# Photolysis of 1,2,5-Selenadiazoles. Formation of Nitrile Selenides

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Dedicated to Professor K. A. Jensen on his 70th birthday

UV photolysis of 1,2,5-selenadiazole, dimethyl-1,2,5-selenadiazole, diphenyl-1,2,5-selenadiazole, diphenyl-1,2,4-selenadiazole and 2,1,3-benzoselenadiazole at room temperature produces nitriles and selenium. At low temperatures (20 K, 85 K) all compounds except the almost photostable 2,1,3-benzoselenadiazole photolyse to very labile transients. Identical transients are formed from diphenyl-1,2,5-selenadiazole and diphenyl-1,2,4-selenadiazole and on the basis of the spectroscopic properties, in particular the IR absorption at 2200 cm⁻¹ (solid nitrogen), it is identified as benzonitrile selenide, $C_6H_5CNSe$. Transients from the photolysis of 1,2,5-selenadiazole and dimethyl-1,2,5-selenadiazole have been detected by low temperature UV spectroscopy. These transients are tentatively assigned the structures HCNSe and CH₃CNSe. Mechanistic studies were undertaken in order to determine the character of the excited states involved. At room temperature 1,2,5-selenadiazole, dimethyl-1,2,5-selenadiazole and diphenyl-1,2,4-selenadiazole photolyse via the singlet state exclusively, with quantum yields of 0.71±0.05, 0.8±0.1 and 0.085±0.05, respectively. Diphenyl-1,2,5-selenadiazole photolyses both via the singlet state (80 %) and the triplet state (20 %) with a total quantum yield of 0.96±0.05.

Benzonitrile sulfide has been generated as a reactive intermediate by thermal and photochemical reactions of a variety of substrates and it has been trapped in 1,3-dipolar cycloaddition reactions with acetylenes, nitriles and maleic anhydride.[1] Furthermore, it has been characterized by low temperature spectroscopic methods.[1c] Acetonitrile sulfide can also be generated thermally [1a,2] and trapped. Since nitrile selenides were unknown a photochemical study of selenadiazoles (Chart 1) was undertaken.
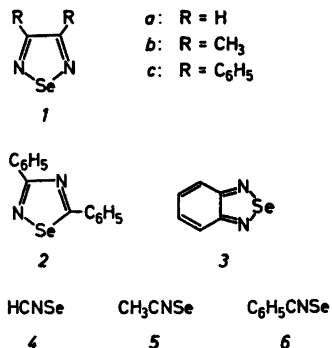


Chart 1.

The photolysis at ambient temperature of systems related to $1a-c$, 2 and 3 has been the subject of several investigations. Photolysis of dimethyl- and diphenyl-1,2,5-thiadiazole gave acetonitrile and benzonitrile, respectively, as well as sulfur.[3] Diphenyl-1,2,5-oxadiazole (diphenylfurazan) was found to give benzonitrile together with products derived from initially formed benzonitrile oxide.[3,4] Nitrile oxides have also been trapped from dimethylfurazan [3] and from benzofurazan.[5] In contrast, diphenyl-1,2,4-oxadiazole photolyses giving products derived from an intermediate nitrene.[6]

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## RESULTS

*Irradiation of compounds 1a−c at room temperature.* In a series of experiments ∼ 10⁻⁴ M solutions of *1a−c* in 96 % ethanol were photo-lysed at 300 ± 20 nm, and the result of photolysis analyzed by UV spectroscopy. Photolysis of substrates *1a* ($\lambda_{max}$ 285 nm, ε 6300 M⁻¹ cm⁻¹) and *1b* ($\lambda_{max}$ 288 nm, ε 7300 M⁻¹ cm⁻¹) only permitted the observation of a continuous absorption due to colloidal selenium. Photolysis of compound *1c* ($\lambda_{max}$ 317 nm, ε 12 700 M⁻¹ cm⁻¹) produced benzonitrile and selenium.

Identical results were obtained with aerated and deoxygenated solutions and no effect of concentration on the product distribution was detected when 10⁻² M solutions were photolysed with the more intense pyrex-filtered light ($\lambda > 300$ nm). Photolysis of *1a* in 96 % ethanol and analysis by titration with silver nitrate gave an 87 % yield of hydrogen cyanide. Analysis by GLC of the photolysis mixture from *1b* in chloroform showed that the formation of acetonitrile was quantitative. Likewise, comparison by UV spectroscopy of the diluted photolysis mixture from *1c* in 96 % ethanol with a reference solution of benzonitrile showed that only formation of benzonitrile had taken place. Compounds *1a−c* thus undergo cleavage to nitriles and selenium.

$$1a-c \xrightarrow{\;hv,\;25\;°C\;} 2RCN + Se$$
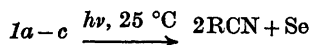
Attempts were made to trap the initially formed benzonitrile selenide (*6*) by irradiation of *1c* in neat dimethyl acetylenedicarboxylate, but without success.

*Irradiation of compounds 2 and 3 at room temperature.* 10⁻⁴ and 10⁻² M aerated solutions of *2* [$\lambda_{max}$ 310 nm (sh), ε 5800 M⁻¹ cm⁻¹] in 96 % ethanol were irradiated with pyrex-filtered light. This produced only benzonitrile and selenium (UV).

$$2 \xrightarrow{\;hv,\;25\;°C\;} 2C_6H_5CN + Se$$
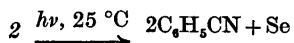
2,1,3-Benzoselenadiazole (*3*, $\lambda_{max}$ 332 nm, ε 15 900 M⁻¹ cm⁻¹), 4 × 10⁻³ M in non-degassed 96 % ethanol, photolysed extremely slowly to a mixture of 2,4-hexadienedinitriles as well as selenium (Chart 2) when irradiated with pyrex-filtered light. The ratios of isomers formed were    cis,cis:cis,trans:trans,trans = 1.0:2.6:2.0.
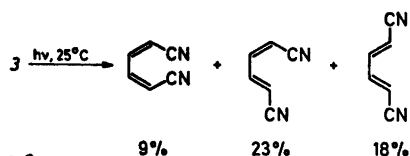
Chart 2.

