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PHOTOLYSIS OF BENZO[c]-1,2,5-SELENADIAZOLE 2-OXIDE. SPECTROSCOPIC EVIDENCE FOR THE FORMATION OF 2-SELENONITROSONITROSOBENZENE AND 2-NITROSO N-SELENOSELENINYLANILINE

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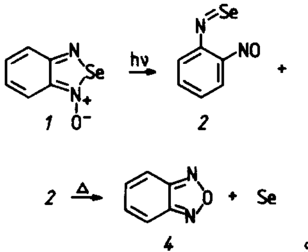
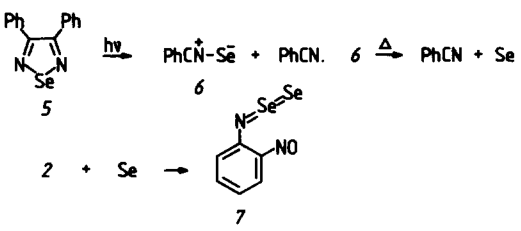
Photolysis of benzo[c]-1,2,5-thiadiazole 2-oxide, the sulfur analogue of the title compound (1, Scheme 1), produces benzo[c]-1,2,5-thiadiazole 1-oxide and 2-thionitrosonitrosobenzene (~ 1:1).[1] The latter compound is a short-lived transient ($k_{25\,^{o}C}$ ~ 200 s^{-1}) which re-forms the starting material. It was identified from its weak absorption at 700 nm (ε 10 $M^{-1}cm^{-1}$) characteristic of nitroso compounds. 2-Thionitrosonitrosobenzene also absorbs intensely at 490 nm (ε 9000 $M^{-1}cm^{-1}$).[1]


Scheme 1


Scheme 2

Irradiation (λ>390 nm) of benzo[c]-1,2,5-selenadiazole 2-oxide (1) in methylene chloride at room temperature produced benzofurazan (4, 96%, Scheme 1) and selenium only.[2] In 2-propanol also benzo[c]-1,2,5-selenadiazole (3, 5%) was isolated. Absorption spectra recorded during irradiation (410 nm) of compound 1 at 100 K in a methanol/ethanol glass (2:5) showed the development of absorption bands at 500 nm (sh), 526 and 560 nm (sh) (Fig. 1) due to an intermediate. At the same time absorption bands due to benzoselenadiazole (3) and benzofurazan (4) appeared at 330 nm and at 250-290 nm respectively. Heating of the sample above 120 K (i. e. before the glass melted) caused the absorption bands due to the intermediate to disappear with concomitant enhancement of the absorption bands due to benzofurazan (Fig. 1). From the spectra, the yields of 3 and 4 were calculated as 40% and 33% respectively. No (or very little) starting material was re-formed. Provided that only compound 4 is formed when the photolysed sample is warmed up, ε_{526} was calculated as 7000 $M^{-1}cm^{-1}$. TLC (using three different eluents) of the concentrated photolysis mixture confirmed that compounds 3 and 4 had been formed.

Fig. 1. UV spectra after photolysis of benzo[c]-1,2,5-selenadiazole 2-oxide (1) with 410±20 nm light. ——, after photolysis at 100 K in a methanol/ethanol glass. Starting material can be seen at 398 nm and at 420 nm. ---, after heating the same sample to 130 K. ..., after photolysis at 85 K of compound 1 in a PVC film, 20 µm thick.

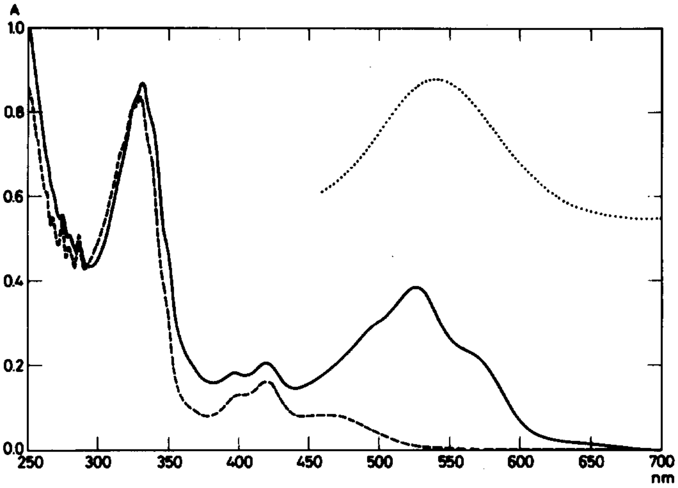


Fig. 2. UV spectra at room temperature of 2-selenonitrosonitrosobenzene (2) in cyclohexane (——), λ_{max} at 540 nm, and in 96% ethanol (---), λ_{max} at 536 nm, obtained by flash photolysis. Intensity in absorbance, arbitrary units.

