Photolysis of 1,2,3-Thiadiazole. Formation of Thiirene by Secondary Photolysis of Thioketene

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Irradiation of 1,2,3-thiadiazole together with diethylamine in liquid solution at room temperature or at 150 K gives rise to *N,N*-diethylthioacetamide in high yield which implies trapping of thioketene during photolysis. Experiments with [4-^{13}C]-1,2,3-thiadiazole at room temperature demonstrate lack of carbon randomization in the thioacetyl group of the trapping product. This excludes thiirene as a potential precursor for thioketene at this temperature.

The products isolated after irradiation of [4-^{13}C]-1,2,3-thiadiazole together with diethylamine in an EPA glass [diethyl ether–isopentane–ethanol (5:5:2)] at 77 K show up to 37 % carbon randomization in the thioketene. This strongly supports a reaction mechanism where thiirene is formed by photolysis of thioketene in solid solution and rapidly reverts to thioketene, resulting in the observed carbon randomization. This process does not occur in liquid solution owing to the extremely small steady-state concentration of thioketene during photolysis.

The photolytic reaction of 1,2,3-thiadiazole in EPA at 77 K was monitored by UV spectroscopy and the spectrum of thioketene is reported.

Light-induced elimination of molecular nitrogen from 1,2,3-thiadiazoles has been the subject of many investigations.[1–20] Depending on the experimental conditions and on the substituents in the 4,5-positions, formation of different products is observed. Kirmse and Horner,[1] who were the first to study this reaction, found that irradiation of substituted 1,2,3-thiadiazoles in benzene or dioxane gave rise to 1,4-dithiafulvenes and 1,4-dithiacyclohexadienes and proposed thioketocarbenes/1,3-biradicals and thioketenes as highly reactive intermediates. The thioketene was suggested to be formed in a Wolff-like rearrangement from the thioketocarbene. Zeller *et al.*[2,3] observed the formation of thiophenes as well as other products and assumed formation of thioketenes and biradicals as intermediates. Strausz *et al.*[4,5] carried out trapping experiments with hexafluoro-2-butyne during gas-phase irradiation of 1,2,3-thiadiazole, 4-methyl- and 5-methyl-thiadiazoles and isolated substituted thiophenes as products. The results were interpreted to imply the formation of thiirene. Irradiation of either 4- or 5-phenyl-1,2,3-thiadiazole in alcohols, was found to give rise to phenylthioketene,[6,7] trapped as the corresponding phenylthioacetic acid ester. It was shown by ^{13}C-labelling that phenylthiirene was an intermediate from 5-phenyl-1,2,3-thiadiazole to the extent of 15 %, while it was not formed from the 4-isomer. Bicyclic thiadiazoles such as 4,5,6,7-tetrahydro-1,2,3-benzothiadiazole[8] and 1,2,3-benzothiadiazole[9] were found to produce thioketenes upon irradiation, but in contrast with the above monocyclic thiadiazoles the intermediacy of thiirenes could be ruled out. A kinetic analysis of the mechanistic scheme for the conversion of thiirenes and their open-chain valence isomers has been presented by Meier and Kolshorn.[10]

The photochemistry of parent 1,2,3-thiadiazole (**1**) has been investigated thoroughly in matrices at cryogenic temperatures. By means of infrared spectroscopy, Krantz and Laureni[11–14] studied ^{13}C- and ^{2}H-labelled 1,2,3-thiadiazoles in matrices at 8 K. They established two reaction pathways for photolysis of **1** under these circumstances, one leading directly to thioketene (**2**) and ethynethiol (**3**), the other forming the same products via the symmetrical thiirene **4**, which causes randomization of the labels. On the other hand, thioketene itself was found capable of undergoing light-induced reactions. Depending on wavelength, it can form either thiirene – which regenerates thioketene with scrambled carbon atoms – or ethynethiol by a 1,3-hydrogen shift. Strausz and coworkers[15–17] have independently provided evidence for the formation of thiirene from the parent 1,2,3-thiadiazole under these conditions by means of IR spectroscopy.

