

## Strong Evidence for Thiazirines as Stable Intermediates at Cryogenic Temperatures in the Photolytic Formation of Nitrile Sulphides from Aryl-substituted 1,2,3,4-Thiatriazole, Thiatriazole 3-Oxide, and 1,3,4-Oxathiazol-2-one

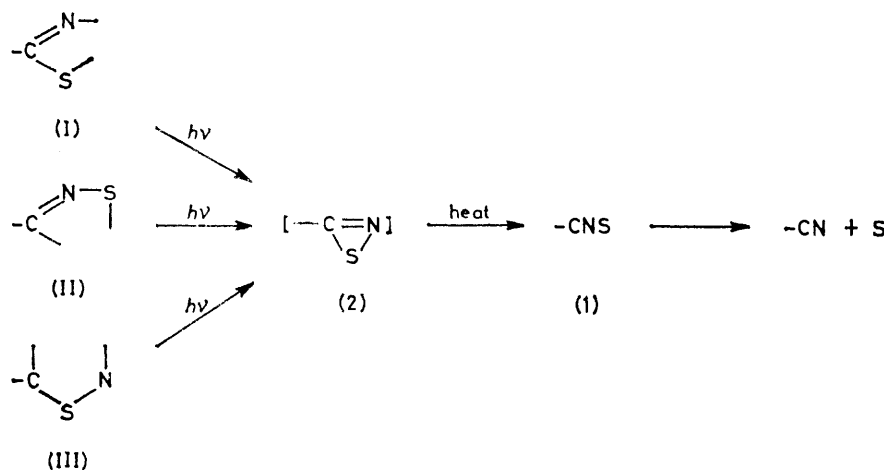
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The photolysis of phenyl-substituted C-, N-, and S-containing heterocyclic compounds embedded in poly(vinyl chloride) (PVC) at 10–15 K has been studied. A compound believed to be phenylthiazirine was formed in each case. It is stable at 10–15 K, and on heating it rearranges to benzonitrile sulphide, which at still higher temperature decomposes to benzonitrile and sulphur.

THIAZIRINES, planar cyclic systems containing 4  $\pi$ -electrons in a cyclic array, are hitherto unknown. They belong to the group of compounds designated antiaromatic by Breslow.<sup>1</sup> The preparation and isolation of the related thiiren and seleniren by photolysis of matrix-isolated 1,2,3-thiadiazole and 1,2,3-selenadiazole,

Since thiazirines, if they exist, would be expected to be stable only at very low temperatures, we have studied the photolytic formation of nitrile sulphides at temperatures around 10–15 K.

The u.v. spectrum of benzonitrile sulphide has been recorded in an EPA glass at 85 K. The molecule was



SCHEME 1

respectively, has been reported recently.<sup>2</sup> Evidence for the transient formation of oxiren<sup>3</sup> and azirine<sup>4</sup> has been obtained, but neither the parent nor derivatives of these molecules have been isolated.<sup>5</sup>

A number of five-membered heterocyclic compounds, described by the general formulae (I)–(III), give rise to the thermally labile nitrile sulphides (1) on irradiation.<sup>6,7</sup> Thiazirines (2) are reasonable precursors of the nitrile sulphides, but the reactions may take place with direct formation of nitrile sulphide without intermediates or, less likely, proceed *via* an individual mechanism in each case.

<sup>1</sup> R. Breslow, *Accounts Chem. Res.*, 1973, **6**, 393; *Chem. Eng. News*, 1965, **43**, 90.

<sup>2</sup> A. Krantz and J. Laurenzi, *J. Amer. Chem. Soc.*, 1977, **99**, 4842.

<sup>3</sup> For recent work see the following papers and references therein: O. P. Strausz, R. K. Gosavi, A. S. Denes, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, 1976, **98**, 4784; H. Kropf and R. Schröder, *Annalen*, 1976, **2325**; K.-P. Zeller, *Tetrahedron Letters*, 1977, **707**; U. Timm, K.-P. Zeller, and H. Meier, *Tetrahedron*, 1977, **33**, 453; E. G. Lewars and G. Morrison, *Canad. J. Chem.*, 1977, **55**, 966.

