Photolysis of 1,2,3-Selenadiazole. Formation of Selenirene by Secondary Photolysis of Selenoketene

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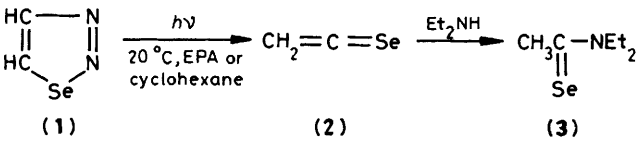
Irradiation of 1,2,3-selenadiazole together with diethylamine in solution at room temperature or at 150 K gives rise to *N,N*-diethylselenoacetamide in near quantitative yield, an indication of the trapping of selenoketene during photolysis. Experiments with ^{13}C-labelled selenadiazole demonstrate lack of carbon randomization in the selenoketene. This excludes selenirene as potential precursor for selenoketene.

After irradiation of 1,2,3-selenadiazole in an EPA-glass or PVC-film at 77 K, carbon randomized selenoketene has been detected in up to 56% yield by i.r. spectroscopy and 78% yield by trapping with diethylamine; the yields are dependent on the experimental conditions. A reaction mechanism is suggested which involves reversible formation of selenirene by photolysis from selenoketene. This process does not occur in liquid solution because of the extremely small steady-state concentration of selenoketene during photolysis.

The photochemistry of 1,2,3-selenadiazole has been little investigated, in contrast to that of 1,2,3-thiadiazole from which thiirene, thioketene, and ethynethiol have been detected after irradiation of matrix-isolated molecules at 8 K.[1,2] Krantz *et al.* described the results of irradiating samples of matrix-isolated 1,2,3-selenadiazole at 8 K, the reactions being monitored by i.r. spectroscopy.[3] New absorption bands for acetylene, ethyneselenole, selenirene, and selenoketene were assigned on the basis of comparisons with sulphur analogues. Meier and Menzel found that irradiation at room temperature of 4-ethoxycarbonyl-1,2,3-selenadiazole leads to formation of two isomeric diselenafulvenes.[4] It was suggested that a 1,3-diradical is formed which rearranges to selenoketene. The fulvenes were assumed to result from a reaction between selenoketene and the diradical.

Here we describe our results for the photochemical fragmentation of the parent 1,2,3-selenadiazole. They show that the first product detectable at 77 K is selenoketene. Selenirene is not the primary product, being produced photochemically from selenoketene; it is not thermally stable at 77 K.

Trapping Experiments.—We have found that irradiation (290 ± 10 nm) of 1,2,3-selenadiazole (**1**) ($\lambda_{max.}$ 285 nm, ε 905 l mol^{-1} cm^{-1}, EPA†)‡ in low concentrations (*ca.* 5 × 10^{-4} M) in cyclohexane or EPA and in the presence of diethylamine (*ca.* 1%) at room temperature gives rise to the formation of *N,N*-diethylselenoacetamide (**3**)§ in high yield (90—100%). With increasing selenadiazole concentrations decreasing amounts of diethyl selenoacetamide are formed and, concurrently, formation of elemental selenium is observed. The quantum yield for disappearance of (**1**) in dilute solutions is not dependent on the presence of diethylamine (0—10%); this excludes the possibility that product formation could result from direct reaction of diethylamine with an excited state of the selenadiazole. Furthermore, the quantum yield for disappearance of (**1**) is not dependent on the presence of oxygen. The overall observations, therefore, indicate that (**1**) undergoes a unimolecular reaction from an excited singlet state to form selenoketene (**2**) either directly or *via* short-lived intermediates. This step is followed by trapping with diethylamine to give (**3**) (see Scheme 1).



(**1**) (**2**) (**3**)

Scheme 1.

Additional information has been obtained by studying the photolysis of dilute solutions of 4- or 5-^{13}C labelled selenadiazole in EPA or cyclohexane in the presence of diethylamine. Sufficient volumes of the solutions were irradiated (300 nm) in order to give 15—20 mg of diethyl selenoacetamide; this was purified by distillation (overall yield up to 80%) and analysed by ^{13}C n.m.r. for carbon randomization. Inspection of the Table shows that *no* randomization takes place when the photolysis is carried out in liquid solution at room temperature or 150 K (expt. nos. 1 and 2). However, we do observe randomization when ^{13}C-labelled 1,2,3-selenadiazole is irradiated in EPA-glass at 77 K but the extent depends on other conditions as well. A high degree of exchange, (39%) [1-^{13}C]diethylselenoacetamide from [4-^{13}C]selendiazole, is observed when the sample is irradiated through quartz for 100 min (expt. no. 8). Minimum exchange (6—9%) is observed when total irradiation for up to 100 min is performed through Pyrex for periods of 10—20 min at a time, these being followed by annealing (heat, melt, recool); this allows primary products to react thermally (see Scheme 1; expt. nos. 3—5). Thus, the degree of scrambling is high when secondary photolysis is favoured.

