Photochemistry of Thiatriazoles. Benzonitrile Sulfide as Intermediate in the Photolysis of Phenyl-Substituted 1,2,3,4-Thiatriazole, 1,3,2-Oxathiazolylio-5-oxide, and 1,3,4-Oxathiazol-2-one

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Abstract: Photolysis of 5-phenyl-1,2,3,4-thiatriazole leads to phenyl isothiocyanate (4.8–7.6%), benzonitrile (65–76%), sulfur, and nitrogen. Product formation takes place from the excited singlet state. Population of the triplet state by energy transfer from excited triplet state benzophenone does not lead to chemical conversion. ^{15}N-labeling experiments show that the extruded nitrogen originates from the N(2)–N(3) positions and that nitrogen scrambling prior to extrusion does not take place. The chemical yield of phenyl isothiocyanate is almost the same in different solvents and over the temperature range 300 to 193 K. At 85 K, photolytic formation of phenyl isothiocyanate is observed without indication of an intermediate (uv and ESR spectroscopy). On the basis of this and the solvent effect, thiobenzoylnitrene is excluded as precursor for the isothiocyanate. Benzonitrile sulfide was trapped during photolysis at room temperature as a cycloaddition product with dimethyl acetylenedicarboxylate in 9% yield. On photolysis in EPA at 85 K, a compound is formed which exhibits a uv absorption spectrum and thermal and photochemical properties identical with those of the compound generated from 4-phenyl-1,3,2-oxathiazolylio-5-oxide and assigned the structure of benzonitrile sulfide.[1] 5-Phenyl-1,3,4-oxathiazol-2-one behaves similarly upon photolysis, giving rise to the same transient absorptions at 85 K. On room temperature photolysis of the latter, benzonitrile sulfide was trapped as a cycloaddition product with dimethyl acetylenedicarboxylate in 22% yield.

Photolysis of heteroaromatic thiatriazoles was first reported by Kirmse.[2] Irradiation of 5-phenyl-1,2,3,4-thiatriazole (I) with uv light afforded benzonitrile (66%), sulfur (76%), and phenyl isothiocyanate (7.3%). Recently Okazaki et al. reported the formation of triplet sulfur atoms on irradiation of thiatriazoles.[3] A scheme for the formation of atomic sulfur was proposed involving primary formation of a thioacylnitrene (II). A thioacylnitrene as intermediate in the formation of isothiocyanate has been proposed for certain thermal processes.[4,5] However, decisive evidence for this type of intermediate has not yet been obtained.[6]

This paper addresses itself primarily to the question of transients in the photolysis of thiatriazoles. First we will explore the formation of benzonitrile and compare the results with its origin from similar heterocyclic systems. Secondly we will consider the photogeneration of phenyl isothiocyanate. Important in these respects is the question of where the individual ring N atoms appear in the respective products.

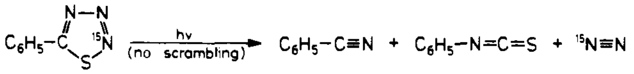
Results and Discussion

States of Excitation. The photoreduction of benzophenone in isopropyl alcohol[7] is effectively quenched by addition of 5-phenyl-1,2,3,4-thiatriazole (see Experimental Section). Energy is therefore transferred (benzophenone, E_T = 287 kJ/mol[7]) with formation of triplet thiatriazole, but analysis showed that all the thiatriazole could be recovered from the photolysis mixture. We can thus conclude that the main route for photolytic product formation goes via the singlet excited state.

Lack of Ring Transposition and Extrusion of Nitrogen. An analytical method based on ^{15}N magnetic resonance spectroscopy was developed which makes it possible to follow nitrogen scrambling at the different positions in the thiatriazole ring. Thus $^{15}N_2$, $^{15}N_3$, and $^{15}N_4$ labeled 5-phenyl-1,2,3,4-thiatriazoles were alkylated by means of triethyloxonium tetrafluoroborate to 3-ethyl-5-phenyl-1,2,3,4-thiatriazolium tetrafluoroborates. The ^{15}N chemical shifts for the three different nitrogen atoms N_2, N_3, and N_4 could then be determined from the ^1H NMR spectra by means of heterodecoupling to be −31 ± 2, −91 ± 2, and −73 ± 2 ppm, respectively.[8] The signals from these compounds in a mixture are well separated, and detection of ring transposition products is possible if only 2% ^{15}N interchange has taken place during photolysis (see Figure 1).