<sup>4</sup> T. L. Gilchrist, C. W. Rees, and C. Thomas, *J.C.S. Perkin I*, 1975, **8**.

generated by irradiation of 5-phenyl-1,2,3,4-thiatriazole (3), 5-phenyl-1,3,4-oxathiazol-2-one (5), or 4-phenyl-1,3,2-oxathiazolium-5-olate (7).<sup>6</sup> Upon heating, decomposition of benzonitrile sulphide took place around 140 K according to Scheme 1 simultaneously with melting of the glass. At room temperature benzonitrile sulphide has been trapped as a cycloaddition product with dimethyl acetylenedicarboxylate by irradiation of each of the substrates (3), (5), and (6)<sup>6</sup> as well as by irradiation of nine other compounds derived from heterocycles of types (I) and (II).<sup>7</sup>

Besides (3), (5), and (7), two other compounds, (4) and (6) have been included in the present investigations.

<sup>5</sup> However, derivatives of thiiren 1-oxide,<sup>a</sup> thiiren 1,1-dioxide<sup>b</sup> and 1-methylthiirenium ion<sup>c</sup> have been prepared: (a) L. A. Carpino and H.-W. Chen, *J. Amer. Chem. Soc.*, 1971, **93**, 785; (b) L. A. Carpino, L. V. McAdams, III, R. H. Rynbrandt, and J. W. Spiewak, *J. Amer. Chem. Soc.*, 1971, **93**, 476; L. A. Carpino and J. R. Williams, *J. Org. Chem.*, 1974, **39**, 2320; (c) G. Capozzi, O. De Lucchi, V. Lucchini, and G. Modena, *J.C.S. Chem. Comm.*, 1975, 248.

<sup>6</sup> A. Holm, N. Harrit, and N. H. Toubro, *J. Amer. Chem. Soc.*, 1975, **97**, 6197.

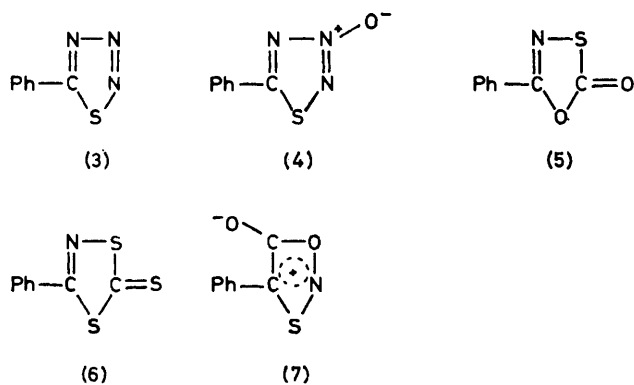
<sup>7</sup> A. Holm and N. H. Toubro, *J.C.S. Perkin I*, in the press.

They all give rise to benzonitrile sulphide at room temperature.<sup>7</sup>

We have recently observed that photolysis of 5-phenylthiatriazole (3) in an argon matrix at 10 K leads to benzonitrile without the apparent intermediacy of benzonitrile sulphide (as shown by u.v. spectroscopy).<sup>8</sup> A possible explanation for this result is that vibrational energy is not sufficiently effectively transferred to the gas matrix and the benzonitrile sulphide formed in a vibrationally excited state is immediately converted into benzonitrile even at 10 K.<sup>9</sup> For the present studies we have employed u.v. spectroscopy and a poly(vinyl chloride) film (PVC) as matrix with the idea that vibrational energy might be more effectively transferred within this matrix material. We have previously described the dramatic thermal stabilization of benzonitrile sulphide which takes place when PVC is used instead of EPA glass. The u.v. spectrum of benzonitrile sulphide could still be observed even after heating the sample to room temperature.<sup>6</sup> This effect is probably related to the high and temperature-insensitive viscosity of the polymer and a positive volume of activation for the process involved. Combination of the effects here mentioned may explain the successful detection of a photolytically formed precursor of benzonitrile sulphide, believed to be phenylthiazirine, as described below.