Spectroscopy.—The phototransformation of 1,2,3-selenadiazole in the absence of diethylamine has been monitored by u.v./visible spectroscopy in EPA-glass at 80 K (Figure 1). Irradiation causes disappearance of the selenadiazole absorption (Figure 1, trace A) and appearance of a weaker band at 266 nm (Figure 1, trace B). Continued irradiation causes no further observable transformation. However, the absorption band at 266 nm vanishes at *ca.* 95—100 K when the sample is warmed slowly. Simultaneously, a relatively strong band at 372 nm is formed (Figure 1, trace C). Reversion to starting material is not

† EPA = diethyl ethyl–isopentane–ethanol (5:5:2).
‡ Reported as $\lambda_{max.}$ 282 nm (ε 900 l mol^{-1} cm^{-1}).[5]
§ Identified by comparison with authentic material (F. Malek-Yazdi and M. Yalpani, *Synthesis*, 1977, 328) after column chromatography (u.v. spectroscopy and ^1H n.m.r.).

Table. Irradiation (254 nm (quartz tubes)[a] or >290 nm (Pyrex tubes)) of [4-^{13}C]- or [5-^{13}C]-4*H*, 5*H*-1,2,3-selenadiazoles [(5.4—7.5) × 10^{-5} M in EPA[b]] in the presence of diethylamine (1%)

Expt. no.	Label	Temp. (K)	Yields as % found by u.v. spectroscopy and by isolation U.v.	Isol'n	Irrad'n intervals (min) interrupted by annealing	Total irrad'n time (min)	Percent scrambling in the isolated ethylselenoacetamide[d]
1*	5-^{13}C	293				85	*ca.* 0[c]
2*	5-^{13}C	156				116	*ca.* 0[c]
3*	5-^{13}C	77	73	26	10	100	8
4*	5-^{13}C	77	86	34	20	100	9
5*	4-^{13}C	77	42	23	20	100	6
6*	5-^{13}C	77	95	62	100	100	31
7*	5-^{13}C	77	84	80	200	200	26
8†	4-^{13}C	77	96	41	100	100	39

[a] Pyrex tubes* (2.2—3.5 cm i.d.) or quartz tubes† (1 cm i.d.). [b] Except expt. no. 1 in cyclohexane. All liquid samples were purged with argon during irradiation. [c] Noise level 1—2%. [d] Determined by ^{13}C n.m.r. ($CDCl_3$).

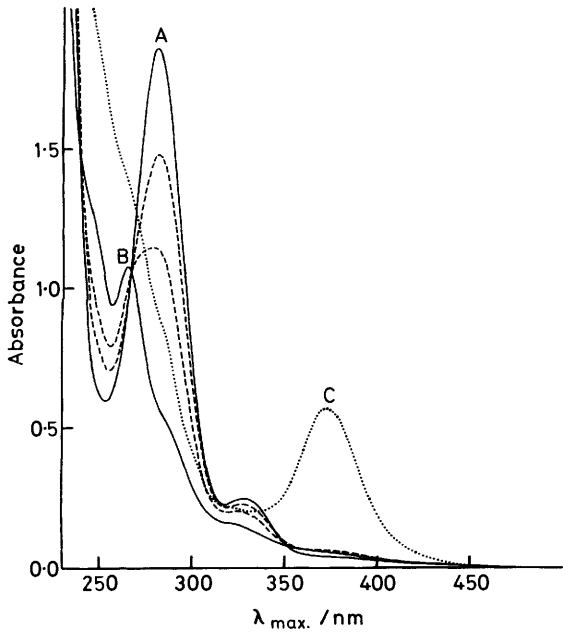


Figure 1. Stepwise photolysis (290 ± 35 nm) of 1,2,3-selenadiazole in EPA frozen at 80 K. Intermediate spectra are shown in dashed lines: A, Initial spectrum; B, final spectrum after photolysis; C, spectrum recorded after cautious heating to *ca.* 95—100 K.

