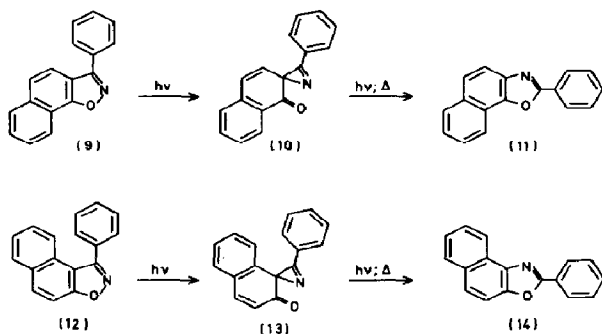


The photochemistry of benzisoxazoles depends strongly on the substituent R at position 3.

(4c) yields salicylonitrile exclusively in non-polar solvents; (4a) with about equal and rather low quantum yields the oxazole (8a) and *N*-methylsalicylamide [2c]; (4b), however, yields almost exclusively the oxazole (8b). In protic polar solvents such as water, methanol, or propanol-2 all three compounds are almost quantitatively converted into the corresponding oxazoles with high quantum yields. The naphthisoxazoles (9) and (12) behave like (4b), *i.e.* they form oxazoles in both polar and non-polar solvents.



Scheme 3

I.r. spectra

I.r. spectra were measured with a NaCl cell of 0.1 mm optical pathlength, suitable for low temperature work [4]. Since relatively high concentrations of the transients have to be generated in order to take their *i.r.* spectra, the concentration of the starting material has to be high too. Therefore the exciting light will be absorbed within a very thin layer. If the intermediate itself is photoreactive and the shape of the u.v. absorption spectra does not allow selective excitation of the starting material, care has to be taken to minimize excitation of the transient. This is achieved to some extent by choosing a solvent which is still fluid enough at the applied low temperature to allow the intermediate to diffuse into volume layers which are not penetrated by light. We used CH₂Cl₂ as the solvent for the illumination of (4b), (9), and (12), and CD₃OD for (4a). In the latter case CH₂Cl₂ could not be used because (4a) forms oxazole only in protic solvents, as mentioned above. Two new *i.r.* bands develop if the compounds listed in Table 1 are illuminated with 254 nm light. They disappear if the samples are allowed to warm up to room temperature.

U.v. spectra

U.v. measurements were carried out in the solvents methanol, propanol-2, and dichloromethane with a Cary 17 spectrophotometer. Compounds (4b), (9), and (12) were excited with 254 nm light, compound (4a) at 280 nm.

In order to minimize excitation of photoproducts, the optical density of the solution at the wavelength of excitation was adjusted to the rather high value of about 3 and only small amounts of the solute were photolyzed.

With all four compounds a transient was observed with an absorption spectrum extending to longer wavelengths than the starting material. Its lifetime at room temperature varies from compound to compound. At sufficiently low temperatures [(4a), $-96\text{ }^{\circ}\text{C}$; (4b), $-80\text{ }^{\circ}\text{C}$; (9) and (12), $-30\text{ }^{\circ}\text{C}$] the u.v. absorption spectra could be recorded. After warming to room temperature the transients disappeared and the absorption bands of the corresponding oxazoles were observed. In the case of compounds (9) and (12) the simultaneous decay of the transient and the formation of the oxazole could be observed at room temperature with the Cary 17 spectrophotometer at fixed wavelengths. The corresponding first order rate constants for the transient decay and product formation agree very well. Similar experiments were carried out with (4a) and (4b) by means of flash excitation (see below). Exclusive excitation of the transient at the above mentioned temperatures in the long wavelength region with a cutoff filter that absorbs all light below 320 nm has different effects depending on the starting material. The transients generated from (4b), (9), and (12) are at least partly converted into the oxazoles (8b), (11), and (14), respectively, by the long wavelength excitation; whereas the transient from (4a) yields mainly, if not entirely, the starting material. All four transients are to some extent converted into the oxazoles if they are excited with 254 nm light.

Flash experiments

Flash experiments were carried out with solutions of (4a) and (4b) in different solvents. The apparatus used has been described elsewhere [5]. Flashing a solution of (4b) at $20\text{ }^{\circ}\text{C}$ in propanol-2 or methanol reveals the existence of a transient with a half-life of 1.34 s in propanol-2 and 0.16 s in methanol. It has an absorption maximum at 350 nm in both solvents. Neither (4b) nor the final product (8b) absorb in this wavelength region and the decay of the transient can be observed at 350 nm without interference from other compounds. At 313 nm, however, the final product (8b) has the highest extinction coefficient and its build-up can be observed. It occurs with exactly the same first-order rate constant as the decay of the transient measured at 350 nm. A similar transient with an absorption maximum at 350 nm and a half-life of 0.041 s is observed if one flashes a solution of (4a) in methanol. In this case, however, the build-up of (8a) cannot be followed kinetically because there exists no suitable wavelength region where the extinction coefficient of (8a) is higher than that of (4a).

The temperature dependence of the transient decay is depicted in Fig. 1. The flash experiments have been carried out between $+40$ and $-20\text{ }^{\circ}\text{C}$. Below $-20\text{ }^{\circ}\text{C}$ the rate constants become too small to be determined accurately with the flash apparatus. The values for temperatures around $-60\text{ }^{\circ}\text{C}$ predicted from the extrapolated Arrhenius plot (cf. Fig. 1) agree very well with the values which were determined in this temperature region with a Cary 17 spectrophotometer at a fixed (350 nm) wavelength. At the temperatures at which the u.v. spectra were recorded (see above) the calculated lifetimes of these transients are 230 ± 70 min.