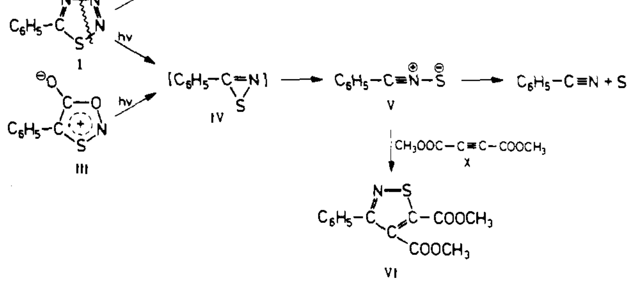
[2-^{15}N]-5-Phenyl-1,2,3,4-thiatriazole was photolyzed until approximately 50% of the starting material had been consumed. The thiatriazole remaining was alkylated with triethyloxonium tetrafluoroborate and the product analyzed by the NMR method described. The analysis clearly showed that all labeled nitrogen atoms remained in the 2-position.

The nitrogen formed during irradiation of [2-^{15}N]-5-phenyl-1,2,3,4-thiatriazole was analyzed by means of high resolution mass spectrometry. It was found that it originated exclusively from the N_2–N_3 positions.



Formation of Benzonitrile via Benzonitrile Sulfide. a. Trapping Experiments. Benzonitrile sulfide (V) is believed to be formed in the photochemical reactions of 4-phenyl-1,3,2-oxathiazolylio-5-oxide (III).[1,9] Thus Gotthardt found that irradiation of III in neat dimethyl acetylenedicarboxylate (X) afforded dimethyl 3-phenyl-1,2-thiazole-4,5-dicarboxylate (VI)[9] (Scheme I).

Scheme I



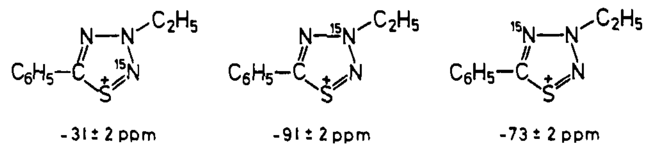
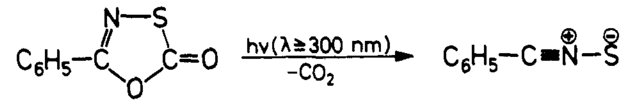


Figure 1. ^{15}N chemical shifts of 3-ethyl-5-phenyl-1,2,3,4-thiatriazolium tetrafluoroborate. Ammonium nitrate as internal reference.

We have irradiated 5-phenyl-1,2,3,4-thiatriazole (I) at room temperature in neat X and found 9% VI among the products. This strongly suggests the formation of benzonitrile sulfide from the thiatriazole (Scheme I).

Preliminary investigations of 5-phenyl-1,3,4-oxathiazol-2-one (XI) have proved this to be a third precursor for photolytic formation of benzonitrile sulfide. On irradiation in methylene chloride, benzonitrile is formed in 60% yield and, on irradiation through Pyrex glass in neat X, compound VI is formed in 22% yield:[10]

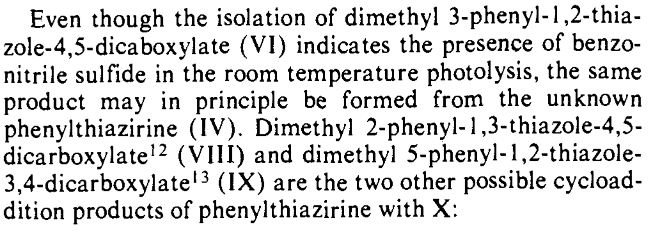


XI V

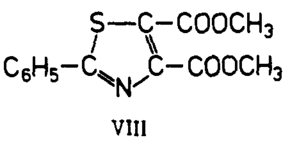
Although the structure of XI may be suggestive of direct formation of benzonitrile sulfide, the thiazirine IV as intermediate cannot be excluded.

Atomic sulfur formed on photolysis of I,[3] III, and XI could be responsible for the formation of VI by reacting with one molecule of X and one molecule of benzonitrile. Strausz and coworkers have shown that triplet or singlet sulfur generated photochemically from carbonyl sulfide reacts with two molecules of acetylene to yield thiophene.[11] To investigate whether VI is formed by a similar mechanism, an exchange experiment was carried out. *p*-Tolunitrile was photolyzed together with I in neat X, the rationale being that dimethyl 3-*p*-tolyl-1,2-thiazole-4,5-dicarboxylate (VII) should be formed along with VI if this mechanism were operating (Scheme II). Authentic VII was used as a comparison standard but was not found to be present in the samples taken at different stages of photolysis. We therefore discard active sulfur as a source for VI.