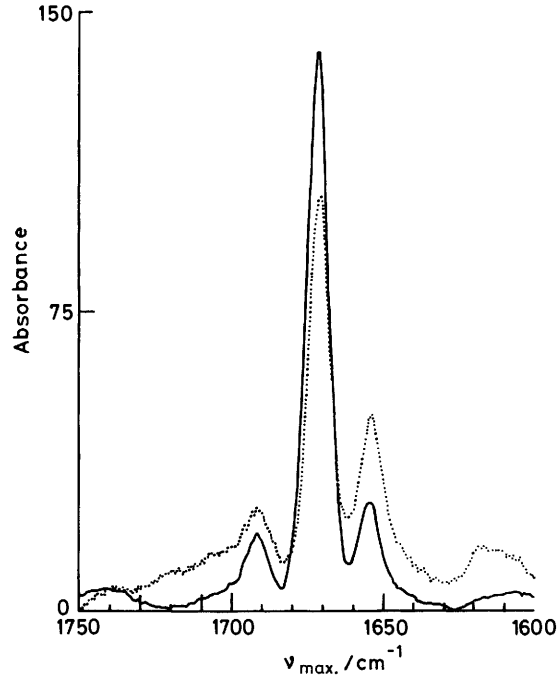


Figure 2. Selenoketene ($H_2{}^{12}C{=}{}^{12}C{=}Se$, 1 691; $H_2{}^{13}C{=}{}^{12}C{=}Se$, 1 672; $H_2{}^{12}C{=}{}^{13}C{=}Se$, 1 654 cm^{-1}) formed upon irradiation (290 ± 10 nm) of [4-^{13}C]-1,2,3-selenadiazole (90% ^{13}C) in PVC at 77 K monitored by i.r. spectroscopy. Full line: absorbance (× 100). Dotted line [absorbance (× 200)]. Same sample after further irradiation with unfiltered light from an Osram HBO mercury source.

observed. At higher temperatures the 372 nm band disappears gradually along with melting of the EPA glass (*ca.* 140 K). Spectroscopically the same observations have been made using poly(vinyl chloride) (PVC) instead of EPA as solvent, but the thermal events took place at higher temperatures during warm-up and with wider temperature intervals. Thus, appearance of the 372 nm band cannot be linked to a reaction with the solvent.

Basically the same experiment was duplicated using i.r. spectroscopy to monitor the reaction. The sample was a solid solution of 1,2,3-selenadiazole in PVC cast as a thin film. Irradiation (290 ± 10 nm) caused the selenadiazole (782 cm^{-1}) to disappear while a very strong band grew at 1 691 cm^{-1}. This absorption can be assigned to selenoketene[3,6] which consequently is responsible for the u.v. absorption at 266 nm. No new absorptions were visible in the i.r. region when the selenoketene was degraded during warm-up. Apparently, the i.r. absorptions corresponding to the compound absorbing at 372 nm in the u.v. region are hidden by the strong i.r. bands of PVC. Although it must be a thermal product of selenoketene, we have no suggestion as to its structure.

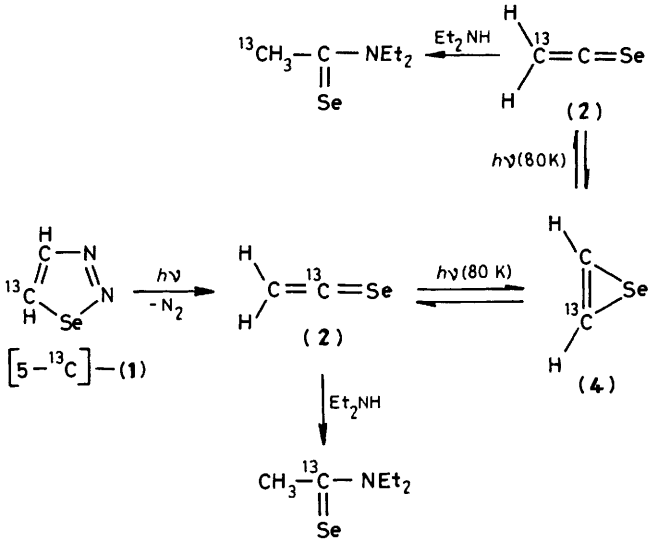
Irradiation of 4-^{13}C labelled 1,2,3-selenadiazole (90% ^{13}C) in PVC at 77 K monitored by i.r. spectroscopy provides further significant information. Upon irradiation (290 ± 10 nm) a strong band appeared at 1 672 cm^{-1} while the selenadiazole absorptions disappeared. In Figure 2 (full line) the relevant heterocumulene i.r. region is depicted after complete conversion of selenadiazole. The strong band at 1 672 cm^{-1} is assigned to $H_2{}^{13}C{=}{}^{12}C{=}Se$, the weak band at 1 691 cm^{-1} to $H_2{}^{12}C{=}{}^{12}C{=}Se$[3,6] and the weak band at 1 654 cm^{-1} to $H_2{}^{12}C{=}{}^{13}C{=}Se$. From the spectrum it is calculated, that $H_2{}^{12}C{=}{}^{12}C{=}Se$ corresponds to *ca.* 9% of the total amount as expected (same isotopic purity of starting material).