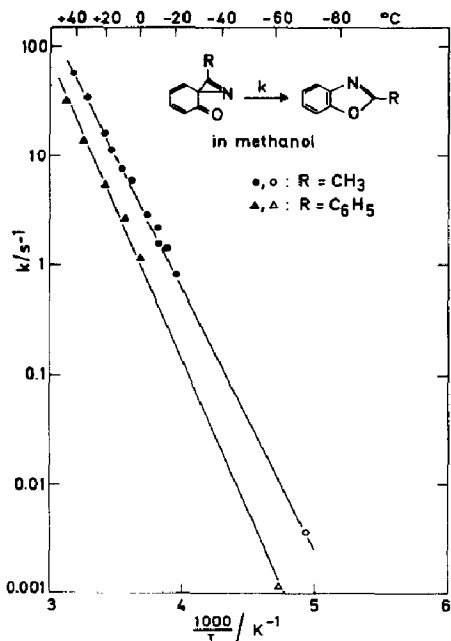


Fig. 1. Arrhenius plot of the decay of azirine (6a) (●, ○) and (6b) (▲, △) in methanol. Solid symbols: rate constant k determined by flash photolysis; open symbols: rate constant k determined with a Cary 17 spectrophotometer. In the latter case a solution was illuminated in a thermostated 1 cm quartz cell inside the Cary cell compartment for a few minutes and the decay of the optical density afterwards monitored at 350 nm with constant chart speed. $k = 2.2 \times 10^9 \exp(-11,000/RT)$, (6a); $k = 1.6 \times 10^{10} \exp(-12,700/RT)$, (6b).

Discussion

The i.r. absorption bands observed at low temperatures (Table 1) are characteristic for azirine ring systems ($1770 - 1790 \text{ cm}^{-1}$) [3] and ketones (1650 cm^{-1}). We therefore assign the structures (6) (Scheme 2), (10) and (13) (Scheme 3) to these low temperature intermediates. Since after warming to room temperature the azirines disappear and the corresponding oxazoles are formed, it is plausible to assume that the azirines are precursors of the final products, as indicated in Schemes 2 and 3.

To prove this assumption one has to link the i.r. results with the experiments in the u.v. region. In the latter case it is quite evident from the observed rate constants that the transients with absorption maxima around 350 nm are precursors of the oxazoles. In three cases the build-up of the photoproduct and the decay of the transient could be compared directly [compounds (4a), (9), and (12)]. Furthermore, the absorption spectra determined by means of flash spectroscopy at higher temperatures and the "steady state" absorption spectra at lower temperatures are identical. The Arrhenius plot of decay rates measured by flash photolysis between $+40$ and -20 °C predicts values at still lower temperatures which were confirmed experimentally with the Cary 17 spectrophotometer (cf. Fig. 1).

TABLE 1

Location of i.r. peaks generated during the illumination of isoxazole solutions with 254 nm light.

Compound	Solvent	Temp. (°C)	I.r. maxima (cm ⁻¹)
4a	CD ₃ OD	-90	1780, 1650
4b	CH ₂ Cl ₂	-50	1790, 1650
9	CH ₂ Cl ₂	-30	1770, 1661
12	CH ₂ Cl ₂	-30	1776, 1647

It remains, however, to be shown that these transients are identical with the azirines observed in the i.r. region. If this is the case they should have the same lifetime at a given temperature. It is not easy to perform kinetic experiments in the i.r. region with these systems. We measured the lifetime of the azirine and ketone i.r. peak in one case with a solution of (4b) in CH₂Cl₂ at -50 °C which agreed well with the lifetime of the transient absorption at 350 nm in CH₂Cl₂ at the same temperature.

Taking all the other experimental data into account, we feel it justified to assume that the photochemical conversion of all four isoxazoles investigated proceeds via azirines, as indicated in Schemes 2 and 3.

The azirines observed here are much more unstable than (2). This is not surprising because the rearrangements of (6), (10), and (13) to the corresponding oxazoles convert the cyclohexadienone structure of the azirines into the aromatic system of the final products. Preliminary experiments show that the lifetimes of the azirines are considerably longer in non-polar solvents. This might be an indication for the involvement of polar structures such as (7) during the decay of the azirines. The short lifetime of (6a) and its photochemical reactivity require sufficiently low temperatures, relatively high solute concentrations and a suitable wavelength of excitation in order to produce measurable amounts of the transients. Illumination of (4a) with 254 nm light for instance results in a much lower steady state concentration than excitation at 280 nm, where (4a) has an absorption maximum and (6a) absorbs much less. This might be the reason why (6a) has not been detected in previous investigations [2c].

It is interesting to note in this context, that the azirine (6a) behaves similarly to the azirine (2) with respect to long wavelength excitation (see above). Singh and Ullman reported [1a, b] that (2) is entirely converted back into the isoxazole (1) if its long wavelength band is excited selectively. The distinct difference in the photoreactivity of (6b), (10), and (13) under long wavelength excitation compared with that of (6a) merits further investigations.

TABLE 2

Compound	Solvent	U.v. maximum (nm)	Lifetime at 20 °C (s)
6a	methanol	350	0.041
6b	propanol-2	350	1.34
10	propanol-2	350 (shoulder)	3000
	hexane		7000
13	propanol-2	350 (shoulder)	500
	hexane		750

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- 4 A detailed description of the cell will be published elsewhere.
- 5 E. W. Förster, K. H. Grellmann and H. Linschitz, *J. Am. Chem. Soc.*, 95 (1973) 3108.