The three isomeric 2,4-hexadienedinitriles, which are known compounds,[7] were identified by elemental analysis and IR spectroscopy (see Experimental).

Irradiation of *cis,cis*-2,4-hexadienedinitrile in ethanolic solution ($\lambda_{max}$ 260 nm) through quartz gave a mixture of the isomers *cis,cis: cis,trans:trans,trans* = 1.0:2.6:1.7. This result indicates that photoequilibration among the isomers is taking place during photolysis of *3*.

*Irradiation of compounds 1c and 2 at low temperature.* Irradiation of compound *1c* at low temperature was performed in a variety of media [poly(vinyl chloride) (PVC), diethyl ether, isopentane, ethanol 5:5:2 (EPA), nitrogen] and the reactions followed by spectroscopy. The best UV results were obtained in a PVC film, *ca.* 20 μm thick. Irradiation at 85 K with 300 nm light gave rise to new absorptions at 255 nm (ε 13 000 − 25 000 M⁻¹ cm⁻¹), 340 nm
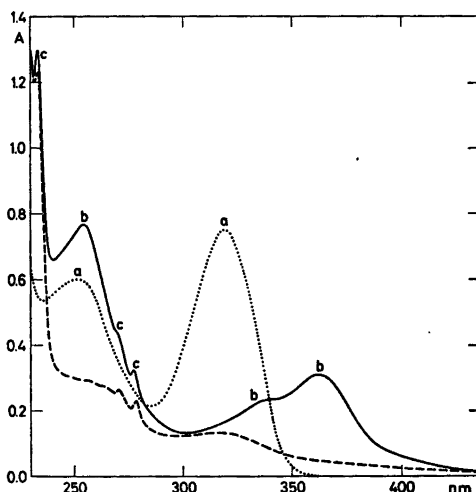


*Fig. 1.* UV spectra after photolysis at 85 K of diphenyl-1,2,5-selenadiazole (*1c*) in PVC film, 20 μm thick, with 300 ± 20 nm light. a, starting material at 85 K, $\lambda_{max}$ 320 nm, b, benzonitrile selenide at 255 nm, 340 nm and 362 nm, c, benzonitrile. ---, after heating from 85 K to room temperature. Absorptions from starting material and benzonitrile can be seen.

and 362 nm ($\varepsilon$ 5000 − 10 000 M⁻¹ cm⁻¹) (Fig. 1). Simultaneously, absorptions from benzonitrile appeared at 233, 270 and 278 nm. Upon prolonged photolysis at 300 nm or on heating above ~240 K the absorption bands at 255, 340 and 362 nm disappeared. Simultaneously, the absorption bands from benzonitrile increased in intensity (Fig. 1). The new absorption bands were assigned to benzonitrile selenide. This assignment is based on the thermal and photochemical properties, on the IR results discussed below and on the results of the following experiment with compound *2*.

When compound *2* was irradiated in PVC under similar experimental conditions, absorptions from the same transient appeared at 258, 325 and 360 nm ($\varepsilon$ 5000 − 10 000 M⁻¹ cm⁻¹) together with absorptions from benzonitrile at 233 and 277 nm (Fig. 2). Bands from the transient were less distinct in this experi-
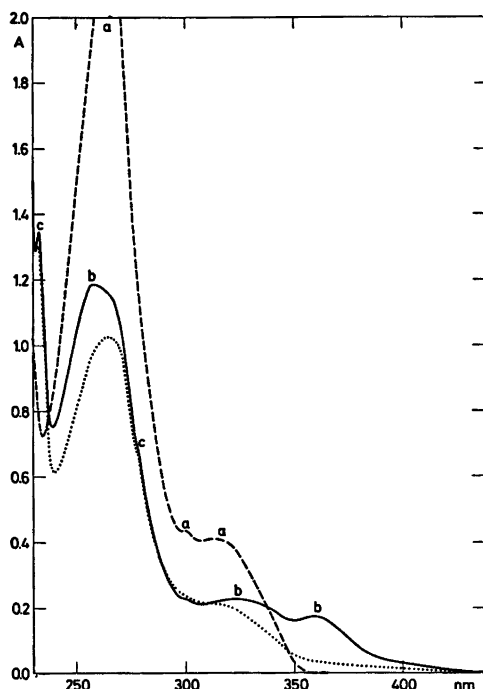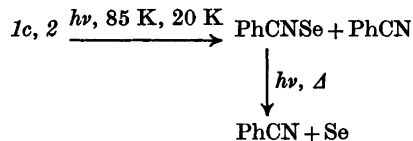
ment due to the greater photostability of *2* relative to *1c*.

$$1c, 2 \xrightarrow{h\nu,\ 85\ K,\ 20\ K} PhCNSe + PhCN$$

$$\downarrow h\nu, \Delta$$

$$PhCN + Se$$

By irradiation of *1c* in frozen EPA (diethyl ether, isopentane, ethanol 5:5:2) at 85 K the same spectroscopic feature (Table 1) resulted, although competitive photolysis of the benzonitrile selenide formed made its absorptions less intense. Prolonged irradiation at 300 nm, selective excitation of product absorptions at 360 nm or heating above 110 K caused the benzonitrile selenide bands to disappear with simultaneous enhancement of the absorption bands from benzonitrile. Selenium was precipitated when samples were heated from cryogenic temperatures.