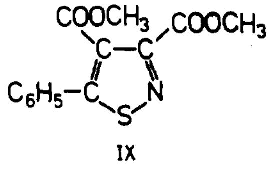
Scheme II



Even though the isolation of dimethyl 3-phenyl-1,2-thiazole-4,5-dicaboxylate (VI) indicates the presence of benzonitrile sulfide in the room temperature photolysis, the same product may in principle be formed from the unknown phenylthiazirine (IV). Dimethyl 2-phenyl-1,3-thiazole-4,5-dicarboxylate[12] (VIII) and dimethyl 5-phenyl-1,2-thiazole-3,4-dicarboxylate[13] (IX) are the two other possible cycloaddition products of phenylthiazirine with X:



VIII



IX

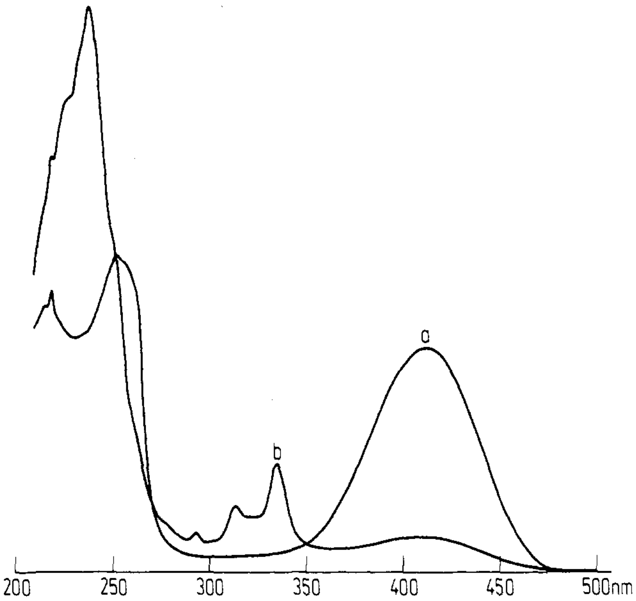


Figure 2. Uv-visible absorption spectra recorded before and after photolysis (λ 420 ± 14 nm; approximately 85% conversion) of 4-phenyl-1,3,2-oxathiazolylio-5-oxide (a) (λ_{max} 410 nm (log ϵ 3.95), 256 (4.06); dioxane[9]) at 85 K in EPA to benzonitrile sulfide (b).

Neither of the two latter products was observed in the room temperature photolysis of 5-phenyl-1,2,3,4-thiatriazole despite their stability under the photolytic conditions. Attempts to generate VIII and/or IX from III at 85 K (chosen in preference to I because of spectral advantages) were likewise unsuccessful. VI was obtained in 8% yield as in the room temperature photolysis.[9] Failure to find VIII and IX does not of course imply the absence of an intermediate thiazirine.

Support for benzonitrile sulfide as the common intermediate in the photolysis of I, III, and XI leading to VI is obtained from recent investigations by Howe and Franz.[14] Kinetic measurements were reported as evidence for thermal formation of benzonitrile sulfide at 125°C from 5-phenyl-1,3,4-oxathiazol-2-one (XI). Dimethyl 3-phenyl-1,2-thiadiazole-4,5-dicarboxylate (VI) was obtained in 90% yield when the thermolysis was carried out in the presence of X. Benzonitrile sulfide thus actually undergoes the cycloaddition process leading to VI since phenyl thiazirine is a very unlikely intermediate in the pyrolysis of XI (vide infra).

b. Low Temperature Absorption Spectroscopy. Previously we described how the light induced transformations of 4-phenyl-1,3,2-oxathiazolylio-5-oxide (III) at 85 K in EPA glass[15] could be monitored with absorption spectroscopy.[1] On irradiation with 420 ± 14 nm light, new absorptions appeared at 335 nm (log $\epsilon \sim 3.5$-4), 324, 313, 295, and 240 (Figure 2). Irradiation of the 335-nm band or warming to room temperature caused disappearance of the bands with simultaneous formation of benzonitrile. The bands were tentatively assigned to benzonitrile sulfide (V) with the exception of the 324-nm absorption. This was assigned to 2-(nitrosomercapto)-2-phenylketene.[1]