The area of the 1 654 cm^{-1} band constitutes 11% of the sum of the absorptions at 1 654 and 1 672 cm^{-1}. This procedure makes the figures comparable with those obtained in the trapping experiments, since the unlabelled isomers are invisible in the ^{13}C n.m.r. spectrum.

Upon continued irradiation with unfiltered light (OSRAM HBO 200) a gradual increase of the 1 654 cm^{-1} band is observed at the expense of the 1 672 cm^{-1} absorption. The process was continued until the 1 654 cm^{-1} band was 24% of the sum of the two (Figure 2, dotted line).

Thus it is established, that the carbon atoms of selenoketene change positions when the molecule is irradiated. The minor amount of $H_2C=^{13}C=Se$ apparent in trace A is presumably produced during build-up of selenoketene, since the u.v. absorption spectra of 1,2,3-selenadiazole and selenoketene overlap to a great extent making rephotolysis inevitable.

A band at 3 318 cm^{-1} assigned to HC≡C–SeH, was reported by Krantz *et al.*[3] to be formed during irradiation of 1,2,3-selenadiazole under matrix conditions at 10 K but has not been observed in our experiments. It is also pertinent to note that the strong band at 729 cm^{-1} due to HC≡CH has not been observed either.



Scheme 2.

Discussion

The trapping experiments with diethylamine demonstrate photochemical formation of selenoketene[6] from 1,2,3-selenadiazole in almost quantitative yield at room temperature. The ^{13}C-labelling experiments at room temperature and in liquid solution down to 150 K show that the carbon atoms never became equivalent on the reaction pathway to selenoketene. That is, selenirene is *not* involved.

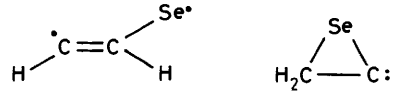
Identification of selenoketene as the first photoproduct stable at 77 K is based primarily on the i.r. spectrum (*vide infra*). U.v. spectra of selenoketenes with which the u.v. spectrum of the photochemically generated parent selenoketene can be directly compared have not been reported. So far, room temperature stability seems conditioned by the presence of substituents that interfere with the electrophilic carbon and the π-system of the ketene moiety. Thus, Schaumann *et al.*[7] have reported on the preparation of trimethylsilyl(1-methylallyl)selenoketene [291 (log ε 3.3) and 554 nm (1.3)]. Considering the expected bathochromic effect of these substituents, the values found here for the parent (266 nm, log ε *ca.* 2.7) are consistent with the findings quoted. The long wavelength absorption expected in selenoketenes is too weak to permit observation in the concentration range employed in this work.

Selenoketene appears to be extremely reactive[6] and steady-state concentrations during photolysis in liquid solution must be very small. In contrast to this, selenoketone ($\lambda_{max.}$ 262 nm) is stable in an EPA-glass or PVC-film at liquid nitrogen temperatures and is thus accessible for secondary photolysis. The latter can be largely avoided by repeated annealing since the selenoketene generated is periodically removed from the irradiation zone before significant amounts build up. Without annealing, continued irradiation after formation of the selenoketene caused 39% exchange of the carbon atoms in selenoketene by the trapping experiments and 28% in the i.r. experiment. The absolute figures are insignificant inasmuch as they are dependent on the degree of re-photolysis and thereby on many experimental parameters. Thus, it is unambiguously established, that the carbon atoms of selenoketene can change positions in a photochemical reaction.

We have not observed acetylene (729 cm^{-1}) during the low-temperature i.r. experiments and do not consider a hypothetical (photo)reaction between acetylene and selenium atoms to be part of the rationalization of these experiments. It is more logical to involve selenirene (Scheme 2).