Experiments were also undertaken in nitrogen matrix with the primary aim of obtaining characteristic absorptions of benzonitrile selenide in the infrared. UV photolysis at 300 nm of *1c* after deposition in solid $N_2$ at 20 K gave valuable data, although competitive photolysis of the benzonitrile selenide so formed remained a serious problem. The UV and IR spectra from these experiments are shown in Figs. 3 and 4. These spectra were recorded from the *same* sample.

The UV spectrum in Fig. 3 shows the two lowest lying transitions of benzonitrile selenide at 356 and 390 nm. The longer wavelength band also appears as a maximum in EPA but as a continuum in PVC (Figs. 1 and 2). The IR spectrum (Fig. 4) consists of two bands in the



*Fig. 2.* UV spectra after photolysis at 85 K of diphenyl-1,2,4-selenadiazole (*2*) in PVC film, 20 $\mu$m thick, with 300 ± 20 nm light. a, starting material at 85 K, $\lambda_{max}$ 313 nm, b, benzonitrile selenide at 258 nm and 360 nm, c, benzonitrile. ...., after heating from 85 K to room temperature. Absorptions from starting material and benzonitrile can be seen.

*Table 1.* The UV absorptions of benzonitrile selenide, *6*.

| Compound | Medium | Absorption/nm | | | |
|---|---|---|---|---|---|
| *1c* | PVC | 255 | 340 | 362 | *a* |
| *2* | PVC | 258 | 325 | 360 | *a* |
| *1c* | EPA | 254 | 325(sh) | 357 | 384 |
| *1c* | $N_2$ | | | 356 | 390 |

*a* The long wavelength absorption cannot be located in PVC since site effects render the absorption bands broad.
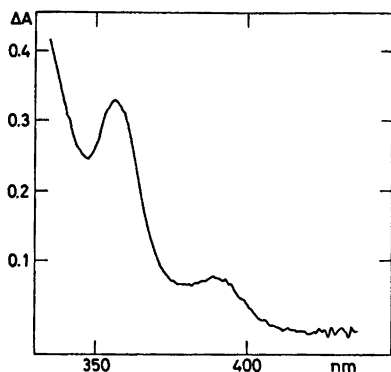
*Fig. 3.* UV spectrum after photolysis at 20 K of diphenyl-1,2,5-selenadiazole (*1c*) in a nitrogen matrix with 300 ± 10 nm light. The bands at 356 and 390 nm are assigned to benzonitrile selenide.
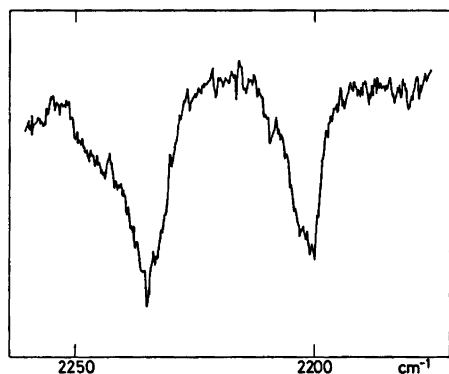


*Fig. 4.* IR spectrum after photolysis at 20 K of diphenyl-1,2,5-selenadiazole (*1c*) in a nitrogen matrix with 300 ± 10 nm light. The bands are assigned to benzonitrile selenide, 2200 cm$^{-1}$, and benzonitrile, 2235 cm$^{-1}$. Intensity in transmission.

2300 − 1900 cm$^{-1}$ region, benzonitrile at 2235 cm$^{-1}$ and benzonitrile selenide at 2200 cm$^{-1}$. Irradiation of the matrix with pyrex-filtered light caused the absorptions in the UV spectrum and the absorption in the IR spectrum at 2200 cm$^{-1}$ to disappear. Simultaneously, the benzonitrile band was slightly enhanced in intensity.

IR absorptions of benzonitrile selenide were also observed at 85 K when *1c* in a PVC film (0.5 M, 100 μm thick) was irradiated in the long wavelength part of its absorption ($\lambda_{max}$ ~ 320 nm) with 330 nm light. However,

the maximum intensity of the absorption at 2190 cm$^{-1}$ was only small.

The extremely small quantum yield for photolysis of *3* at 85 K prevented spectroscopic detection of primary products from this species.

*Irradiation of compounds* 1a − b *at low temperature.* These irradiations were carried out in PVC, EPA and argon. Spectra corresponding to the irradiation products of compounds *1a − b* in PVC with 300 nm light are shown in Figs. 5 and 6. Absorption bands for the photolysis product of compound *1a* were found at 237 nm ($\varepsilon$ ~ 18 000 M$^{-1}$ cm$^{-1}$) and ~ 255 nm (shoulder) and absorption bands for the photolysis product of *1b* at 233 nm ($\varepsilon$ ~ 25 000 M$^{-1}$ cm$^{-1}$) and ~ 252 nm (shoulder). These bands disappeared upon prolonged photolysis with pyrex-filtered light ($\lambda$ > 300 nm) and upon heating above *ca.* 220 K. No new absorptions resulted (HCN and CH$_3$CN does not absorb above 200 nm [8]).