Further information about these elusive intermediates has been obtained by Strausz and coworkers by irradiating certain substituted 1,2,3-thiadiazoles at cryogenic temperatures. Triplet thiobenzoylphenylmethylene was detected by EPR spectroscopy from the photolysis of

4,5-diphenyl-1,2,3-thiadiazole at 77 K.[18] On warming the sample, a rearrangement took place to give diphenylthioketene. It was shown that photolysis of argon-matrix isolated 4-acetyl-5-methyl-1,2,3-thiadiazole gives rise to the respective thiirene via thioacetylacetylmethylene.[19] It is of interest with respect to the latter type of compound, that Schrauzer and Kisch[20] had earlier trapped thiobenzoylphenylmethylene as an iron carbonyl complex by irradiation of 4,5-diphenyl-1,2,3-thiadiazole.

This paper describes the photolysis of the related parent 1,2,3-thiadiazole in liquid and solid polar solutions at room temperature and at 77 K. By means of trapping experiments, isotopic labelling and UV–VIS spectroscopy, it is shown, that the primary photoprocess under these circumstances does not involve thiirene. This species can, however, be formed in a secondary photochemical reaction from thioketene.

Trapping experiments. Irradiation (250–350 nm, quartz) of 1,2,3-thiadiazole (**1**, λ_{max} 247 nm, log ε 3.26, EPA* in low concentrations (10^{-4}–10^{-2} M) in EPA together with diethylamine (ca. 1 %) at room temperature gave rise to the formation of *N,N*-diethylthioacetamide (**5**)† in 75 % yield. The quantum yield disappearance of **1** in dilute solutions was found to be independent of the presence of diethylamine (0–10 %). This finding excludes the possibility that product formation could result from direct reaction of diethylamine with an excited state. Furthermore, the quantum yield disappearance of **1** did not depend on the presence of oxygen.

Additional information was obtained by carrying out the trapping experiments with solutions (10^{-3}–10^{-2} M) of [4-^{13}C]-1,2,3-thiadiazole in EPA under various conditions as specified in Table 1. The *N,N*-diethylthioacetamide formed in the room temperature experiments (expt. No. 1) was purified by vacuum distillation, in a typical run leaving ca. 11 mg (ca. 25 %) to be analyzed by ^{1}H and ^{13}C NMR spectroscopy for carbon randomization. In all other experiments at lower temperatures, *N,N*-diethylthioacetamide was the only product formed, and the sample did not require any further purification before spectroscopy.

Inspection of Table 1 reveals that *no* [1-^{13}C]-*N,N*-diethylthioacetamide was formed when the photolysis was carried out in liquid solution at room temperature or at 150 K at which temperature EPA is fluid (expts. Nos. 1 and 2). However, carbon randomization was observed in the product after irradiation in EPA-glass at 77 K. About 37 % of the molecules pass a stage in which the carbon atoms are equivalent giving rise to 18.5 % [1-^{13}C]-*N,N*-diethylthioacetamide. This amount appeared insensitive to irradiation time (expts. Nos. 3 and 4) and wavelength (expt. No. 6). EPA was exchanged for a 1:1 mixture of methanol and ethanol (expt. No. 5) in order to investigate whether the local viscosity of the matrix could alter the scrambling ratio. This glass has a microscopic viscosity ca. 10^9 times that of EPA,[23,24] but the result remained unchanged.