The same intermediate (V) was observed as a photoproduct of 5-phenyl-1,2,3,4-thiatriazole (I) at 85 K in EPA glass as shown in Figure 3. Bands appeared at 335, 313, 295, and 240 nm, identical with those appearing on photolysis of III. However, the bands appear weak since they overlap with those of the starting material. Thus photodegradation of both starting material and benzonitrile sulfide occurs side-by-side. The latter leads to benzonitrile. Heating the sample to the melting point of the glass likewise caused formation

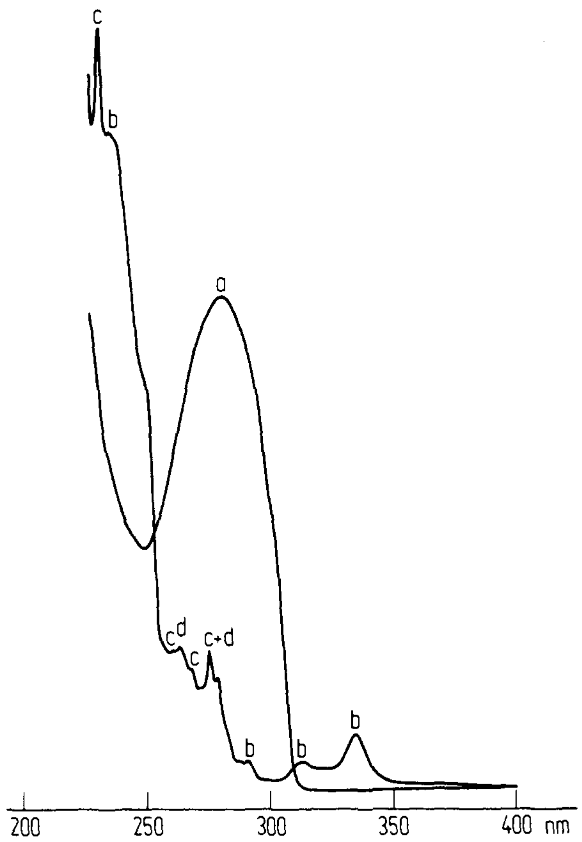


Figure 3. Uv absorption spectra recorded before and after photolysis (λ 280 ± 14 nm; almost quantitative conversion) of 5-phenyl-1,2,3,4-thiatriazole (a) (λ_{max} 280 nm (log ϵ 4.03)[2]) in EPA at 85 K to benzonitrile sulfide (b), benzonitrile (c), and phenyl isothiocyanate (d).

of benzonitrile. The transient thus exhibits the same characteristics as the transient generated from III.[1]

Similarly investigation of 5-phenyl-1,3,4-oxathiazol-2-one (XI) has demonstrated this to be a third parent compound for the same intermediate. On photolysis in EPA glass at 85 K, the spectral absorptions were again found at 335, 313, 295, and 240 nm. In this case, peak overlap of the transient with the starting material is even more disturbing than in the thiatriazole case, and the absorptions, although distinct, are very weak (Figure 4).

Since radicals and nitrenes can be excluded as intermediates (vide infra), the fragments common to the three heterocycles permit only two alternative transients, IV and V. In the present study, no new observations have been made that necessitate revision of the earlier tentative structure assignment of the intermediate to benzonitrile sulfide. In sum our conclusions are based on the isolation of VI via room temperature photolysis of I, III, and XI in neat X, on the photochemical and thermal properties of the transient, and also on the expected properties of the unknown phenylthiazirine. This is a so-called antiaromatic compound for which a high ground state energy can be expected.[16] Cyclobutadiene, the best known compound of this type, is obtained photolytically at 8 K but is transformed when heated to 35 K.[17] Similarly trialkylcyclopropenes exhibit the highest pK_a values yet recorded, 62–65, stressing the extraordinary high energy content of the corresponding antiaromatic cyclopropenyl anions.[18] In our investigations, the transient obtained was unchanged in the EPA glass at 85 K for about 3 hr, and decomposition was observed only when the glass was heated to its melting point around 140 K. Preliminary photolytic experiments with III in a PVC plastic film has shown that the uv spectrum of V can be traced even at room temperature when heating from 85 K over a period of 2.5 hr. These observations rule out phenylthiazirine and strongly support the structure assignment to benzonitrile sulfide.