The same spectroscopic behaviour was found when *1a* was photolysed in frozen EPA at 85 K with 300 nm light. The spectrum of the product had maximum absorption at 233 nm ($\varepsilon$ ~ 19 000 M$^{-1}$ cm$^{-1}$) and this product disappeared when the matrix was heated above 110 K. No new absorptions resulted. Selenium was precipitated from samples heated from cryogenic temperatures.
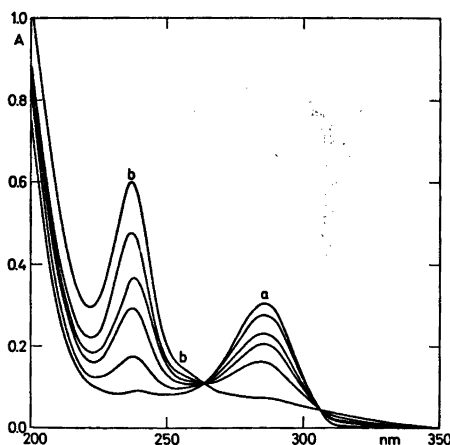


*Fig. 5.* UV spectra after photolysis at 85 K of 1,2,5-selenadiazole (*1a*) in PVC film, 20 μm thick, with 300 ± 20 nm light. a, starting material at 287 nm, b, photoproduct at 237 and 255 nm.
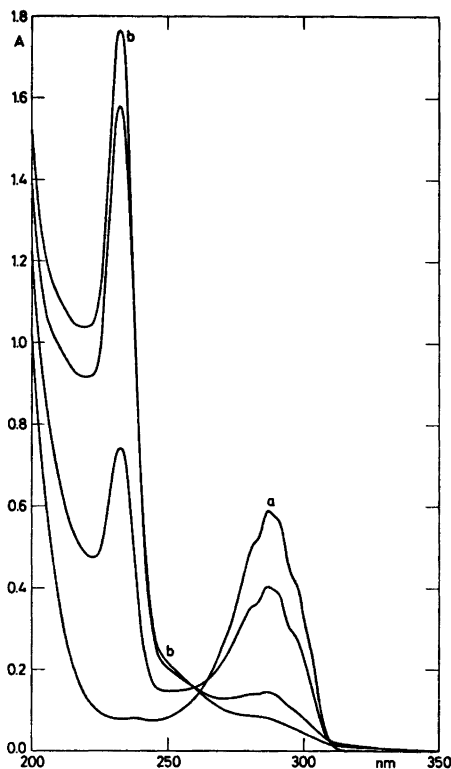
*Fig. 6.* UV spectra after photolysis at 85 K of dimethyl-1,2,5-selenadiazole (*1b*) in PVC film, 20 μm thick, with 300 ± 20 nm light. a, starting material at 287 nm, b, photoproduct at 233 and 252 nm.

The argon matrix experiments were carried out at 20 K with guest-host ratios of 1/10 000 – 1/1000. The results of these experiments are shown in Fig. 7. The absorption bands for the photolysis products of *1a* and *1b* with maxima at 233.0 and 230.2 nm, respectively, possess vibrational fine-structure * which is not observed in PVC or EPA at 85 K. The products were photolabile and disappeared on further irradiation at 300 nm. This problem of secondary photolysis prevented IR detection of the intermediates and it could not be circumvented by consecutive application and photolysis or by photolysis with plane-polarized light. Thus irradiation of *1a* in argon (1/5000) with 300

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* Photoproduct from *1a*, 230.8, 233.0, 235.3, 238.1, 241.2 and 244.4 nm. Photoproduct from *1b*, 223.4, 225.7, 227.9, 230.2, 232.3 and 234.8 nm.

nm light produced sharp bands at 2044.8 and 2046.5 cm$^{-1}$ and a weak broad band at 2091 cm$^{-1}$. The two sharp bands are assigned to the radical CN (2046.0 cm$^{-1}$ in Ar,[9] the splitting of the band is due to site-effects) and the band at 2091 cm$^{-1}$ to HCN-monomer.[10] Additional bands from HCN-oligomers [10b] were observed, especially when a more concentrated gas mixture (1/1000) was irradiated.

Photolysis of compound *1b* in argon (1/5000) at 300 nm led to absorptions from acetonitrile at 2250 and 2252 cm$^{-1}$ (site effect),[11] from the CN radical as a doublet at 2046 cm$^{-1}$,[9] and from hydrogen cyanide monomer at 2090 cm$^{-1}$.[10] In addition, bands from hydrogen cyanide oligomers were present.[10b]

An interesting detail in these IR experiments with compounds *1a* and *1b* was the occurrence of a green emission when the photolysed matrix was slowly heated. We tentatively assign this emission to chemiluminescence from the reaction $Se + Se \rightarrow Se_2 + h\nu$. Diselenium is known to fluoresce when excited in the gas phase.[12]

IR experiments were also performed with PVC films (100 μm thick). PVC is sufficiently transparent between 2800 and 1400 cm$^{-1}$. The experiments were carried out at 85 K and at 20 K with UV light of different wavelength (255, 295 and 330 nm). However, the product distribution was independent of the experimental conditions chosen. The only observed products were hydrogen cyanide at 2095 and 2070 cm$^{-1}$ and acetonitrile at 2250 cm$^{-1}$.
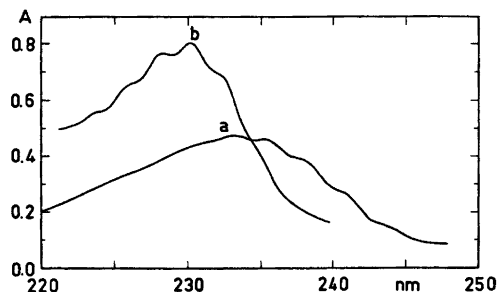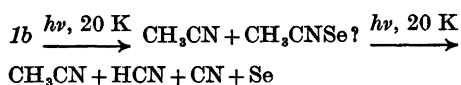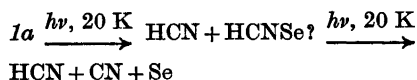


*Fig. 7.* UV spectra after photolysis at 20 K of 1,2,5-selenadiazole (*1a*), guest-host ratio 1/5000, and of dimethyl-1,2,5-selenadiazole (*1b*), guest-host ratio 1/10 000, in argonmatrices with 300 ± 10 nm light. a, photoproduct from *1a*, $\lambda_{max}$ 233.0 nm, b, photoproduct from *1b*, $\lambda_{max}$ 230.2 nm.