The only change in the experimental procedure which caused a substantial change in the carbon randomization was annealing (expt. No. 7), which reduced the scrambling ratio to approximately half the value in comparison with

Table 1. Irradiation[a] of [4-^{13}C]-1,2,3-thiadiazole[b] in the presence of diethylamine.[c]

Expt. No.	*T*/K	Total irradiation time/min	Percentage [1-^{13}C]-label in *N,N*-diethylthioacetamide formed[d]	
			^{1}H NMR	^{13}C NMR
1	298	150	–	<0.6
2	150	165	<2	<0.6
3	77	165	17.8	18.5
4	77	285	–	18.3
5[e]	77	285	18.3	16.5
6	77	225[f]	17.9	16.5
7	77	165[g]	9.6	9.2

[a] 250–350 nm, Rayonet Reactor RPR208, RU3000-lamps, through quartz. [b] Conc. (20.1–1.3) × 10^{-3} M; in EPA except expt. No. 5. [c] 1 %. [d] Determined by NMR spectroscopy. [e] Instead of EPA, a matrix consisting of MeOH–EtOH (1:1) was employed. [f] In the last 60 min the RUL-3000 lamps were replaced by RUL-2537 lamps, which emit exclusively at 254 nm. [g] Every 20 min of irradiation was interrupted by annealing, i.e., warming the sample to room temperature and recooling it for 15 min before continuation; see the text.

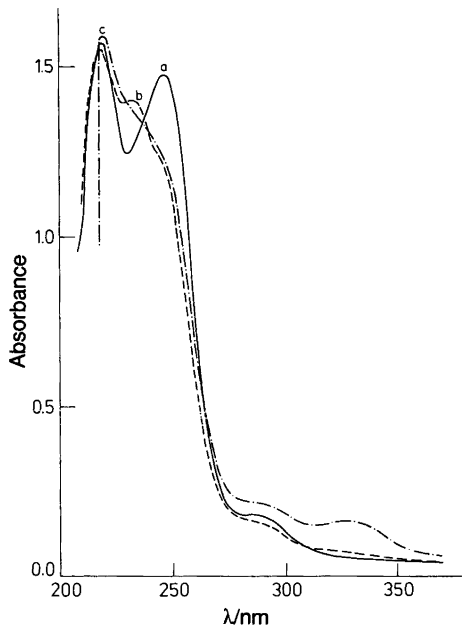
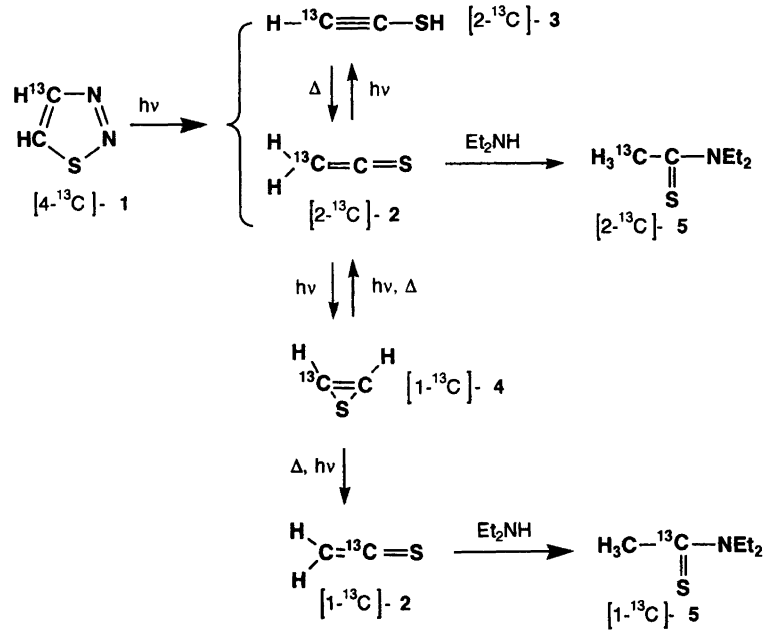


Fig. 1. Stepwise photolysis (265 ± 35 nm) of 1,2,3-thiadiazole in EPA frozen at 80 K. a, initial spectrum; b, final spectrum after photolysis; c, spectrum recorded after cautious heating to ca. 95–100 K.

* EPA = diethyl ether–isopentane–ethanol (5:5:2).

† Identified by comparison with authentic material,[21,22] λ_{max} 274 nm (EtOH), ε 1.24×10^4 M^{-1} cm^{-1}.



