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SPECTROSCOPIC EVIDENCE FOR THE FORMATION OF BENZONITRILE SELENIDE AS AN INTERMEDIATE IN THE LOW TEMPERATURE PHOTOLYSIS OF DIPHENYLSELENADIAZOLES

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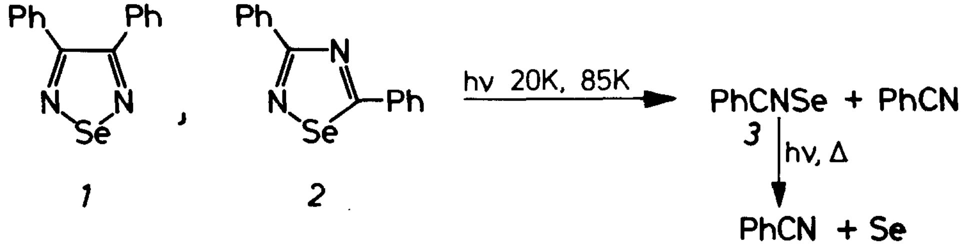
Benzonitrile sulfide has been generated as a reactive intermediate by thermal[1-5] and photochemical[6-9] reactions of various substrates. It has been characterized by low temperature spectroscopic methods[9] and trapped in 1,3-dipolar cycloaddition reactions with acetylenes,[1,2,6-9] nitriles[3,5] and maleic anhydride.[4] Since nitrile selenides were unknown, a photochemical study of diphenyl-1,2,5-selenadiazole[10] (1) and diphenyl-1,2,4-selenadiazole[11] (2) was undertaken in the hope of obtaining evidence for formation of benzonitrile selenide (3).

Irradiation at room temperature of 1 and 2 in ethanol with pyrex filtered light produced benzonitrile quantitatively. Attempts to trap benzonitrile selenide (3) by irradiation of compound 1 in neat dimethyl acetylenedicarboxylate were unsuccessful.



Absorption spectra recorded during the course of irradiation of compound 1 at 85 K in a poly(vinyl chloride) (PVC) film (Fig. 1) showed the development of absorption bands due to an intermediate at 255 nm (ε 13000-25000 $M^{-1}cm^{-1}$), 340 and 362 nm (ε 5000-10000 $M^{-1}cm^{-1}$). At the same time absorption bands due to benzonitrile appeared at 233, 270 and 278 nm. The absorption bands due to the intermediate decayed when irradiation at 300 nm was continued or when the sample was heated above ∿ 240 K, whilst the absorption bands due to benzonitrile increased in intensity (Fig. 1). On the basis of this and the following experiments the intermediate was identified as benzonitrile selenide, 3.

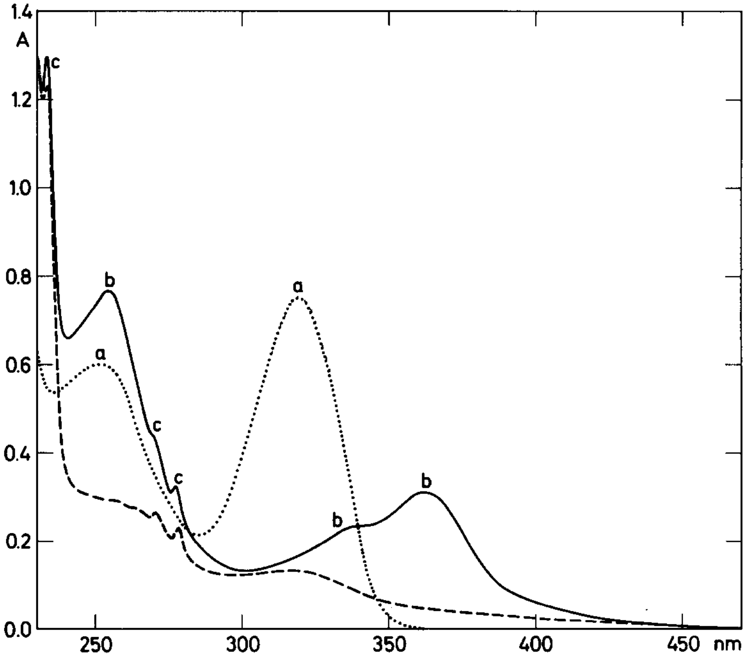


Fig. 1. UV spectra measured after photolysis at 85 K of diphenyl-1,2,5-selenadiazole (1) in PVC film, 20 µm thick, at 300±20 nm: a, starting material at 85 K (λ_{max} 320 nm). b, benzonitrile selenide at 255, 340 and 362 nm. c, benzonitrile. ----, after heating the sample to room temperature. Absorption due to starting material and benzonitrile can be seen.

Spectra recorded during photolysis of compound 2 in PVC under similar experimental conditions (spectra not shown) showed the development of absorption due to the same intermediate at 258, 325 (shoulder) and 360 nm (ε 5000-10000 $M^{-1}cm^{-1}$) together with absorptions due to benzonitrile. UV absorptions of benzonitrile selenide were also observed during photolysis in frozen EPA (diethyl ether, isopentane, ethanol, 5:5:2) at 85 K but competitive photolysis of the product formed rendered the absorptions at 254, 325 (shoulder), 357 and 384 nm less intense. Prolonged photolysis or heating of the sample above 110 K caused the benzonitrile selenide bands to disappear with concomitant enhancement of the absorption due to benzonitrile. The transition at 384 nm could not be detected during photolysis in PVC (Fig. 1) since site effects lead to broadening of the absorption bands.