*Table 2.* Quantum yields of reaction ($\Phi_r^\circ$) and reactive state of selenadiazoles at room temperature.

| Compound | $\Phi_r^\circ$ | Reactive state, unsensitized |
|---|---|---|
| *1a* | 0.71(5) at 285 (12) nm | Singlet |
| *1b* | 0.8 (1) at 290(8) nm | Singlet |
| *1c* | 0.96(5) at 317 (8) nm | Singlet + triplet |
| *2* | 0.085(5) at 310 (10) nm | Singlet |

The results of the low-temperature experiments with compounds *1a* and *1b* are summarized below.

$$1a \xrightarrow{h\nu,\ 20\ K} HCN + HCNSe? \xrightarrow{h\nu,\ 20\ K} HCN + CN + Se$$

$$1b \xrightarrow{h\nu,\ 20\ K} CH_3CN + CH_3CNSe? \xrightarrow{h\nu,\ 20\ K} CH_3CN + HCN + CN + Se$$

*Quantum yields.* Quantum yields for chemical reaction, $\Phi_r^\circ$, were measured in 96 % ethanol at room temperature with samples stirred and deoxygenated with a stream of argon. The wavelength of light used corresponds to that of maximum absorption of the solutions. The measured quantum yields are given in Table 2 (see also Experimental Section). $\Phi_r^\circ$ (*1c*) in heptane, benzene and ethanol were identical within 5 % deviation.

*Quenching and sensitization experiments.* In order to determine the multiplicity of the excited states involved experiments were carried out with added quenchers (oxygen, $E_S = 23$ kcal/mol [13],* and piperylene, $E_T = 57 - 59$ kcal/mol [14a]) and sensitizers (xanthone, $E_T = 74$ kcal/mol,[13] and thioxanthone, $E_T = 65$ kcal/mol [13]).

Triplet sensitized photolysis of compounds *1a* and *1b* was studied in PVC films (100 $\mu$m thick) with xanthone ($\sim$0.5 M) as sensitizer and with acceptor concentrations of *1a* or *1b* $\sim$0.5 M. Irradiation was carried out at 85 K and at 195 K. Xanthone was excited selectively with 363 nm light (interference filter). Only absorptions from hydrogen cyanide and acetonitrile were detected (IR).

* 1 kcal = 4.184 kJ.

Analogous experiments with compounds *1c* and *2* were performed in poly (methyl methacrylate) (PMMA, 50 $\mu$m thick) at room temperature with thioxanthone as sensitizer and with concentrations of donor and acceptor $\sim$0.1 M. When the sensitizer was selectively excited at 395 nm (interference filter), benzonitrile was readily formed (IR, 2220 cm$^{-1}$) from compound *1c* but sensitized photolysis of *2* did not occur even on prolonged photolysis.

The effect of quenching with piperylene and oxygen was measured relative to deoxygenated samples. The rate of photolysis of selenadiazoles *1a* (in heptane) and *1b* (in benzene) was insensitive to saturation of solutions with oxygen (1 atm) and also insensitive to concentrations of piperylene up to 0.3 M. However, the photoreaction of diphenylselenadiazole, *1c*, (in ethanol), was partly quenched by oxygen ($\Phi_r = 0.33 \pm 0.05$).

The degree of quenching of *1c* in benzene was studied as a function of the concentration of added piperylene. The so-called Stern-Volmer plot is shown in Fig. 8, where the ratio $\Phi_r^\circ/\Phi_r$ is depicted as a function of piperylene concentration. Irradiation was carried out at $320 \pm 7$ nm. Under these conditions, light absorption by piperylene is negligible. Also shown in Fig. 8 is the insensitivity of $\Phi_r(2)$ to the presence of piperylene. The mechanistic consequences of these experiments are discussed in the next section and summarized in Table 2.

*Luminescence of excited states.* Compounds *1a* − *c* did not luminesce in liquid solution at room temperature, but in frozen EPA at 77 K compounds *1b* − *c* were found to phosphoresce. No fine structure could be seen in the spectra. Compound *1a* did not luminesce at 77 K. Quantum yields of emission were measured relative to compounds with known quantum yields. Phosphorescence lifetimes (EPA, 77 K) were measured using the rotating chopper of the phosphorescence accessories in the emission spectrophotometer (see Experimental Section). Emission data are given in Table 3.

## DISCUSSION

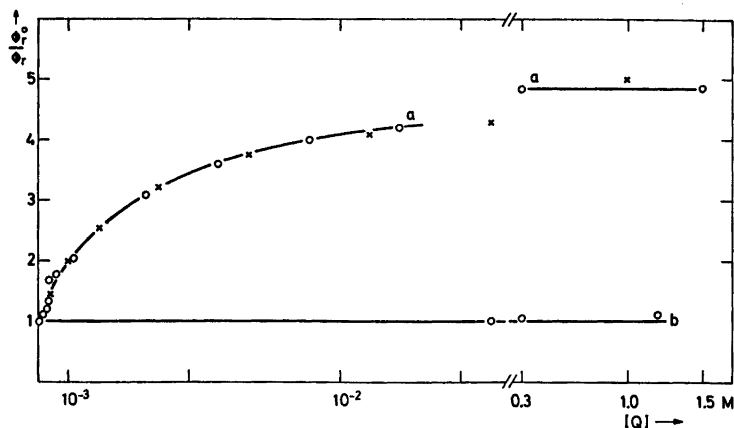*Photolysis of compounds* 1a − c *and* 2. It is concluded from the low temperature UV spectra in Figs. 1 and 2 that compounds *1c*

*Fig. 8.* Plots of $\Phi_r^\circ/\Phi_r$ against concentration of piperylene in benzene at room temperature. a, diphenyl-1,2,5-selenadiazole (*1c*) (4.0 × 10⁻⁴ M in benzene, $\lambda_{ex}$ 320 ± 7 nm) and b, diphenyl-1,2,4-selenadiazole (*2*) (4.6 × 10⁻⁴ M in benzene, $\lambda_{ex}$ 310 ± 20 nm). ×, calculated values using $a = 4$ and $k_q\tau = 1600$ M⁻¹, see Discussion.

and *2* photolyse to benzonitrile and a common intermediate, which is identified as benzonitrile selenide on the basis of its properties: (i) Photolysis or warming from cryogenic temperatures produces benzonitrile exclusively. (ii) In nitrogen matrix the IR absorption at 2200 cm⁻¹ (Fig. 4, 2190 cm⁻¹ in PVC) disappeared on photolysis, *and the UV bands of the same sample (Fig. 3) disappeared simultaneously*.