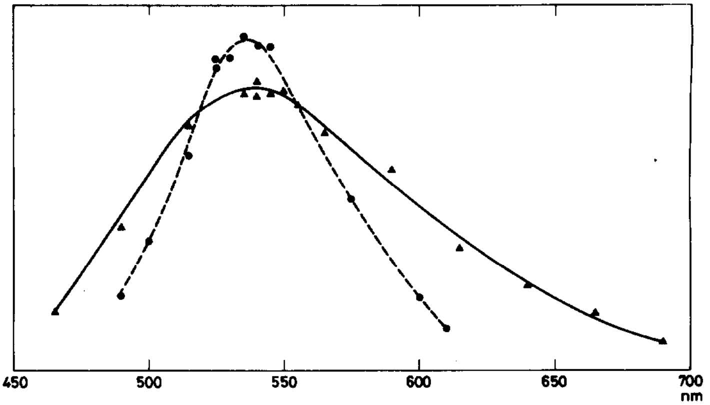
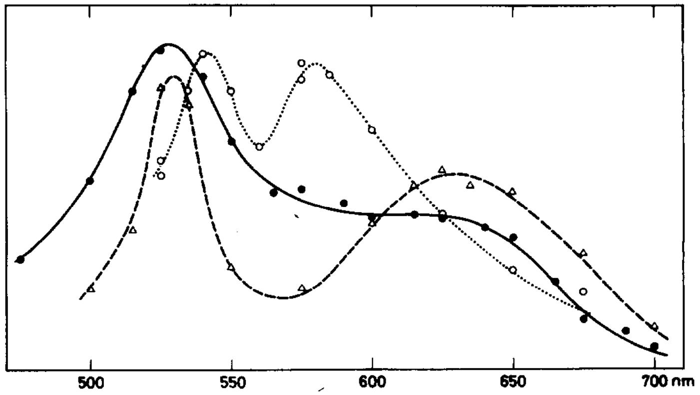


Fig. 3. UV spectra of 2-nitroso N-selenoseleninylaniline (7) in cyclohexane (——), λ_{max} at 530 nm and 615 nm, in acetonitrile (---), λ_{max} at 530 nm and 630 nm and in 96% ethanol (...), λ_{max} at 540 nm and 580 nm. Spectra were obtained by flash photolysis of mixtures of 1 and 5. Intensity in absorbance, arbitrary units.



Flash photolysis of compound 1 was performed in aerated as well as in degassed 2×10^{-5} M solutions (96% ethanol and cyclohexane) using pyrex filtered flash light (λ>300 nm). In both solvents absorptions due to transients were observed (Fig. 2, λ_{max}(EtOH) 536 nm, $\lambda_{max}(C_6H_{12})$ 540 nm) which decayed in a first order reaction. The lifetime and intensity of these absorptions were unaffected by the presence of oxygen. Activation parameters at 25 °C for disappearance of the transient in ethanol were calculated using an Arrhenius plot: $\underline{k}$ = 2340±40 s^{-1}, $\Delta H^{\ddagger}$ = 3.7±0.2 kcal/mol, $\Delta G^{\ddagger}$ = 12.9±0.0 kcal/mol and $\Delta S^{\ddagger}$ = -30.7±0.8 cal/deg. mol. $\underline{k}_{25\ ^oC}(C_6H_{12})$ = 1800 s^{-1}. From the UV spectra obtained, it is concluded that the same transient is formed at low temperature as well as at room temperature. Furthermore, the specific rate at 120 K was calculated as 0.05 s^{-1} (Arrhenius plot). The order of magnitude of this rate is consistent with the results of the low temperature experiment.