Scheme 1.

expt. No. 3. This procedure implied melting of the glass, thereby allowing primary products to react thermally. The solution was then frozen and left to equilibrate for 15 min before continuing the irradiation. This cycle was repeated eight times, thereby reducing the degree of rephotolysis of thermally labile intermediates compared with uninterrupted irradiations.

Independent experiments proved the labelled photoproduct *N,N*-diethylthioacetamide to be photostable under the conditions used.

UV–VIS spectroscopy. The phototransformation of 1,2,3-thiadiazole in the absence of diethylamine was monitored by UV–VIS spectroscopy in EPA-glass at 80 K (Fig. 1). Irradiation (λ 265 ± 35 nm) caused disappearance of the thiadiazole absorption band (Fig. 1, trace a) and consecutively recorded spectra showed an isosbestic point at 236 nm (not shown). The spectrum of the photoproduct(s) obtained after complete transformation of the thiadiazole is shown in Fig. 1, trace b, exhibiting an absorption band at 234 nm. Continued irradiation caused no further observable transformations. When the sample was warmed slowly to room temperature, the absorption band at 234 nm vanished at 95–100 K. Concurrently, a relatively strong band at 330 nm was formed (trace c). Reformation of starting material was not observed. The 330 nm band disappeared gradually along with melting of the EPA glass which occurred at ca. 140 K.

Discussion

The peak value at 234 nm in the electronic absorption spectrum of the photoproducts observed after photolysis of 1,2,3-thiadiazole in EPA at 80 K is assigned to the unsubstituted thioketene in analogy to the corresponding experiment with 1,2,3-selenadiazole.[25] The value agrees with the spectra of the few substituted thioketenes characterized so far.*

Thioketene is thermally highly labile as evidenced by the disappearance of the 234 nm absorption band at 90–100 K. In this temperature range microscopic domains in the EPA glass undergo temporary softening and diffusion becomes possible.[29] The simultaneous appearance of an absorption band at 330 nm is tentatively assigned to the formation of a dimer of thioketene, as the reaction cannot be linked to a reaction with the solvent. Similar phenomena have been observed for selenoketene.[25]

The insensitivity of the photolysis rate of 1,2,3-thiadiazole in solution at room temperature towards the presence of oxygen and diethylamine indicates a unimolecular reaction from an excited singlet state of **1** to form thioketene – either directly or via short-lived intermediates. The trapping experiments with diethylamine (see Scheme 1) demonstrate quantitative formation of thioketene upon photolysis of 1,2,3-thiadiazole in ethanol and EPA. ^{13}C-Labelling experiments in liquid solution at room temperature and 150 K show that the carbon atoms never become equivalent on the reaction pathway to thioketene. That is, thiirene is not involved as a primary photoproduct from 1,2,3-thiadiazole under these circumstances.

Steady-state concentrations of thioketene (**2**) during photolysis in liquid solution at room temperature or 150 K must be very small. In contrast, the photolysis experiments with [4-^{13}C]-labelled **1** in solid EPA (77 K) show that thio-

* Bis(trifluoromethyl)thioketene absorbs at 239 nm,[26] di-*tert*-butylthioketene at 239 nm,[27] and isopropyl(*tert*-butyl)thioketene at 240 nm.[28] The long-wavelength absorption also expected in thioketenes is too weak[26–28] to permit observation in the concentration range employed in this work.

ketene under these conditions is accessible for secondary photolysis (see Table 1, expts. Nos. 3–7), whereby a symmetrical molecule, i.e. thiirene (**4**), is formed since a maximum of ca. 18 % of the product appeared as [1-^{13}C]-*N,N*-diethylthioacetamide. This value was not changed by increased irradiation time (expts. Nos. 3 and 4), by a ca. 10^9 increase in viscosity of the matrix (expt. No. 5) or by shifting the irradiation to lower wavelength (expt. No. 6). The amount of secondary photolysis was only diminished by frequent annealing of the reaction mixture, whereby the thioketene generated was periodically removed from the irradiation zone before significant amounts could build up (expt. No. 7).