These properties are very similar to the properties of benzonitrile sulfide,[1c] which absorbs at 2185 cm⁻¹ in PVC [15] and features a UV spectrum with the same profile as that of benzonitrile selenide shown in Figs. 1–3, except that the maxima of the selenide are red-shifted. Benzonitrile selenide is thermally less stable than the sulfide.[1c] This probably explains why trapping experiments were unsuccessful.

*Table 3.* Phosphorescence data of selenadiazoles *1b* and *1c* in EPA at 77 K.

| Compound | $\lambda_{max}$/nm [b] | $\Phi_p$ | $\tau_p/10^3$ s |
|---|---|---|---|
| *1b* [a] | 455 | 0.14(3) | 2.5(1) |
| *1c* [a] | 538 | 0.33(8) | 1.7(1) |

[a] Samples of *1b* and *1c* (∼10⁻⁴ M) were excited at 280–290 nm and 310–320 nm, respectively. [b] Spectra were corrected.

A comparison of the two spectra in Fig. 7 shows that 1,2,5-selenadiazole (*1a*) and dimethyl-1,2,5-selenadiazole (*1b*) photolyse to different products. This excludes possible common intermediates, *e.g.* Se$_n$, CN, HSe and C₂N₂ as candidates for the assignment of the spectra. Since the positions and the intensities of the maxima are only slightly different (Figs. 5, 6 and 7) we assume that the two primary products differ only by the substitution of the hydrogen with a methyl group. Their thermal stabilities are comparable to the stability of benzonitrile selenide. The two intermediates must display weak absorptions in the near ultraviolet since photolysis with 300 nm light caused degradation of all material absorbing in this spectral region. The nitrile selenides HCNSe (*4*) and CH₃CNSe (*5*) are expected to photolyse to nitriles and selenium, neither of which absorbs above 200 nm. This tentative assignment is further supported by the observation of chemiluminescence, believed to originate from dimerization of selenium atoms.

On the other hand photolysis of *1a* as well as *1b* caused formation of CN radicals observed at 2046 cm⁻¹. This result is only consistent with the assumption that HCNSe/HCN and CH₃CNSe/CH₃CN are the sole primary photoproducts of *1a* and *1b* if the two nitrile selenides can produce CN radicals, at least partially, upon irradiation. As mentioned, the analogy to benzonitrile selenide makes us believe, that

extrusion of selenium is the prevailing photo-lytic pathway. Alternatively, the CN radicals are formed directly from *1a* and *1b* or from primary photoproducts of these with structures different from *4* and *5*. HSeNC and $CH_3SeNC$ could be such precursors, but intermediates with this structure would probably rearrange thermally to selenocyanates, RSeCN. Methyl selenocyanate, a stable compound, was not formed when *1b* was photolysed at room tem-perature and no absorption from methyl selenocyanate (2152 $cm^{-1}$ [16]) was observed in the IR experiment in PVC.

In conclusion, the origin of the CN radicals remains unknown and the definite assignment of the spectra corresponding to the irradiation products of *1a−b* must await further experi-ments.

*Mechanistic results.* The photodegradation of compounds *1a* and *1b* could not be quenched by oxygen or piperylene. Neither the triplet energy (63 kcal/mol) nor the triplet lifetime (2.5 ms at 77 K) of *1b* can be prohibiting factors in triplet energy transfer from *1b* to oxygen or piperylene. Thus we conclude, that the photoactive state of *1b* and probably *1a* too, is a singlet state.
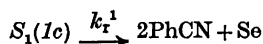
The photoreactions of *1a* and *1b* could be triplet-sensitized by using xanthone, demon-strating the reactivity of the triplet states. But these are apparently not populated on direct excitation at room temperature.

The curvature of the Stern-Volmer plot for quenching of *1c* (Fig. 8) indicates that two photoactive states are involved. At high piper-ylene concentrations the plot is linear with a slope of zero. These results are interpreted by assuming that *triplet-1c* ($T_1(1c)$) and *singlet-1c* ($S_1(1c)$) are leading to products but only the triplet state can be quenched.

Excitation:

$$S_0(1c) \xrightarrow{h\nu} S_1(1c)$$
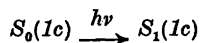
Chemical reaction of excited singlet:

$$S_1(1c) \xrightarrow{k_r^1} 2PhCN + Se$$

Internal conversion:

$$S_1(1c) \xrightarrow{k_{ic}} S_0(1c)$$

Intersystem crossing:

$$S_1(1c) \xrightarrow{k_{isc}} T_1(1c)$$

Chemical reaction of triplet:

$$T_1(1c) \xrightarrow{k_r^3} 2PhCN + Se$$
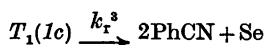
Unimolecular decay of triplet:

$$T_1(1c) \xrightarrow{k_d^3} S_0(1c)$$
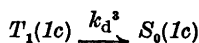
Bimolecular quenching of triplet:

$$T_1(1c) + Q \xrightarrow{k_q} S_0(1c) + T_1(Q)$$
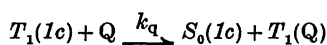
If a photoreaction takes place from an excited singlet and triplet state but only the triplet reaction can be quenched, the kinetic expression has the following form:[17]

$$\Phi_r^\circ/\Phi_r = (1+a)(1+k_q\tau[Q])/(1+a+k_q\tau[Q])$$

$a$ is the ratio of triplet to singlet reaction and $\tau = 1/(k_r^3 + k_d^3)$.

