Photorearrangement of 2-Phenyloxazole

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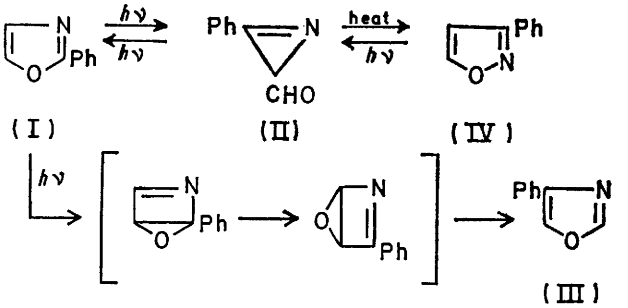
Summary Irradiation of 2-phenyloxazole (I) in benzene or cyclohexane gives 3-phenyl-2*H*-azirine-2-carbaldehyde (II) [thermally converted into 3-phenylisoxazole (IV)] and 4-phenyloxazole (III).

We have reported[1] that irradiation of 2,5-diphenyloxazole gives 3,5-diphenylisoxazole, 4,5-diphenyloxazole, and 2,4-diphenyloxazole. The conversion of 2,5-diphenyloxazole into 3,5-diphenylisoxazole was thought to involve the intermediacy of 2-benzoyl-3-phenyl-2*H*-azirine, but this species was not isolated. We have now found that 3-phenyl-2*H*-azirine-2-carbaldehyde (II) is obtained on irradiation of 2-phenyloxazole (I).



Irradiation (100 W high-pressure mercury lamp; 80°; 38 h; under nitrogen) of a solution (3·1 × 10^{-2}M) of (I) in benzene, followed by chromatography on silica gel, gave the azirine (II) (11·9%), m.p. 44°, and 4-phenyloxazole (III)[2] (2·2%), together with starting material (I) (34·9%). A trace of 3-phenylisoxazole (IV)[3] was also detected (n.m.r. spectrum).

The structure (II) was supported by i.r. absorptions at 1774 (2*H*-azirine C=N[4,5]), 2820, 2720, and 1712 cm^{-1} (aldehyde). The u.v. absorption [241 nm (ϵ 15,000)] was similar to those of 3-phenyl-2*H*-azirine[4] and 2-aroyl-3-aryl-2*H*-azirines,[5] and the longer-wavelength tail of the band showed a shoulder at 335 nm (ϵ 110) suggestive of a carbonyl $n \rightarrow \pi^*$ band. The n.m.r. spectrum showed doublets at δ 2·88 (=NCH, 1H, *J* 7 Hz) and 8·95 (CHO, 1H, *J* 7 Hz) and aromatic signals at δ 7·5—8·0 (5H).

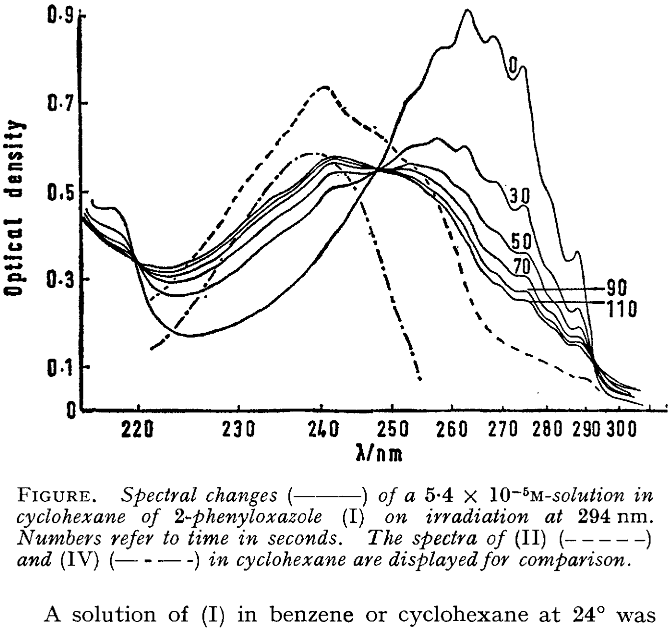


Figure. *Spectral changes* (———) *of a* 5·4 × 10^{-5}M-*solution in cyclohexane of* 2-*phenyloxazole* (I) *on irradiation at* 294 nm. *Numbers refer to time in seconds. The spectra of* (II) (- - - - -) *and* (IV) (— - — -) *in cyclohexane are displayed for comparison.*

A solution of (I) in benzene or cyclohexane at 24° was irradiated with 294 nm light† and the reaction was monitored by u.v. spectroscopy and g.l.c. Concomitant with the decrease of the absorption band (264 nm) of the starting material (I), a new band at 241 nm appeared. This change indicated the formation of the azirine (II); the formation of (IV) [$\lambda_{max.}$ 239 nm (ϵ 10,500)] was not observed (see Figure). The formation of (II) and (III) was also shown by g.l.c. but no (IV) was detected. Under the same conditions, (III) gave no isomeric product. Thus the azirine (II) is not derived from (IV) but directly from (I).

It is generally known that 2*H*-azirines are photochemically or thermally formed from isoxazoles.[5-7] Irradiation of (IV) also led to compounds (I) and (II). Irradiation of

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† The selected light (*ca.* ± 7·5 nm width) was obtained from a concave radiating monochromator (2 kW xenon-discharge lamp, Japan Spectroscopic Company, model CRM-FA).

(II) gave the starting oxazole (I) regardless of the wavelength of the light,‡ although the disappearance of (II) was very slow with light of long wavelengths. However, heating (II) at 200° for 28 h in benzene gave the isoxazole (IV) in 77% yield. The resistance to the conversion of (II) into (IV) under irradiation contrasts with the specific photorearrangements of 2-aroyl-3-aryl-2*H*-azirines to 3,5-diarylisoxazoles[5] but is analogous to the photorearrangement of 2-benzoyl-2,3-diphenyl-2*H*-azirine to 2,4,5-triphenyloxazole.[7]

In the photorearrangements of oxazoles proceeding with formal interchange of adjacent ring atoms carrying substituents, we believe that the initial photoproduct is an azirine species which undergoes further photochemical or thermal rearrangement to an isoxazole. The conversion of (I) into (III) could well proceed *via* a bicyclic intermediate as in the photorearrangement of 2,5-diphenyloxazole to 4,5-diphenyloxazole.[1]

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‡ 255, 282, 327, or 335 nm.

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