#### EXPERIMENTAL

Compounds (3)–(7) were obtained as described elsewhere.<sup>7</sup> Poly(vinyl chloride) films were prepared<sup>10</sup> by dissolving *ca.* 1 mg of the heterocyclic compound (resulting absorbance *ca.* 1) and 250 mg of PVC (I.C.I., Corvic D 65/13) in tetrahydrofuran (10 ml), passing the solution through basic alumina, and allowing it to evaporate in a covered dish (10 cm diam.) overnight. A small strip of the



film (corresponding to less than  $10^{-3}$  mg of heterocycle) attached to metallic copper was placed in a He-quartz glass double-walled flow tube, which was supplied by a feed-back system to an evaporation resistor in the He container, allowing any temperature between 10 and *ca.* 300 K to be

\* Photolysis experiments with 4-phenyl-1,3,2-oxathiazolium-5-olate in EPA at 85 K demonstrate that the optimum amount of benzonitrile sulphide generated from the oxathiazole is of similar absorbance measured at the 340 nm band of the nitrile sulphide and at the 410 nm band of the oxathiazole ( $\epsilon$   $8.3 \times 10^3$  l mol<sup>-1</sup> cm<sup>-1</sup>) (unpublished results).

<sup>8</sup> A. Holm and B. Nelander, unpublished results.

established. The flow tube was placed in the sample chamber of a Cary 14 recording spectrophotometer. Irradiations were performed in the sample chamber with an Osram HBO

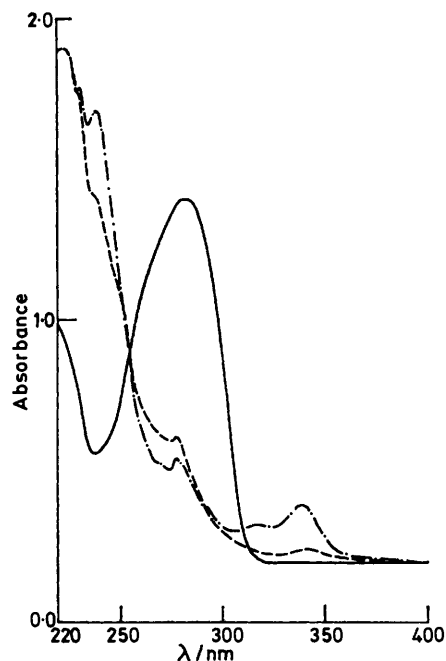


FIGURE 1 U.v. absorption spectra of 5-phenyl-1,2,3,4-thiatriazole (3) at 10–15 K in PVC before (a; —) and after photolysis (b; ---) ( $\lambda$   $280 \pm 14$  nm; almost quantitative conversion), and after subsequent warming to *ca.* 150 K (c; - · - · -)

200 high-pressure mercury lamp equipped with monochromator (Figures 1–3, and 5) or with a Varian VIX 300 W xenon lamp [Figure 4 and compound (6)]. During irradiations the temperature was maintained at 10–15 K.

#### RESULTS

5-Phenyl-1,2,3,4-thiatriazole (3).—The spectra before and after irradiation ( $\lambda$  280 nm) are shown in Figure 1. The most prominent change is the disappearance of the thiatriazole absorption around 280 nm and appearance of absorptions in the area of the previous minimum at 240–250 nm. Absorptions are observed [Figure 1(b)] at 340 and 240 nm assigned to benzonitrile sulphide<sup>6</sup> and at 277 and 231 nm assigned to benzonitrile.<sup>6</sup> We are not able to identify new bands indicative of compounds other than those mentioned here. However, on heating the sample a characteristic change takes place with formation of significant amounts of benzonitrile sulphide as shown in Figure 1(c). A general increase in absorption is noted [Figure 1(c)] and it seems not to be possible to associate the appearance of benzonitrile sulphide with the disappearance of specific bands in spectrum 1(b). If we assume a molar absorption coefficient ( $\epsilon$ ) for benzonitrile sulphide (340 nm band) of  $\geq 7 \times 10^3$  l mol<sup>-1</sup> cm<sup>-1</sup>,\* the amount corresponding to the

\* Cf. B. R. Henry and W. Siebrand, 'Organic Molecular Photophysics,' ed. J. B. Birks, Wiley, New York, 1973, vol. 1, ch. 4; F. Legay, 'Chemical and Biochemical Applications of Lasers,' ed. C. Bradley Moore, Academic Press, New York, 1977, vol. II, ch. 2.