Although Krantz and Laureni[3] have found that the selenirene structure is stable at 10 K in solid argon, this seems not to be the case at liquid nitrogen temperatures. Obviously, thermal decomposition of selenirene can give rise to an equal mixture of [1-^{13}C]- and [2-^{13}C]-selenoketenes, the two carbon atoms becoming equivalent in the symmetrical selenirene. Depending on the quantum yields and reversibility of the primary step more than 78% of the selenoketene molecules are involved in this cycle of trapping experiments with maximum scrambling; in the i.r. experiment the figure is 48%.

In Scheme 1, the photoreactions of selenadiazole and selenoketene and the thermal reaction of selenirene do not necessarily have to be concerted. Intermediates like the biradical (**5**) and/or the carbene (**6**) may be involved.



(**5**) (**6**)

Strausz and co-workers[8] have demonstrated the formation of a triplet biradical upon irradiation of diphenyl-1,2,3-thiadiazole. Likewise, nitrogen extrusion from 1,2,3-selenadiazole may lead to (**5**) as the primary product. However, the work described in this paper implies that any primary product from 1,2,3-selenadiazole must form, exclusively, selenoketene. The ring carbene (**6**) features two hydrogens located on one carbon atom. Accordingly, it has high priority when hypothetical intermediates in the interconversions between selenirene and selenoketene are being considered. A further C_2H_2Se isomer, acetyleneselenol, can probably be formed photolytically from selenirene.[1,3] However, since selenirene is thermally unstable at 77 K and concentrations cannot build up, acetyleneselenol is not observed (2 050 and 581 cm^{-1}) under our conditions.

To sum up, the experiments presented in this paper demonstrate that selenirene is not the primary photoproduct when 1,2,3-selenadiazole is photolysed in fluid solution or in frozen EPA glass at liquid nitrogen temperatures. Furthermore, it has been shown that the carbon atoms of selenoketene can change positions in a photochemical reaction. The mechanism for this step is suggested to involve selenirene. A comparison with experiments in solid argon matrices[1-3] reveals that

although the two sets of conditions are very different, the results described here may be applied to the rationalization of both sets of results.

Experimental

^1H and ^{13}C N.m.r. spectra were obtained on a JEOL FX 90 Q Fourier Transform n.m.r. spectrometer using $CDCl_3$ as solvent and $SiMe_4$ as internal standard. Room temperature u.v./visible spectra were obtained on a UNICAM SP 800 spectrophotometer. Low-temperature u.v./visible spectra were recorded on a Cary 14 instrument using a cryostat as previously described.[9] Low-temperature i.r. spectra were obtained using a cryostat constructed in this department as previously described[10] and PVC films[11] from PVC, Corvic D60/13, I.C.I. Approximately 15 mg of the particular 1,2,3-selenadiazole to 300 mg of PVC were used. The i.r. spectra were recorded and the data stored digitally with a Perkin-Elmer 580 i.r. spectrometer interfaced with a RC 4000 computer (Ballerup, Denmark). The ratio-recording system of this spectrometer allows true transmission spectra to be obtained at cryogenic temperatures. These spectra have then been converted into the absorbance spectra which are shown in Figures 2 and 3. Two types of light sources were used for the photolytic reactions. An Osram HBO-200 high-pressure mercury lamp was used unscreened or equipped with a monochromator (typical bandwidth 20 nm). For the preparative experiments in EPA glasses and solutions a Rayonet RPR-208 photochemical reactor with RUL 3000 lamps was employed.

[1-^{13}C-] *and* [2-^{13}C]-*Acetaldehyde Semicarbazone.*—[1-^{13}C]- or [2-^{13}C]-ethanol (90% enriched, KOR Incorporated) (0.95 g) was diluted with water (6 ml) and added dropwise to Beckmann's solution (20 ml) [potassium dichromate (300 g), water (1 500 ml), and concentrated sulphuric acid (135 ml)] at 80 °C. The solution was purged with a moderate stream of nitrogen which at the same time ensured stirring and carried the acetaldehyde formed *via* a condenser to a trap containing semicarbazide hydrochloride (1.3 g) and sodium acetate (1.5 g) in water (5 ml). The trap was cooled in ice. Acetaldehyde semicarbazone, which generally is precipitated in *ca.* 1 h, was filtered off and dried *in vacuo* over concentrated sulphuric acid (yield, 1.3 g), m.p. 160—164 °C. This material was sufficiently pure for the preparation of selenadiazole.

