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Photoreaction of 3-Azido-5,7-di-t-butyl-2,1-benzisothiazole. Spectroscopic Detection of a Thionitroso Intermediate

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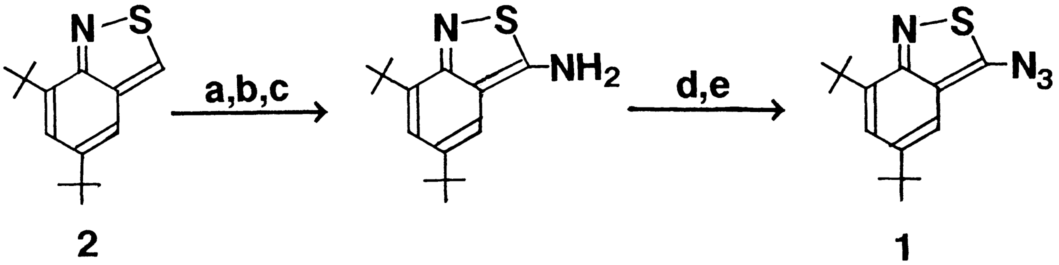
Photoreaction of the title compound at cryogenic temperatures produced a highly reactive 2,4-di-t-butyl-6-cyanothionitrosobenzene which showed a visible absorption around 470 nm.

Although thiocarbonyl compounds have extensively been studied in recent years, our knowledge on thionitroso compounds, the corresponding nitrogen analog, is relatively scarce.[1)] In connection with our continuing work on nitrogen-sulfur compounds,[2)] we report here on the spectroscopic detection (UV-VIS and IR) of a thionitroso compound using the photoreaction of azidoisothiazole **1**. Although Joucla and Rees reported the generation of a thionitroso intermediate in the photoreaction of azidoisothiazole derivatives, its intermediacy was confirmed only by chemical trapping.[1a)]

Compound **1** was synthesized from **2**[2b)] by amination,[3)] diazotization and subsequent reaction with sodium azide (20% from **2**).[4)]



(a) n-BuLi. (b) $N_3CH_2SiMe_3$. (c) H_3O^+. (d) $NaNO_2$-HCl. (e) NaN_3.

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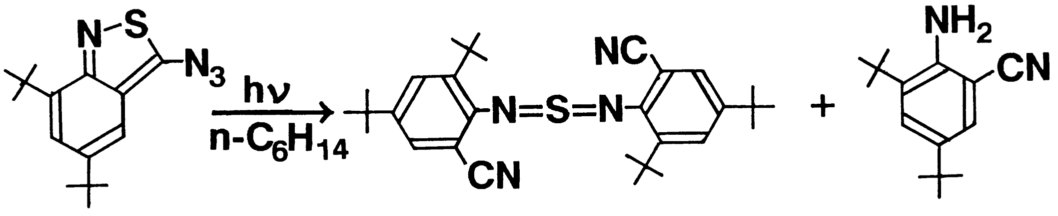
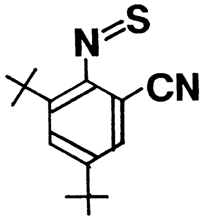
Irradiation of a hexane solution of **1** with a high pressure Hg lamp at 0 °C gave **3** (78%) and **4** (16%).[4,5]



1 **3** **4**



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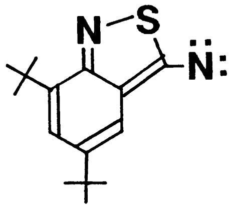

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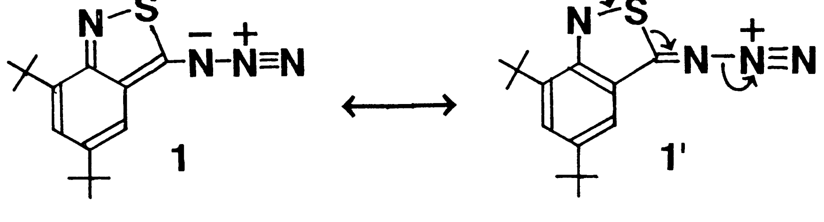
When the photoreaction (≥320 nm) of **1** in an argon matrix at 12 K was followed by electronic spectroscopy, a new band was observed around 470 nm (456 and 483 nm) at the expense of a strong 353 nm absorption of **1** (Fig. 1a). Monitoring by IR spectroscopy of the reaction under similar conditions revealed appearance of a band due to a cyano group (2225 cm^{-1}) along with concomitant decrease of the azide absorption (2130 cm^{-1}) (Fig. 1b). This strongly suggests that the initial intermediate, which has an absorption around 470 nm (ε 4700), can be assigned to thionitroso compound **5**, excluding the possibility of nitrene **6**. The band around 470 nm was also observed in the photoreactions in organic glass (70-80 K) such as EPA (ether:pentane:ethanol 5:5:2), 2-methyltetrahydrofuran, 3-methylpentane, and isopentane, although it disappeared above 90 K, suggesting the high reactivity of **5**.