<sup>10</sup> N. Geacintov, G. Oster, and T. Cassen, *J. Opt. Soc. Amer.*, 1968, **58**, 1217.

band in spectrum 1(b) is *ca.* 5% and in spectrum 1(c) *ca.* 20% based on converted starting material.

An approximately ten times more concentrated solid solution of thiatriazole in PVC than that used for the spectra in Figure 1 was irradiated, but apart from a general broadening in the absorptions above 300 nm as compared with the spectrum in Figure 1(b) no new bands were apparent.

In another series of experiments phenylthiatriazole was irradiated to the same degree of conversion as in Figure 1(b) [Figure 2(a)], and subsequently irradiated at selected wavelengths. Irradiation within the bands of benzonitrile sulphide<sup>6</sup> (340, 317, 293, and 240 nm) at either 340 or 293 nm caused rapid decomposition into benzonitrile. On subsequent heating benzonitrile sulphide was formed as mentioned above. On the other hand, irradiation for a longer period around 240–250 nm caused no significant change in

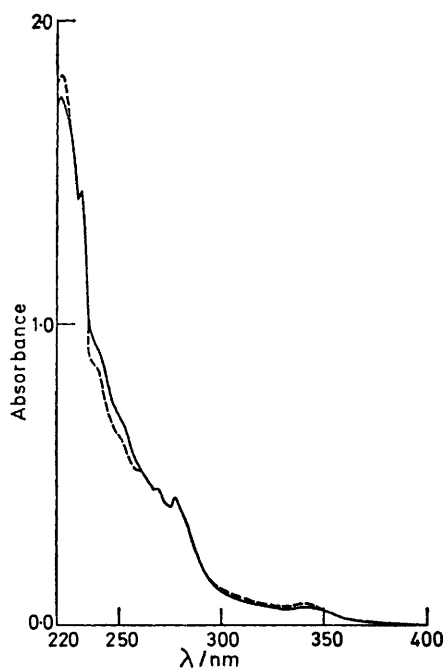


FIGURE 2 U.v. absorption spectra of 5-phenyl-1,2,3,4-thiatriazole at 10–15 K in PVC irradiated to the same degree of conversion as in Figure 1(b) (a; —) and subjected to subsequent irradiation (b; - - -) ( $\lambda$  240–250 nm)

the nitrile sulphide concentration (measured at 340 and 240 nm) [Figure 2(b)].

**5-Phenyl-1,2,3,4-thiatriazole 3-Oxide (4).**—The photolytic conversion of compound (4) was conducted to the extent of *ca.* 40% ( $\lambda$  280 nm) shown in Figure 3(b). On heating benzonitrile sulphide was formed [Figure 3(c), 340 and 240 nm] but in smaller amounts than from phenylthiatriazole [Figure 1(c)]. This is only partly explicable by the relatively low conversion of (4).

**5-Phenyl-1,3,4-oxathiazole-2-one (5).**—As seen from the spectra in Figure 4, compound (5) is significantly converted on irradiation ( $\lambda$  270 nm). On heating, however, only a small amount of benzonitrile sulphide (340 nm) was formed [Figure 4(c)].

**5-Phenyl-1,3,4-dithiazole-2-thione (6).**—This compound was studied because of the presence of a longwave chromophore<sup>7</sup> permitting irradiation in the region above 300 nm, in contrast to the above compounds. However, irradiation

( $\lambda$  350 nm) resulted in a slow decrease in the concentration of (6), but benzonitrile sulphide was not formed either during irradiation or during the subsequent controlled heating to room temperature.