Since $\Phi_r^\circ$ was estimated to be 1.0, all radia-tionless deactivation must be negligible, *i.e.* $k_{ic} \ll k_{isc} + k_r^1$ and $k_d^3 \ll k_r^3$. Consequently, $\tau \approx 1/k_r^3$. The limiting value of the kinetic expres-sion at high quencher concentrations is

$$\lim_{[Q] \to \infty} \Phi_r^\circ/\Phi_r = 1 + a = 5 \quad \text{(Fig. 8)}$$

Thus $a = 4 = k_{isc}/k_r^1$. By using $a = 4$ and by simple iteration $k_q\tau$ is calculated to $1600 \pm 400$ $M^{-1}$. The simulated values are seen to fit the experimental curve satisfactorily (Fig. 8). The diffusion controlled bimolecular quenching constant depends on structures and on relative triplet energies of donor and acceptor.[14b] Usually, $10^9$ $M^{-1}s^{-1} < k_q < 10^{10}$ $M^{-1}s^{-1}$.[14b] In conclusion, the lifetime of $T_1(1c)$ in benzene at room temperature is $1.6 \times 10^{-7} s < \tau < 1.6 \times 10^{-6} s$.

Since $\Phi_p$ (*1c*, 77 K, EPA) was estimated to $\sim 0.33$ the quantum yield for chemical reaction in EPA at 77 K cannot exceed 0.67. This result and the fact that the triplet lifetime at 77 K in EPA is three orders of magnitude greater than the lifetime at room temperature in benzene solution shows that the ring cleavage from the triplet state is associated with an activation barrier.

The photochemical reaction of diphenyl-1,2,4-selenadiazole (*2*) could not be quenched with piperylene (Fig. 8) and unlike compounds *1a−c* triplet sensitized photolysis using thioxanthone was inefficient. The photoactive state is therefore the excited singlet state.

The difference in energy between $S_1$ and $T_1$ of heterocycles [$\Delta E(S_1,T_1)$] is generally $> 3000$ cm$^{-1}$ for $\pi - \pi^*$ states but $\leq 2500$ cm$^{-1}$ for $n - \pi^*$ states.[18] $\Delta E(S_1,T_1)$ for *1b−c* was determined as the difference in onset-energy between the UV absorption bands [$\sim 310$ nm (*1b*) and $\sim 350$ nm (*1c*)] and the phosphorescence bands [$\sim 390$ nm (*1b*) and $\sim 450$ nm (*1c*)]. This gave the values $\Delta E(S_1,T_1)$ $\sim 7000$ cm$^{-1}$ for *1b* and $\sim 6000$ cm$^{-1}$ for *1c* indicating that the lowest states are $\pi - \pi^*$ in character.

Spin forbidden processes are affected by heavy atoms in the molecule and a decrease in triplet lifetime is expected when oxygen, sulfur and selenium analogues are compared.[19]

The measured lifetimes (Table 3) are therefore reasonable for $T_1(\pi - \pi^*)$ states of *1b* and *1c*.

## EXPERIMENTAL

*Compounds.* *1a−c* were prepared according to Ref. 20, *2* according to Ref. 21 and *3* according to Ref. 22.

*Polymer films.* Poly(methyl methacrylate) (PMMA) was prepared by polymerization of neat monomer initiated by azobis-isobutyronitrile at 60−80 °C. The monomer was carefully purified by distillation through a Vigreux column. Poly(vinyl chloride) (PVC), Corvic D60/13, was used without further purification. Films were prepared using the solvent casting technique.[23]

*Photolyses at room temperature.* Irradiation of *1a−c*, *2* and *cis,cis*-2,4-hexadienedinitrile was carried out using a Bausch and Lomb SP-200 mercury point source with or without monochromator as specified. (Typical monochromator band width was $\sim 20$ nm). In the sensitization experiments selective excitation was ensured by use of interference filters (363 nm and 395 nm). Photolysis of *1c* in dimethyl acetylenedicarboxylate was performed with a Rayonet reator, type RPR-208 with RUL 3000 Å lamps. Compound *3* was irradiated with an internal light source, type Hanovia Q-700, cooled with tap water. Stirring was ensured. Photolysis mixtures were analyzed with either a Unicam SP-800 A spectrophotometer, a Perkin-Elmer 337 grating infrared spectrophotometer or with a Pye Unicam 104 gas chromatograph connected to a Varian Aerograph model 477 electronic integrator.

Preparative layer chromatography (PLC) was performed using plates with a 2.5 mm thick layer of silica gel (Merck PF $_{254+366}$). The plates were developed with a mixture of benzene, light petroleum and acetone, 7:7:1. Quantum yields for chemical reaction were measured using the potassium trisoxalatoferrate(III) actinometer.[24] In this case the highly stabilized 150 W Xe/Hg superpressure point source of the fluorescence spectrophotometer (see below) was used. Deoxygenation and stirring were effected with argon.

*Photolyses at low temperature.* As light source at liquid nitrogen and dry ice temperatures, the Bausch and Lomb mercury source mentioned above was used. The low temperature UV cell, cooled with liquid nitrogen, is described in Ref. 1c. Spectra were recorded on a Cary 14 instrument. The IR cryostat used for irradiation of polymer films down to liq. N$_2$ temperatures was constructed by the group in Copenhagen. The film is kept between two KBr discs in a copper cavity. The hollow walls of the cavity are filled with liquid nitrogen. High vacuum is maintained around the probe. IR spectra were recorded on the Perkin-Elmer 337.