The upper limit of ca. 37 % thiirene formation from irradiated thioketene strongly indicates a competing photochemical pathway, most probably giving rise to ethynethiol (**3**). In matrices at cryogenic temperatures,[11] **3** is formed along with thioketene and can also be produced photochemically from thioketene via a 1,3-hydrogen shift. In either case, the label is maintained in the thioketene, which **3** probably (re)forms very fast when viscosity permits. As described above (UV–VIS spectroscopy), irradiation at 265 nm of thioketene in UV concentrations in EPA at 80 K, did not cause observable transformations. However, the sample concentration in the UV experiment is approximately 100 times lower than in the trapping experiments thus rendering possible rephotolysis of thioketene at the wavelength employed in the latter case only.

Our results show that 254 nm light can generate thiirene from thioketene. Thiirene is unlikely to be stable under our conditions, breaking down either photochemically or thermally. But its intermediacy is unquestionable, since in a third of the molecules the carbon atoms are equilibrated as a consequence of secondary photolysis. The results do not imply that the photoreactions of **1** and **2** and the thermal reactions of thiirene are concerted. They may proceed via biradicals and/or carbenoid intermediates as discussed in previous investigations.[11,18,20]

It is noteworthy that the closely related parent 1,2,3-selenadiazole exhibits very similar photochemical properties under the same conditions.[25]

Experimental

Low-temperature UV spectra were recorded on a Cary 14 instrument using a cryostat previously described.[30] Routine IR spectra were obtained on a Perkin-Elmer 157 instrument.

NMR measurements. NMR spectra were recorded on a JEOL FX 90Q instrument at 2.1 T in $CDCl_3$ solutions (0.5–1 %) at 27 °C. For control, both ^{1}H and ^{13}C NMR spectra were used for determination of the degree of scrambling. To allow for signal quantization the ^{13}C NMR spectra were recorded with a pulsewidth of 20 degrees and a pulse delay of 60 s. The ^{1}H decoupling was turned off, except for data acquisition, in order to eliminate the difference in contribution of the nuclear Overhauser effect to the methyl and the thiocarbonyl carbon atom signals. This last condition was found to be very important and amounted to a factor of almost 2 in the relative intensity. In the ^{1}H NMR spectra the distribution of the ^{13}C label was estimated from the intensity of the one-bond and two-bond coupling patterns between the ^{13}C label and the methyl protons ($^1J_{CH}$ = 129.2 Hz, $^2J_{CH}$ = 5.5 Hz). Nearly identical results were obtained from both types of spectrum to within experimental error.

Chemical preparations. All ^{13}C-labelled substances described were prepared according to described procedures with necessary minor modifications and the identity of the products obtained were confirmed by elemental analysis and spectroscopic comparison with authentic unlabelled material. The synthesis of [2-^{13}C]-2-oxopropanoic acid is a modification of the original procedure without isolation of the intermediate amide. References to the original literature are given.

Preparation of [1-^{13}C]*acetyl bromide.*[31] Benzoyl bromide (16.22 ml, freshly distilled) was added to [1-^{13}C]acetic acid (2 g, AEG, 90 % enriched) and the mixture was refluxed for 15 min at 60–70 °C after which the [1-^{13}C]acetyl bromide could be distilled out slowly at 70 °C. Yield 3.87 g, 95 %.

Preparation of [2-^{13}C]*acetyl cyanide.*[31] [1-^{13}C]acetyl bromide (3.87 g, freshly distilled) was added to copper(I) cyanide (2.9 g, dried over sulfuric acid) and the mixture was refluxed for 2.5 h at 100 °C. [2-^{13}C]Acetyl cyanide was distilled from the solution at 93–94 °C. Yield 1.5 g, 69 %.