**4-Phenyl-1,3,2-oxathiazolylium-5-olate (7).**—Irradiation

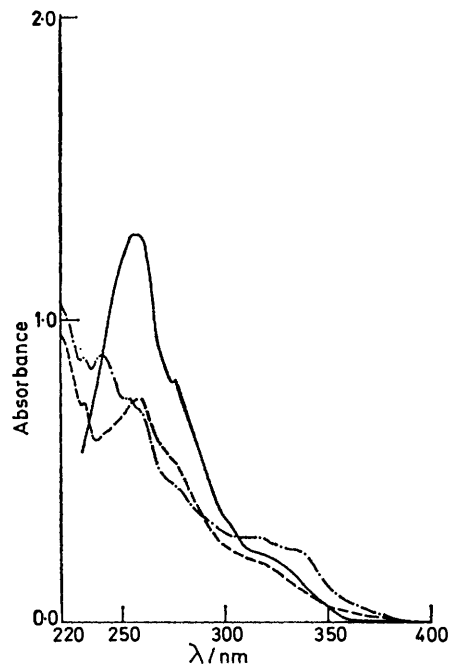


FIGURE 3 U.v. absorption spectra of 5-phenyl-1,2,3,4-thiatriazole 3-oxide (4) at 10–15 K in PVC before (a; —) and after photolysis (b; - - -) ( $\lambda$  280  $\pm$  14 nm; *ca.* 40% conversion), and after subsequent warming to *ca.* 150 K (c; - · - · -)

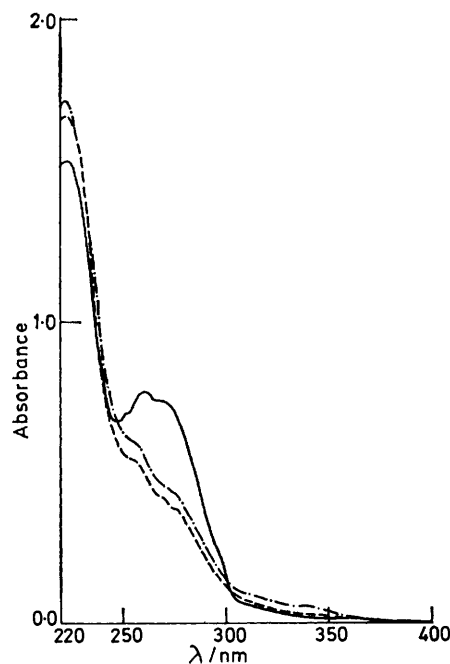


FIGURE 4 U.v. absorption spectra of 5-phenyl-1,3,4-oxathiazole-2-one (5) at 10–15 K in PVC before (a; —) and after photolysis (b; - - -) ( $\lambda$  270  $\pm$  14 nm) and after subsequent warming to *ca.* 150 K (c; - · - · -)

( $\lambda$  420 nm) led to formation of small amounts of benzonitrile sulphide [Figure 5(b)] [*ca.* 5% based on 75% conversion of (7)]. However, only a 2% increase in the amount of

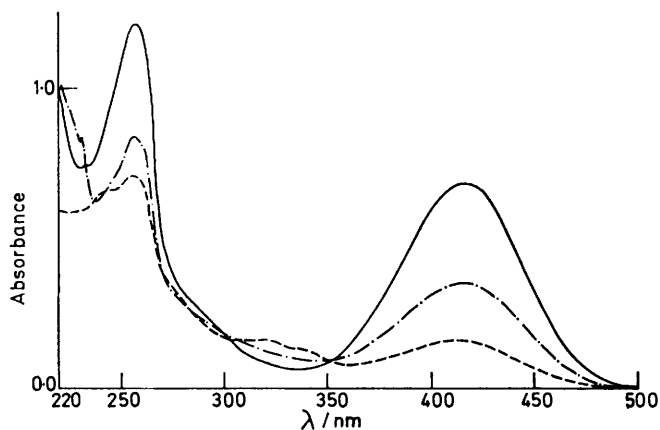


FIGURE 5 U.v.-visible absorption spectra of 4-phenyl-1,3,2-oxathiazolylum-5-olate (7) at 10–15 K in PVC before (a; —) and after photolysis (b; - - -) ( $\lambda$  420  $\pm$  14 nm; *ca.* 75% conversion), and after subsequent warming to room temperature (c; - · - · -)