[4-^{13}C]- *and* [5-^{13}C]-*Selenadiazole.*—A two-phase mixture consisting of selenium dioxide (2 g) in water (15 ml) and [1-^{13}C]- or [2-^{13}C]-acetaldehyde semicarbazone (1.3 g) in chloroform (10 ml) was stirred and refluxed at 50 °C for 1 h. Formation of elemental selenium and gas evolution was noted. The phases were separated after cooling and the aqueous phase as well as some solid material was washed with a small amount of chloroform. The combined chloroform phases were washed with water (1 ml) and saturated aqueous sodium hydrogencarbonate (1 ml) and then dried (Na_2SO_4). The solvent was removed under reduced pressure and the remaining selenadiazole then distilled under reduced pressure (0.01 Torr, 70 °C by flask-to-flask distillation (liquid nitrogen trap) (yield, 0.27 g, 10% based on labelled ethanol) of [4-^{13}C]- or [5-^{13}C]-1,2,3-selenadiazole.

Photolysis of 1,2,3-*Selenadiazole in the Presence of Diethylamine.*—Irradiation (290 ± 10 nm) of 1,2,3-selenadiazole in cyclohexane (10^{-4} M) in the presence of 1% diethylamine was monitored by u.v. spectroscopy; oxygen was not removed. Irradiation for 900 s produced 32% of selenoacetamide [$\lambda_{max.}$ 301 nm (ε 14 000 l mol^{-1} cm^{-1}, ethanol)]. Complete conversion produced a total of 95% selenoacetamide. In a parallel experiment under otherwise identical conditions, diethylamine was not added before the selenadiazole had been irradiated for 900 s. Still, 56% selenoacetamide could be produced in the continued reaction proving that the photolysis rate is independent of the presence of diethylamine.

In the presence of 10% diethylamine identical irradiation results were obtained. Similarly, irradiation of 1,2,3-selenadiazole (10^{-4} M) in cyclohexane in the presence of diethylamine (1%) and under an argon atmosphere gave diethyl selenoacetamide in 95% yield.

Photolysis of [4-^{13}C]- *and of* [5-^{13}C]-1,2,3-*Selenadiazole in EPA at* 77 K.—In each of the following experiments 500 ml of an approximately 3 × 10^{-4} M-solution of [4-^{13}C]- or [5-^{13}C]-1,2,3-selenadiazole in EPA [ether–isopentane–ethanol (5:5:2)] containing diethylamine (1%) was irradiated (≈300 nm) in liquid nitrogen through the walls of a Pyrex or quartz Dewar using the experimental conditions specified below. The conversion of selenadiazole was monitored by u.v. spectroscopy and when the expected conversion had taken place the solvent was removed under reduced pressure and the remaining *N,N*-diethylselenoacetamide isolated by flask-to-flask distillation (0.01 Torr, water-bath kept at 70 °C). The identity and purity were checked by ^1H- as well as ^{13}C n.m.r. spectroscopy. ^{13}C N.m.r. ($CDCl_3$, 5 mm tube with $SiMe_4$ as internal standard; pulse, 2 μs; repetition 30 s, data points 16 K): CH_3(2)-CSe(1)N[CH_2(3 and 3′)CH_3(4 and 4′)]$_2$, 200.9 (1), 36.4 (2), 52.0 and 47.1 (3 and 3′), and 12.5 and 11.2 p.p.m. (4 and 4′). Assignments are based on comparison with CH_3(3)CH_2(2)-CSe(1)N[CH_2(4 and 4′)CH_3(5 and 5′)]$_2$, 208.8 (1), 40.3 (2), 11.3 (3), 51.9 and 46.3 (4 and 4′), or 14.3 and 13.3 p.p.m. (5 and 5′).

Photolysis of [5-^{13}C]-1,2,3-*Selenadiazole in EPA at* 150 K *and in Cyclohexane at Room Temperature.*—An approximately 3 × 10^{-4} M solution (500 ml) of [5-^{13}C]-1,2,3-selenadiazole in EPA (150 K) or in cyclohexane (293 K) in the presence of diethylamine (1%) was irradiated (≈300 nm) for 130 and 85 min respectively to give *N,N*-diethylselenoacetamide in 60 and 69% yield respectively (u.v. spectroscopy) or 27 and 50% yield respectively (actual isolation as described above). In both cases the 1-^{13}C labelled amides were obtained with a content of randomized ^{13}C less than 1—2%, a limit being determined by the noise level of the ^{13}C n.m.r. spectra.

Acknowledgements

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