Preparation of [2-^{13}C]-*2-oxopropanoic acid.*[32] Hydrochloric acid (conc., 0.54 ml) was added to [2-^{13}C]acetyl cyanide (1.5 g, freshly distilled) at 0 °C. The solution was allowed to warm, and after a while a vigorous, exothermic reaction occurred. The amide precipitated when the reaction mixture was cooled but was not isolated. The mixture was subjected to reduced pressure (15 mmHg) for 15 min and hydrochloric acid (4 M, 4.1 ml) was added. The mixture was stirred at 90 °C for 60 min. After being cooled, it was extracted with 5×7 ml diethyl ether. The combined ether extracts were dried ($MgSO_4$) and the solvent evaporated off under reduced pressure. The [2-^{13}C]-2-oxopropanoic acid was used without further purification. Yield 1.02 g, 54 %.

Preparation of [2-^{13}C]-*2-(2-ethoxycarbonylhydrazono)propanoic acid.*[33] A solution of hydrazinocarboxylic acid ethyl ester (1.5 g) in toluene (ca. 1 ml) was added to [2-^{13}C]-2-oxopropanoic acid (1.02 g) at ca. 45 °C. The resulting solution was stored for 2 days at 5 °C. The hydrazone was collected as white crystals and dried. Yield 1.61 g, 80 %.

Preparation of [4-^{13}C]-*1,2,3-thiadiazole-4-carboxylic acid.*[33] Thionyl chloride (5 ml) was added to [2-^{13}C]-2-(2-ethoxy-

carbonylhydrazono)propanoic acid (1.61 g) and the mixture set aside for 24 h at room temperature. The yellow crystals of [4-^{13}C]-1,2,3-thiadiazole-4-carboxylic acid were collected, washed three times with cold hexane and dried. Yield 0.58 g, 48 %.

Preparation of [4-^{13}C]-*1,2,3-thiadiazole.*[33] [4-^{13}C]-1,2,3-thiadiazole-4-carboxylic acid was pyrolyzed at 250 °C in N_2 for ca. 30 s. The [4-^{13}C]-1,2,3-thiadiazole was distilled under reduced pressure (0.01 Torr) into a cooled (liq. N_2) receiver. Yield 43.8 mg, 72 %.

Photolysis of 1,2,3-thiadiazole in the presence of diethylamine. Irradiation (250 ± 20 nm) of an aerated solution of 1,2,3-thiadiazole (10^{-4} M) and diethylamine (1 %) in EtOH at room temperature was monitored by UV spectroscopy. Irradiation for 100 min produced 30.3 % thioacetamide (λ_{max} 274 nm, log ε 4.093, EtOH). Complete conversion produced 75 %. In another experiment under otherwise identical conditions, diethylamine was not added until the thiadiazole had been irradiated for 100 min. Even so, 45 % thioacetamide could be produced in the continued reaction proving that the photolysis rate is independent of the presence of diethylamine. Purging with argon during photolysis did not influence the rate of formation of thioacetamide or its chemical yield. Identical results were obtained with diethylamine in 10 % concentration.

Photolysis of [4-^{13}C]-*1,2,3-thiadiazole in EPA at 77 K, 150 K and room temperature.* 25 ml of a solution of [4-^{13}C]-1,2,3-thiadiazole (1×10^{-2}–1.3×10^{-3} M) in EPA or MeOH–EtOH (1:1) in the presence of diethylamine (1 %) were placed in a cylindrical container (quartz) within a quartz Dewar. The space between the container and the wall of the Dewar was filled with either liq. N_2 (77 K), ethanol (room temperature) or an ethanol slush, the temperature of which was maintained at ca. 150 K (thermocouple) by means of frequent and adequate addition of liq. N_2. The sample was irradiated (Rayonet Reactor RPR208 with RUL3000 or RUL2537 lamps) for 150–285 min (see Table 1 in the text). In the annealing experiments, the conversion of thiadiazole could be monitored by UV spectroscopy on samples taken out. When the desired degree of conversion was reached, the sample was thawed and the solvent removed under reduced pressure. The remaining thioacetamide was investigated by means of NMR spectroscopy (*vide supra*).

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