The evidence for the assignment of structure $\underline{2}$ to the transient is based on the following observations: (i) It exhibits a UV absorption at 526-540 nm ($\varepsilon \sim$ 7000 $M^{-1}cm^{-1}$) having the same profile as that of 2-thionitrosonitrosobenzene ($\lambda_{max} \sim$ 490 nm, ε 9000 $M^{-1}cm^{-1}$) except that the maximum for the selenium containing transient is red-shifted with respect to that for the thionitroso compound. Due to the low quantum yield for photolysis of compound $\underline{1}$, any absorption above 700 nm could not be detected. While the thionitroso compound re-forms the starting material thermally, the transient ($\underline{2}$) extrudes selenium. Extrusion of a selenium atom from compounds with monocoordinated selenium bonded to nitrogen can be a very fast process, e. g. from benzonitrile selenide (see below). (ii) A hypothetical benzo[c]- 1,2,5-selenadiazole 1-oxide may not decompose thermally into $\underline{4}$ and selenium in a frozen glass at 120 K and a highly reactive nitrene (o-nitrenomonoselenonitrobenzene) would be expected to re-close even faster at room temperature due to the o-substitution.

The transient assigned structure $\underline{2}$ was found to react with selenium atoms generated by flash photolysis of either diphenyl-1,2,5-selenadiazole ($\underline{5}$, Scheme 2) or dimethyl-1,2,5-selenadiazole. Photolysis of $\underline{5}$ at room temperature gave benzonitrile and selenium only.[3] Photolysis at low temperature also produced benzonitrile selenide ($\underline{6}$), identified by IR and UV spectroscopy.[3] $\underline{6}$ decays at 25 °C with $\underline{k}$ = 10960±140 s^{-1} (cyclohexane),[4] i. e. it is considerably shorter lived than is compound $\underline{2}$. When mixtures of compound $\underline{1}$ (2×10^{-5} M) and compound $\underline{5}$ (2×10^{-5} M in cyclohexane, 96% ethanol or acetonitrile) were flashed using pyrex filtered light, a new transient, decaying in a first order reaction, was formed.[5] The UV spectra of this transient are shown in Fig. 3. Since the same UV spectra were obtained from mixtures of compound $\underline{1}$ and dimethyl-1,2,5-selenadiazole, the transient formed must result from a chemical reaction between free selenium atoms and the photoproduct of compound $\underline{1}$. On the basis of the following discussion the new transient is assigned as 2-nitroso N-selenoseleninylaniline, $\underline{7}$.

By comparison of the UV spectra in Fig. 3 with the UV spectra of compound $\underline{2}$ (Figs. 1 and 2) it is concluded that a compound with a more extended π-electron system has been formed. In a chemical reaction between compound $\underline{2}$ and selenium atoms, several sites of attack are possible, but according to the concept of hard and soft acids and bases[6] the soft electron deficient selenium atom should attack the selenium atom bonded to nitrogen in preference to the nitrogen and oxygen centers. Thus, in an attempted preparation of p-dimethylaminothionitrosobenzene by treatment of p-dimethylaminonitrosobenzene with phosphorus pentasulfide at room temperature, p-dimethylamino N-thiosulfinylaniline was unexpectedly formed.[7] Neither the thionitroso compound nor the dithionitro compound has been prepared. After reaction of diselenium dichloride with 2,4,6-trimethylaniline at room temperature (analogous to the reactions with disulfur dichloride leading to N-thiosulfinylanilines, Ref. 8) most of the aniline could be recovered.[4]

2,4-Di-t-butyl-6-methyl N-thiosulfinylaniline shows intense UV absorptions at 476 (ε 2190 $M^{-1}cm^{-1}$) and 536 nm (ε 1190 $M^{-1}cm^{-1}$ in hexane) and 2,4,6-trimethyl N-thiosulfinylaniline at 462 and 540 nm (pentane).[8] No remarkable solvent effect was found in the UV spectra of the former compound.[9] In contrast, the solvent effect is rather pronounced in the UV spectra of p-dimethylamino N-thiosulfinylaniline (λ_{max}(MeOH) 538 nm, ε 39000 $M^{-1}cm^{-1}$, $\lambda_{max}(C_6H_{12})$ 510 nm, Ref. 7). Probably the electronic transition in the latter compound is a charge-transfer transition. The large hypsochromic solvent shift in the spectra of 7 is remarkable, but an even larger shift was found for N-thionitrosodimethylamine.[10] This was regarded as strong evidence for extensive hydrogen bonding in ethanol.

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