The matrix experiments at 10 and 20 K were performed using the apparatus in Newcastle which is based on an Air Products Displex CS-202 closed-cycle Helium refrigerator.[25] Irradiations were carried out with a Philips HPK-125 W medium pressure Hg arc and an Applied Photophysics high radiance monochromator (band width $\sim 10$ nm). UV spectra were recorded on a Perkin-Elmer 356 spectrophotometer. IR spectra were recorded on a Grubb Parsons Spectromajor spectrophotometer calibrated with gaseous DCl.

*Emission spectra.* These were obtained on a Perkin-Elmer MPF-3 fluorescence spectrophotometer with corrected spectra and phosphorescence accessories. Lifetimes were calculated from decay curves, stored by means of a Tektronix 549 oscilloscope using a chopper frequency of $\sim 100$ Hz. Quantum yields of phosphorescence ($\Phi_p$) at 77 K were measured relative to compounds with known quantum yields. If two solutions absorb the same fraction of light at a given wavelength the ratio of the quantum efficiencies can be determined as the ratio of the areas of the corrected emission spectra. These areas were determined by cutting and weighing. The areas of the phosphorescence spectra from each sample were reproducible within 10 %. Quantum yields of the standards were taken from Ref. 26. $\Phi_p$ (*1b*) was measured relative to benzoic acid ($\Phi_p$ 0.27) and phenanthrene ($\Phi_p$ 0.11). Solutions were excited at $280−285 \pm 10$ nm. $\Phi_p$ (*1c*) was measured relative to anthraquinone ($\Phi_p$ 0.41) and benzil ($\Phi_p$ 0.67). Solutions were excited at $310−317 \pm 7$ nm.

*Photolysis of 1,2,5-selenadiazole in ethanol at room temperature.* 1,2,5-selenadiazole (0.058 g) in 96 % ethanol (20 ml) was photolysed through

pyrex until deposition of selenium was complete (24 h). The photolysis mixture was poured into water (50 ml) and titrated potentiometrically with 0.050 M silver nitrate. The yield of hydrogen cyanide was measured to 87 %.

*Photolysis of dimethyl-1,2,5-selenadiazole in chloroform at room temperature.* Dimethyl-1,2,5-selenadiazole (0.108 g) in chloroform (20 ml) was photolysed through pyrex for 20 h. The photolysis mixture was filtrated and analyzed by GLC (10 % SE-30 on Gaschrom Q 100 – 120 mesh, 40 °C). Comparison with a reference solution of acetonitrile in chloroform showed that acetonitrile had been formed quantitatively. Peak areas were reproducible within 10 %.

*Photolysis of diphenyl-1,2,5-selenadiazole in dimethyl acetylenedicarboxylate.* Diphenyl-1,2,5-selenadiazole (1.00 g) was suspended in dimethyl acetylenedicarboxylate (10 ml) and photolysed through pyrex for 5 days, after which most of the starting material had disappeared (TLC). The solvent was evaporated *in vacuo* and separated by PLC. Besides unreacted starting material (0.032 g) 3 fractions (0.148 g, 0.036 g and 0.136 g) were isolated and analyzed with 60 MHz NMR. None of the products contained aromatic protons.

*Photolysis of 2,1,3-benzoselenadiazole in ethanol at room temperature.* 2,1,3-Benzoselenadiazole (1.00 g) was dissolved in 96 % ethanol (1.30 l) and photolysed with the internal light source (see above) until deposition of selenium was complete (7 days). The irradiated mixture was evaporated *in vacuo* and separated by PLC into *cis,cis*-2,4-hexadienedinitrile (0.051 g ∼9 %, m.p. 123 – 124 °C (benzene/light petroleum), Ref. 7, 128 °C), *trans,trans*-2,4-hexadienedinitrile (0.100 g ∼18 %, m.p. 155 – 157 °C (benzene/light petroleum), Ref. 7, 159 – 160 °C) and *cis,trans*-2,4-hexadienedinitrile (0.130 g ∼23 %, m.p. 70 – 71 °C (benzene/light petroleum), Ref. 7, 72 – 73 °C).

*Photolysis of cis,cis-2,4-hexadienedinitrile in ethanol at room temperature.* *cis,cis*-2,4-Hexadienedinitrile (0.020 g) was dissolved in 96 % ethanol (4 ml) and irradiated through quartz for 10 h. The photolysis mixture was analyzed by GLC (10 % poly(propylene glycol) on chromosorb W 60 – 80 mesh, 150 °C). By comparison of peak areas in chromatograms of a standard solution containing the three 2,4-hexadienedinitrile isomers the ratio of isomers *cis,cis:cis,trans:trans,trans* was calculated to 1.0:2.6:1.7. Peak areas were reproducible within 10 %.

*Photolysis of diphenyl-1,2,5-selenadiazole with added piperylene.* Quenching experiments with piperylene were performed according to the following procedure: Stock solutions of *1c* in benzene (4.0 × 10⁻⁴ M) and piperylene (1:25 and 1:250) were prepared. 2.00 ml of the solution of *1c* was transferred to a 3 ml UV cuvette. Piperylene and benzene were then added to give a total volume of 3.00 ml. Prior to and

during photolysis ($320 \pm 7$ nm, 5 min) argon was bubbled through the solution. The lamp of the emission spectrograph (see above) was used as light source. Errors due to evaporation of benzene and piperylene were found to be negligible. 1.00 ml of photolysis mixture was then diluted to 3.00 ml and the absorbance (∼1) measured with UV spectroscopy. This allowed $\Phi_r^\circ/\Phi_r$ to be calculated as $\Delta A^\circ/\Delta A$. To ensure total absorption of light and minimize light absorption by colloidal selenium, the amount of conversions did not exceed 15 %.

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