benzonitrile sulphide was observed on heating, but reformation of the starting mesoionic heterocycle (7) took place to the extent of *ca.* 40% on heating to room temperature [Figure 5(c)].

#### DISCUSSION

Formation of benzonitrile sulphide in significant amounts on heating of irradiated phenylthiaziazole (3) clearly demonstrates the presence of a precursor of the former species, which is stable at 10 K. It remains unchanged at this temperature for several hours. Upon heating, formation of benzonitrile sulphide takes place in a stepwise manner (Figure 6). Formation of benzonitrile sulphide takes place even at very low temperature (*ca.* 20 K continuing to *ca.* 140 K). A similar stepwise decay reaction in a polymer has previously been reported.<sup>11</sup> It may be explained by assuming that the decay of groups of molecules is dependent on their relative orientation in the polymer. At still higher

singlet state of phenylthiaziazole originates from N(2) and N(3) (*ca.* 99.8%) [equation (i)].<sup>6</sup>

In the discussion of the structure of the nitrile sulphide precursor we will first consider the eventual formation of valence tautomers. In the thiaziazole case, four structures (8)–(11) may be considered. Structures (8) and (11) can be excluded since they would lose the 'wrong' nitrogen atoms [N(3) and N(4)]. The valence tautomer (10) apparently cannot give nitrile sulphide. Though structure (9) cannot be excluded, it seems likely that it would revert to thiaziazole on heating.

A diradical (12) or a thioacylnitrene (13) are other candidates for the nitrile sulphide precursor from thiaziazoles [type (I) heterocycles]. Structures (9), (12), and (13) however are incapable of rationalizing the formation of nitrile sulphide from the other heterocyclic compounds investigated. Thus although (4) and (5) give rise only to small amounts of nitrile sulphide on heating the irradiated sample from 10 K, photolysis of compounds (3)–(7) at room temperature with a 1,3-dipolarophile resulted in trapping of benzonitrile sulphide

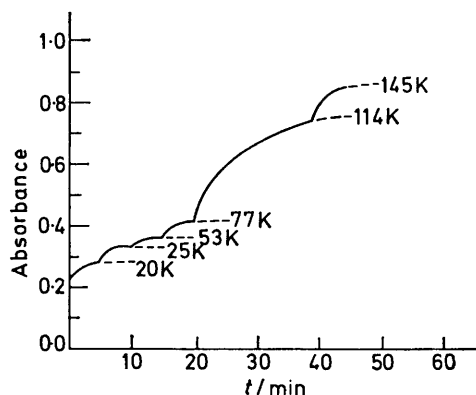
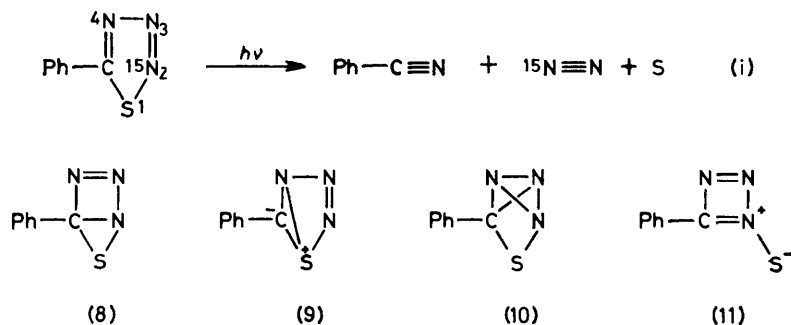


