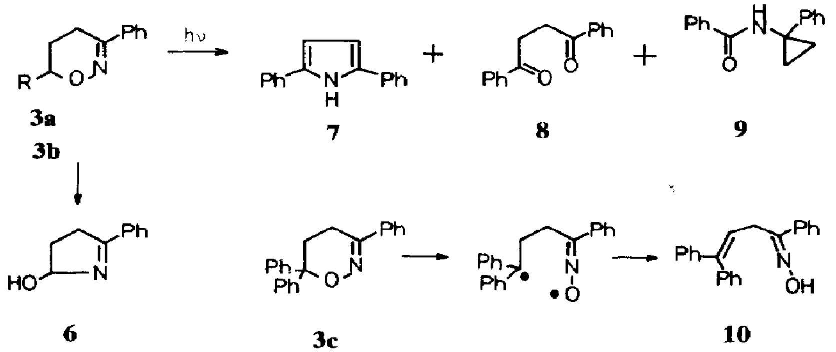

Fig. 3.

from N–O bond fission but the introduction of a phenyl group at position 5 leads to C–O bond fission [4, 5]. Our study was extended to the photochemistry of 3-phenyl-2-isoxazoline **2a** (X ≡ H) and its derivatives 2X possessing electron-donating or electron-withdrawing groups (X ≡ CH_3, OCH_3, or X ≡ CN, NO_2) on the phenyl substituent as well as naphthyl and thienyl groups. It was found that the N–O bond fission does not depend on the electronic character of the substituent but on the magnitude of the singlet energies of the substrates [8].

The photoreactions of six-membered analogues are summarized in Fig. 3 [9]. On irradiation, the 3-phenyl-4,5-dihydro-1,2-oxazine **3a** (R ≡ H) gave quantitatively 5-hydroxy-2-phenylpyrroline **6**, and the 3,5-diphenyl derivative **3b** (R ≡ phenyl) afforded three photoproducts **7**, **8** and **9** in 15%, 21% and 28%

yields respectively. All these products were derived from species arising from cleavage of the N–O bond. In addition, irradiation of the 3,6,6-triphenyl derivative **3c** produced a 1 : 1 mixture of the oximes *syn*-**10** and *anti*-**10** in 80% yields. The dihydro-1,2-oxazine derivatives **3** showed different types of photolysis depending on the substituents. It can be concluded that five-and six-membered cyclic imino ethers exhibit similar photochemical behaviours in the initial step.

In contrast, seven- and eight-membered cyclic imino ethers, *i.e.* 3-phenyltetrahydro-1,2-oxazepine **4** and 3-phenyl-1-oxa-2-aza-2-cyclooctene **5** (Fig. 4), were found to be inert to irradiation. This stability might be attributed to the photochemical equilibrium between *anti*- and *syn*-isomers which was deduced from low temperature photolysis.

In addition to the photoreactions mentioned above, a novel [2 + 2] type of photocycloaddition of the C=N bond of 3-phenylisoxazolines **2** with some aromatics was discovered. 2-Isoxazolines with cyano and methoxycarbonyl groups on the 3-aryl moiety, *e.g.* 2CN and 2E (X ≡ $COOCH_3$), form 1 : 1 adducts with benzene, indene, furan, dihydrofuran and thiophene as shown in Fig. 5. A Diels–Alder reaction of photoproduct **11** with maleic anhydride gave cycloadduct **12** with 80% yield. With *p*-xylene, 2CN undergoes a hydrogen abstraction reaction giving adduct **13** with 58% yield. Azetidine formation, which was induced on

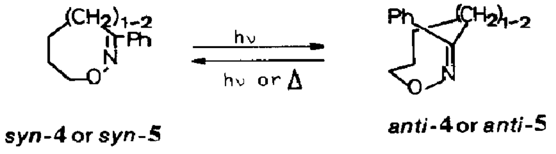

Fig. 4.

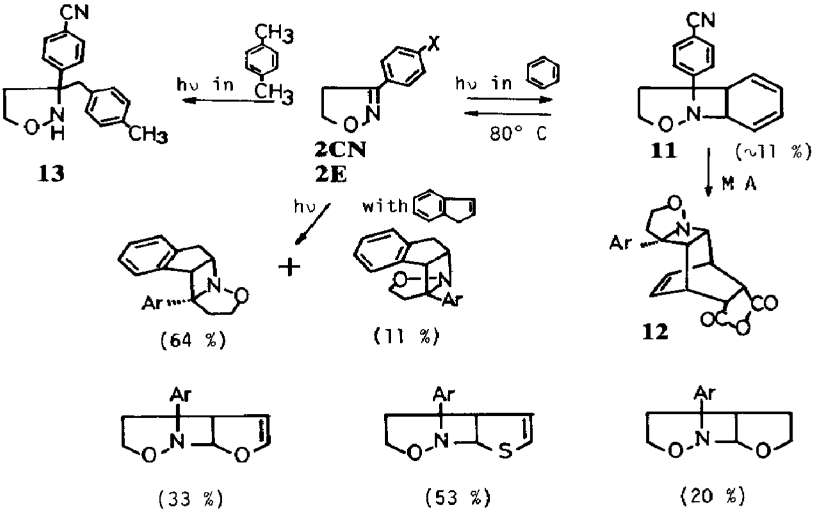

Fig. 5.

irradiation of the C=N–O group, and the hydrogen abstraction reaction are rather uncommon photochemical reactions for the cyclic imino ethers.

In order to learn which excited species, *i.e.* (n,π^*) or (π,π^*) singlet or triplet state, is responsible for the photoreactions of **2a**, the UV and emission spectra were measured at −196 °C. On irradiation at room temperature **2a** immediately undergoes photoreaction (see Fig. 2) without any detectable emission, but at liquid nitrogen temperature the singlet state of **2a** is chemically unreactive and exhibits strong fluorescence. The phosphorescence of **2a** could not be detected even under degassed conditions. Thus it is concluded that the photoreactions of **2a** originate from the (π,π^*) singlet state.

The relationship between rigidity of the ring and photoreactivity should be discussed on the basis of the spectral properties of **2a**, **3a** and **4a**.

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