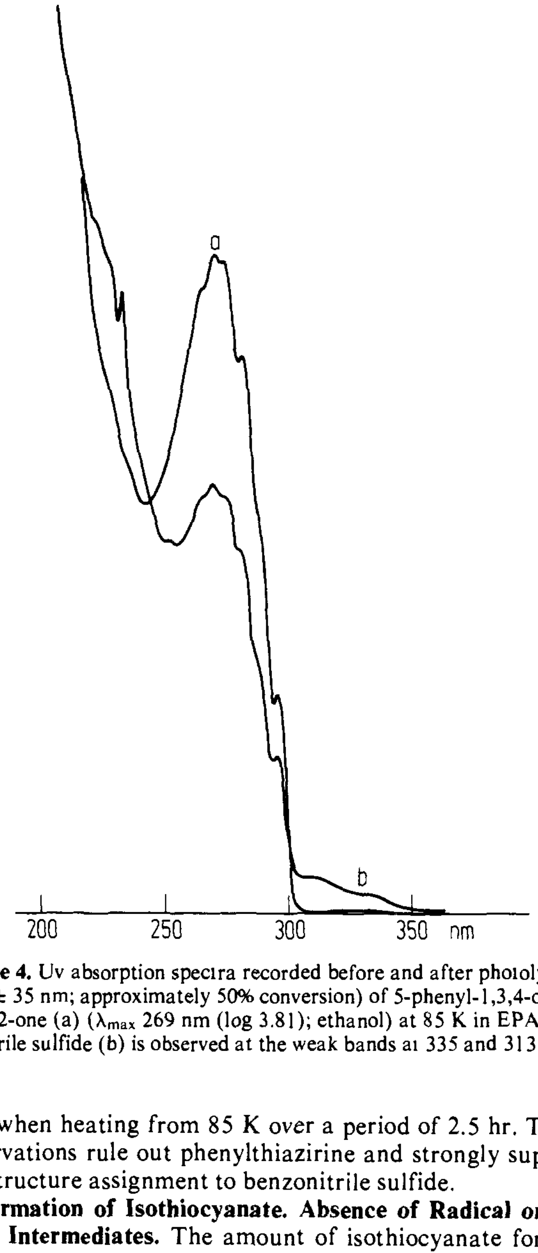
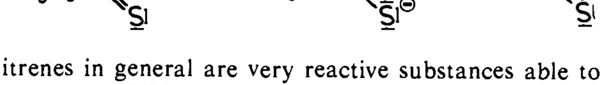


Figure 4. Uv absorption spectra recorded before and after photolysis (λ 260 ± 35 nm; approximately 50% conversion) of 5-phenyl-1,3,4-oxathiazol-2-one (a) (λ_{max} 269 nm (log 3.81); ethanol) at 85 K in EPA. Benzonitrile sulfide (b) is observed at the weak bands at 335 and 313 nm.

Formation of Isothiocyanate. Absence of Radical or Nitrene Intermediates. The amount of isothiocyanate formed on irradiation of 5-phenyl-1,2,3,4-thiatriazole (I) is independent of the solvent employed. By means of calibrated GLC measurements, the yield of isothiocyanate was found to be between 6.0 and 7.6% in such different media as isopropyl alcohol, acetonitrile, methylene chloride, anisole, and dimethyl acetylenedicarboxylate (X). Yields were insensitive to the presence of oxygen. Further only a slight decrease in yield (to 4.6–4.8%) was observed upon lowering the temperature from 300 to 193 K, using methylene chloride as solvent.

The insensitivity of the isothiocyanate yield to changes in the photolytic conditions virtually rules out II as an intermediate.

II:



Nitrenes in general are very reactive substances able to undergo cycloaddition and insertion reactions.[19] Thiobenzoylnitrene may eventually be less reactive than benzoylnitrene, but it seems unlikely that II, if an intermediate in the formation of isothiocyanate, should not be at least partially trapped by any of the above solvents. A particularly favorable reaction pathway of nitrenes is intramolecular insertion in a methyl or methylene group leading to five- or six-membered cyclic products. However, no change in the isothiocyanate yield was observed when photolyzing 5-(2-methylphenyl)-1,2,3,4-thiatriazole (7.6%).

It was similarly found, by means of TLC, that thiobenzamide is not formed on photolysis of I in isopropyl alcohol or in benzene. *N*-Phenylthiobenzamide is also absent in the latter solvent. Furthermore, photolysis of I in dimethyl acetylenedicarboxylate (X) at room temperature or below does not yield dimethyl 2-phenyl-1,3-thiazole-4,5-dicarboxylate (VIII) which would be expected from II and X (vide supra).