Experiments using a nitrogen matrix were also performed with the primary aim of detecting absorption in the infrared. Spectra recorded following irradiation at 300 nm after deposition in solid N_2 at 20 K are shown in Fig. 2. The UV spectrum (left) and the IR spectrum (right) were recorded for the same sample. The two lowest energy UV absorption bands for benzonitrile selenide in this medium were observed at 356 and 390 nm (Fig. 2). The IR spectrum consists of two bands, viz. one due to benzonitrile at 2235 cm^{-1} and one due to benzonitrile selenide at 2200 cm^{-1}. The absorption bands in the UV spectrum and the absorption at 2200 cm^{-1} in the IR spectrum decayed, with concomitant slight enhancement of the IR absorption at 2235 cm^{-1}, when the matrix was irradiated with pyrex-filtered light.

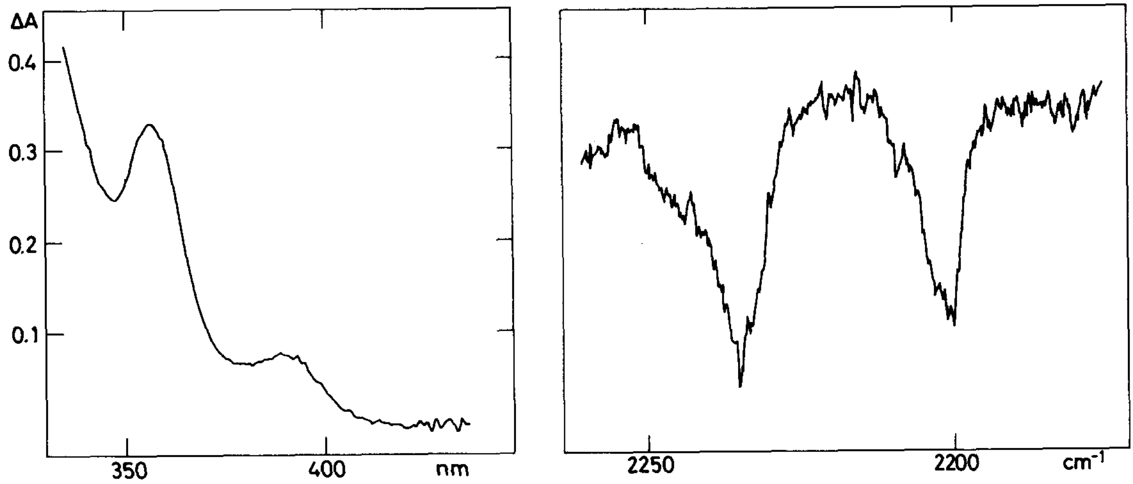


Fig. 2. UV spectrum (left) and IR spectrum (right, intensity in transmission) after irradiation at 20 K of diphenyl-1,2,5-selenadiazole (1) in a nitrogen matrix with 300±10 nm light. The bands at 356 nm and 390 nm in the UV spectrum and the band at 2200 cm^{-1} in the IR spectrum are assigned to benzonitrile selenide.

From the results of low temperature experiments we conclude that the two isomeric diphenylselenadiazoles, 1 and 2, photolyse to give benzonitrile together with a common intermediate identified as benzonitrile selenide on the basis of the following observations: (i) Prolonged photolysis or warming samples up from cryogenic temperatures produces benzonitrile exclusively. (ii) With the nitrogen matrix the IR absorption band at 2200 cm^{-1} (Fig. 2) and the UV absorption bands decayed simultaneously on prolonged irradiation. This behaviour is similar to that of benzonitrile sulfide,[9] which exhibits a UV spectrum having the same profile as that of benzonitrile selenide except that the maxima for the sulfide are blue-shifted with respect to those for the latter. In PVC at 85 K benzonitrile sulfide shows IR absorption at 2185 cm^{-1}.[12]

As expected, benzonitrile selenide is thermally less stable than the sulfide. In EPA glass the selenide decomposes sharply at 110 K. The sulfide decomposes first when the glass is heated to its melting point around 140 K[9] and in a PVC matrix benzonitrile sulfide can still be detected at room temperature.[9] This relative instability of the selenide might explain why trapping experiments with neat dimethyl acetylenedicarboxylate have only been successful with benzonitrile sulfide.

The photolysis of systems related to <u>1</u> and <u>2</u> has been the subject of several studies. Thus photolysis of dimethyl- and diphenyl-1,2,5-thiadiazole at room temperature was found to give acetonitrile and benzonitrile, respectively, as well as sulfur.[13] Photolysis of diphenyl-1,2,5-oxadiazole gave benzonitrile together with products derived from initially formed benzonitrile oxide.[13,14] Acetonitrile oxide has been trapped following photolysis of dimethyl-1,2,5-oxadiazole,[13] and fused 1,2,5-oxadiazoles undergo the same type of reaction.[15] In contrast, diphenyl-1,2,4-oxadiazole photolyses giving products derived from an intermediate nitrene.[16]

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