FIGURE 6 Formation of benzonitrile sulphide as a consequence of stepwise warming after photolysis of 5-phenyl-1,2,3,4-thiaziazole at 10 K in PVC; absorbance measured at 340 nm

in 9, 21, 19, 11, and 8% yields, respectively.<sup>7</sup> Furthermore, several other C-, N-, and S-containing heterocyclic



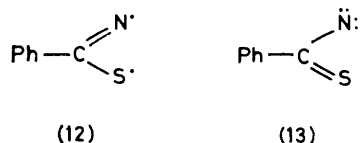
temperatures (*ca.* 220 K) rapid decomposition of benzonitrile sulphide is induced but its spectrum may still be observed at room temperature.<sup>6</sup>

The nitrogen molecule extruded from the excited

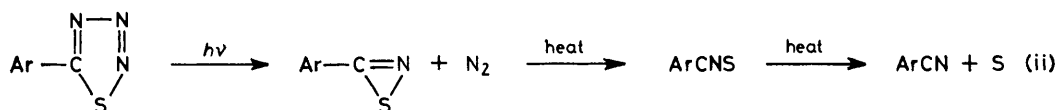
compounds give rise to nitrile sulphide on photolysis at room temperature.<sup>7</sup>

<sup>11</sup> C. David, P. Janssen, and G. Genskens, *Internat. J. Radiation Phys. Chem.*, 1972, **4**, 51.

On the basis of these arguments we consider the hitherto unknown thiazirine to be the most reasonable



nitrile sulphide precursor common to the heterocyclic compounds investigated. The reaction is depicted in equation (ii) with thiazirine as an example.

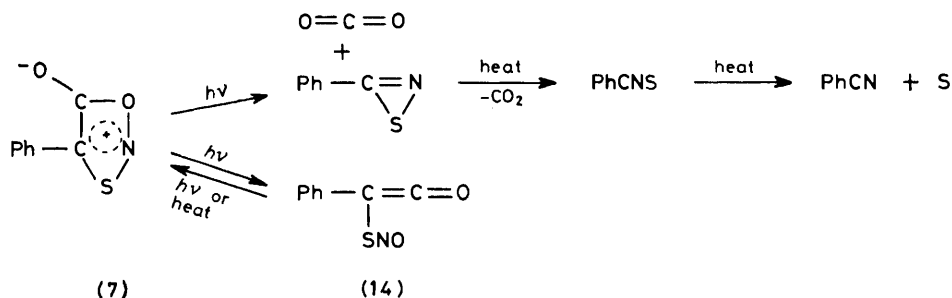


We have no simple explanation for the lack of formation of nitrile sulphide from (6), but the photoreactions in PVC at 10–15 K may of course proceed differently

material on heating of the irradiated sample of (7). It would be tempting to suggest that this reversal is due to a reaction between thiazirine and  $\text{CO}_2$  (Scheme 2). However, it has been demonstrated previously that formation of benzonitrile sulphide is accompanied by formation of a keten (14)<sup>12,13</sup> (Scheme 2). We cannot exclude the possibility that the main product in PVC at 10–15 K is the keten, accompanied by small amounts of the nitrile sulphide as described above. The answers to this question will have to await further studies.

It is a drawback in the inference of the existence of a

thiazirine that no separate spectral peak can be assigned unambiguously to this compound. Its u.v. spectrum should at least feature a strong absorption due to the



SCHEME 2

from the room temperature photolysis. A product analysis under the present conditions is almost impossible because of the very small amounts converted (less than  $10^{-3}$  mg; see Experimental section).

Finally we comment on the reversion to starting

phenyl group. However, the benzenoid regions of the spectra are in all cases complicated, and obscured by the presence of other products and starting material.

[7/1618 Received, 12th September, 1977]

<sup>12</sup> A. Holm, N. Harrit, and N. H. Toubro, *Tetrahedron*, 1976, **32**, 2559.

<sup>13</sup> I. R. Dunkin, M. Poliakoff, J. J. Turner, N. Harrit, and A. Holm, *Tetrahedron Letters*, 1976, 873.