Photolysis at low temperature combined with ESR spectroscopy served as a supplementary indication for the lack of thioacylnitrene (II). Measurements were made on the neat crystals and glassy solutions of I in EPA and MPH[20] at 77 K. No signals were obtained after photolysis of the frozen EPA solution (except for a low intensity signal shown to originate from photodestruction of the matrix) under conditions and concentrations where characteristic changes in the uv spectrum occurred that are associated with formation of both isothiocyanate and nitrile sulfide (vide infra). On the other hand, ESR spectra were obtained after exposure of the sample in a hydrocarbon glass or as crystals to Pyrex filtered light. These spectra were identical and unsymmetrical with broad lines (g_1 = 2.000, g_2 = 2.024, g_3 = 2.040). The radical contains only noninteracting spins, and the signal can be reasonably assigned to that of a thiyl radical.[21] There is no evidence for II which would either be a singlet and not detectable or a triplet and show up as such. Further information concerning the origin of the signal came from low-temperature uv experiments with MPH solutions of I in concentrations as low as a factor of 10 more dilute than those used in the ESR experiments. These spectra showed that aggregates or crystals of I are formed upon cooling, the absorption bands becoming broad and flat. We believe that the ESR signals are due to radical formation within the aggregates but refrain from suggesting a structure for this oligomer. The possible participation of the sulfur atom in the radical formation by reaction with solvent was investigated by photolyzing carbonyl sulfide[22] dissolved in EPA or MPH at 77 K. Strong ESR signals were observed, but neither of the two spectra showed resemblance to that obtained from I in MPH.

The remaining question is whether photochemically generated isothiocyanate is formed via an intermediate, different from a nitrene, or is formed directly from the excited singlet state of the thiatriazole. Since an isothiocyanate-forming intermediate must contain at least one C, one N, and one S atom, only thiobenzoylazide, benzonitrile sulfide (V), and phenylthiazirine (IV) need be considered. Photolysis of III at 300 or 85 K does not give rise to phenyl isothiocyanate. Photolysis of benzonitrile sulfide generated from III at 85 K does not lead to phenyl isothiocyanate but produces benzonitrile exclusively. In contrast, phenyl isothiocyanate is formed photolytically from I at 85 K along with benzonitrile sulfide. The latter can therefore be ruled out as a precursor for phenyl isothiocyanate. Benzonitrile sulfide apparently differs in its photochemical behavior from nitrile oxides which in part rearrange to isocyanates.[23] Thioacylazides are unknown, and attempted synthesis at room temperature leads to the isomeric ring-closed thiatriazoles.[24] CNDO calculations in this laboratory suggest that the ring is ≈13 kcal more stable than the acyclic form.[25]

The thiocarbonyl group is a characteristic chromophore and thiobenzoylazide is expected to absorb in the visible due to a n,π^* transition and in the vicinity of 300 nm by a π,π^* transition.[26] The spectrum of irradiated I in EPA at 85 K (λ 280 ± 14 nm) is devoid of absorptions above 335 nm. Bands can be assigned to either phenyl isothiocyanate, benzonitrile, or benzonitrile sulfide, and no evidence for the intermediacy of thiobenzoylazide is obtained.

In conclusion the overall observations seem to suggest that the isothiocyanate is formed directly in a concerted reaction from the exited singlet state of the thiatriazole or from phenylthiazirine. If phenylthiazirine is an intermediate in the formation of nitrile sulfide from both I and III, it cannot be a precursor for isothiocyanate inasmuch as the latter is observed from I only.

Experimental Section

Room Temperature Photolysis. In the preparative-scale photolysis at room temperature, a low-pressure Hg lamp (Hanau Q-700) fitted with appropriate filters was used. Cooling of the photolysis mixture was ensured by means of tap water. Thin layer chromatography was performed on silica gel. Eluents will be specified.

Low Temperature Uv Spectroscopy. The low temperature uv cell was constructed by the Inorganic Department of this institute. It is in principle a three-walled Dewar made of steel. The six quartz windows are sealed to the steel with indium. The frozen solution is contained in the inner chamber, while high vacuum is maintained in the outer jacket. Heat transport is furnished by a helium atmosphere contained in the middle jacket in contact with liquid nitrogen as well as with the sample cell. In a typical run, the temperature was kept at 85 K except for cooling and heating periods. Spectra were recorded on a Cary 14 instrument and irradiations performed outside the spectrograph with a Bausch and Lomb SP-200 mercury point source equipped with monochromator (typical band width 20 nm).

Electron Spin Resonance. Spectra were obtained on a Japan Electron Optics Laboratory instrument Model JES-ME-1X, using a liquid nitrogen Dewar. *g* values were standardized against Mn^{2+} in MgO.

Irradiation of 5-Aryl-1,2,3,4-thiatriazoles in Different Solvents. Determination of nitrile and isothiocyanate formed upon irradiation of the thiatriazoles was performed by means of gas chromatography directly on the photolysis mixture after addition of benzyl cyanide or phenyl bromide as internal standard. The analysis was carried out on a Pye Unicam 104 chromatograph, dual FID, connected to a Varian aerograph 477 electronic integrator, on a 2 m × 0.25 in. column with 10% SE-30 on Gaschrom Q 100-120 mesh (Applied Science Lab., Inc.) and with nitrogen as carrier gas. (a) Approximately 2.5 × 10^{-2} *M* solutions of 5-phenyl-1,2,3,4-thiatriazole in the appropriate solvent were irradiated at room temperature through quartz until complete transformation (TLC). Yields of phenyl isothiocyanate and benzonitrile (room temperature unless otherwise stated): isopropyl alcohol (6.9, 62%); methylene chloride with oxygen present (7.6, 68%); methylene chloride without oxygen present (6.6, 76%); methylene chloride with oxygen present at 194 K (6.0, 70%); acetonitrile (6.0, 65%); anisole (6.4, —%). (b) Photolysis of 5-(2-methylphenyl)-1,2,3,4-thiatriazole in methylene chloride yielded 2-methylphenyl isothiocyanate (7.6%) and 2-methylbenzonitrile (77%).

Sensitizer Experiments with Benzophenone. Three identical Pyrex flasks containing three different solutions, 1, 2, and 3, were purged with argon and irradiated through 1-cm acetone transmitting ≥330 nm for 3.5 hr. Solutions: (1) benzophenone (25.4 mg) in isopropyl alcohol (10 ml); (2) 5-phenyl-1,2,3,4-thiatriazole (41.2 mg) in isopropyl alcohol (10 ml); (3) 5-phenyl-1,2,3,4-thiatriazole (41.5 mg) and benzophenone (26.0 mg) in isopropyl alcohol (10 ml). After irradiation, solution 1 was evaporated to dryness in vacuo and found to yield 23.1 mg of a solid material which was identified by means of ^{1}H NMR spectroscopy to consist approximately of 95% benzpinacol and 5% unchanged benzophenone. Solution 2 yielded 41.3 mg of unchanged 5-phenyl-1,2,3,4-thiatriazole (≈100%), identified by its ir spectrum. The distillate from solution 3 was collected, benzyl cyanide (25.2 mg) added as internal standard, and the mixture submitted to GLC as described in the foregoing section. Benzonitrile was found to be formed in 1.2% yield. Accordingly, the residue from the evaporated solution showed only a 3.6 mg loss in weight. ^{1}H NMR spectroscopy of the residue revealed a virtually unchanged composition of thiatriazole and benzophenone.

Irradiation of $[2\text{-}^{15}\mathrm{N}]$-5-Phenyl-1,2,3,4-thiatriazole. Loss of Nitrogen. $[2\text{-}^{15}\mathrm{N}]$-5-Phenyl-1,2,3,4-thiatriazole (22 mg) of 95.0% isotopical purity [prepared from $\mathrm{Na^{15}NO_2}$ (95.0% isotopical pure) and thiobenzhydrazide according to standard methods[8,24]] was dissolved in methylene chloride (2 ml) and placed in a Pyrex ampoule. After degassing, the ampoule was evacuated (liquid nitrogen), sealed, heated to room temperature, and irradiated for 3 hr (Osram HBO-200 point source equipped with monochromater, λ 300 ± 10 nm). The ampoule was cooled in liquid nitrogen, attached to a mass spectrometer (AEI-MS 902, double focusing, with a resolution of 10.000), and the nitrogen formed introduced directly. The mass spectrum showed that the nitrogen contained 95.0% of $\mathrm{^{15}N^{14}N}$ (corrected for background) which corresponds to 100.0% loss of nitrogen from position N(2) and N(3).

Transposition Experiments. $[2\text{-}^{15}\mathrm{N}]$-5-Phenyl-1,2,3,4-thiatriazole (123 mg) dissolved in methylene chloride (5 ml) was irradiated through quartz for 4 hr. Methylene chloride and benzonitrile were removed in vacuo and the residue (57 mg), consisting of thiatriazole and sulfur, was washed with a small amount of hexane. After dissolving in methylene chloride (0.25 ml), triethyloxonium tetrafluoroborate (89 mg) in methylene chloride (0.25 ml) was added and the mixture left for 15 hr at room temperature. The solvent was removed in vacuo and the residue washed with dry ether and recrystallized from absolute ethanol, yielding 30 mg of 2-ethyl-5-phenyl-1,2,3,4-thiatriazolium tetrafluoroborate. $^{15}\mathrm{N}$ NMR spectroscopy showed that all $^{15}\mathrm{N}$ remained at the 2-position.[8]

Photolysis of 5-Phenyl-1,2,3,4-thiatriazole in Neat Dimethyl Acetylenedicarboxylate. 5-Phenyl-1,2,3,4-thiatriazole (974 mg) was suspended in dimethyl acetylenedicarboxylate (5 ml) in a Pyrex flask and irradiated. After removal of volatile components in vacuo, the residue was applied to a preparative TLC plate and developed with benzene-petroleum ether 1/1. The band corresponding to VI, found on comparison with an authentic sample,[9] was isolated on elution with chloroform. After evaporation to dryness, the solid material was taken up in ether, applied to a preparative TLC plate, and developed several times with ether-petroleum ether 1/2, until a satisfactorily separated band of VI appeared. On elution with chloroform, 51 mg of material was obtained. On comparison with uv, emission, and ir spectra of an authentic sample of VI, identity was established. VIII[12] could not be observed despite careful investigations; 40% thiatriazole was recovered. The amount of VI isolated corresponds to 8.8% based on converted material.

Irradiation of a Mixture of 5-Phenyl-1,2,3,4-thiatriazole and *p*-Tolunitrile in Dimethyl Acetylenedicarboxylate. 5-Phenyl-1,2,3,4-thiatriazole (993 mg) and *p*-tolunitrile (719 mg) in dimethyl acetylenedicarboxylate (5 ml) were irradiated through Pyrex for 65 hr. The resulting solution was worked up on TLC plates with authentic VI and VII[9] as standards.

Compounds VI and VII could not be satisfactorily separated by the eluents employed, and the band corresponding to the possible mixture of these compounds were isolated and analyzed by means of $^{1}\mathrm{H}$ NMR spectroscopy. On comparison with the $^{1}\mathrm{H}$ NMR spectrum of an authentic mixture of VI and VII, it was found that VI but not VII had been formed.

Irradiation of 4-Phenyl-1,3,2-oxathiazolylio-5-oxide in Dimethyl Acetylenedicarboxylate at 77 K. To dimethyl acetylenedicarboxylate (75 ml) contained in a Pyrex tube (inner diameter 2 cm) was added 0.5 ml of a "stock" solution of 4-phenyl-1,3,2-oxathiazolylio-5-oxide (100 mg) in dimethyl acetylenedicarboxylate (10 ml). After immersion in liquid nitrogen, the sample was irradiated until the yellow color of the glass had almost disappeared (ca. 5 hr). The mixture was heated to room temperature and 0.5 ml of stock solution added. After cooling in liquid nitrogen, irradiation was continued. When all III had been added in this manner, the solvent was removed in vacuo (0.1 mmHg) and the residue applied on a preparative TLC plate. The chromatogram was developed with ether-petroleum ether 2/3 with authentic samples of VI, VIII, and IX[13] applied on the plate for comparison. Bands corresponding to the cycloaddition products were collected and analyzed. Only VI was found, corresponding to 8%. More than ten other products were observed, but attempts to obtain information as to their identity was not undertaken.

Photolysis of 5-Phenyl-1,3,4-oxathiazol-2-one in Neat Dimethyl Acetylenedicarboxylate. 5-Phenyl-1,3,4-oxathiazol-2-one[10] (1.003 g) was suspended in dimethyl acetylenedicarboxylate (5 ml) and irradiated through Pyrex for 88 hr. Products were obtained by means of preparative TLC (vide supra). VI was isolated in 22% yield based on the amount of starting material converted.

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References and Notes

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