These observations lead us to the conclusion that the photoreaction of **1** most likely proceeds via the direct formation of thionitrosobenzene **5** from **1** without the intermediacy of nitrene **6** because of the unique structure of **1** with a probable great resonance contribution of **1'**.



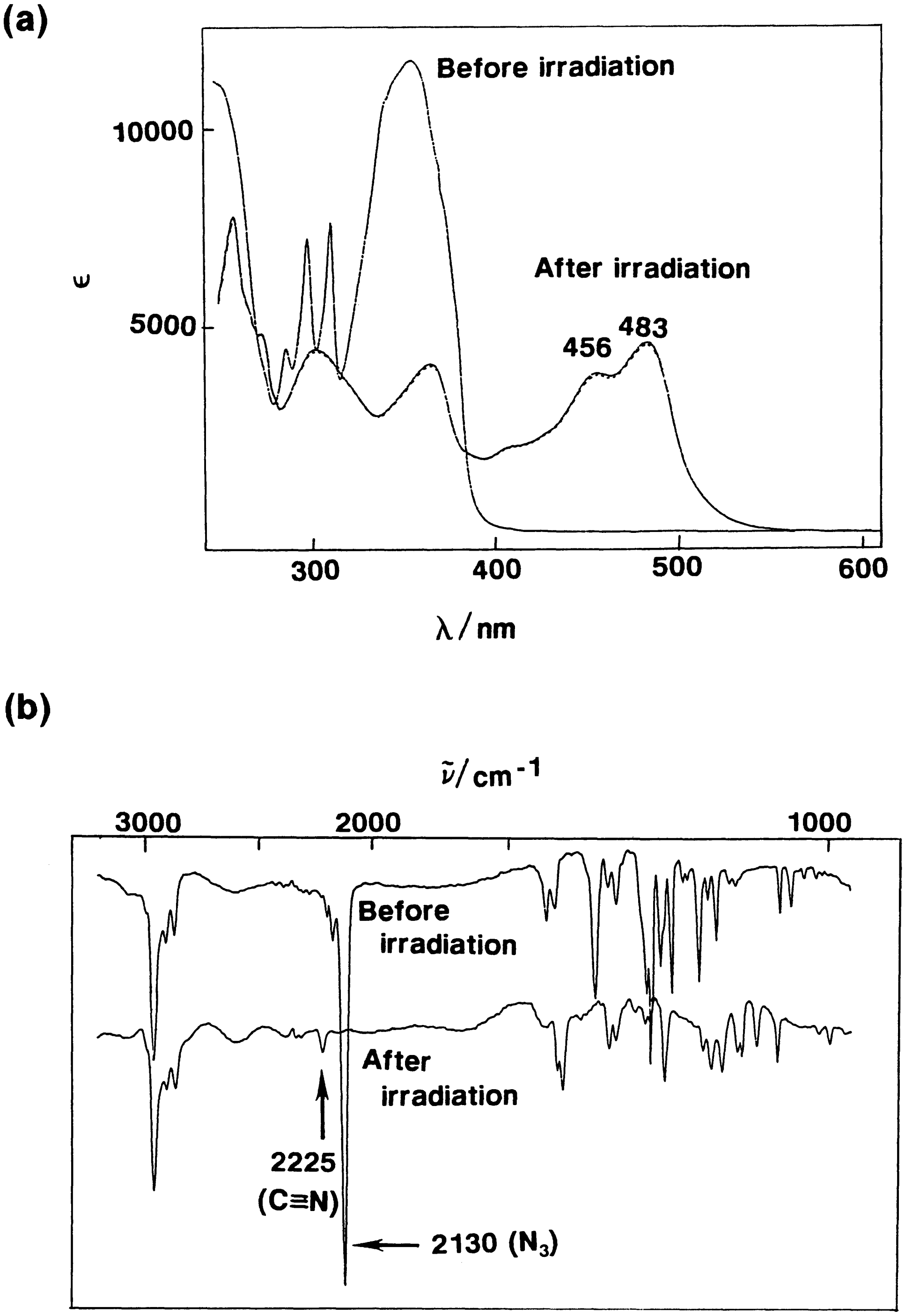


Fig. 1. Photolysis of 1 in argon matrix (12 K) monitored by electronic (a) and IR (b) spectroscopies.

Previously, Pedersen et al. reported that the photolysis of benzo[c]-1,2,5-thiadiazole 2-oxide resulted in the reversible formation of 2-thionitrosonitrosobenzene to which they assigned a visible absorption at 485 nm (ε 8000-9000) (in an argon matrix at 20 K).[6] This interpretation was later questioned, however, by Mayer et al. who carried out extensive calculations on the electronic absorption of thionitroso compounds as well as related sulfur containing species.[7]

We believe that close similarity in the position and coefficient of the absorptions between Pedersen's compound and ours strongly suggests that thionitrosobenzene derivatives have a rather strong absorption band around 470-490 nm in contrast to Mayer's calculations.

References

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2) a) Y. Inagaki, R. Okazaki, and N. Inamoto, Bull. Chem. Soc. Jpn., 52, 1998 (1979); b) Y. Inagaki, R. Okazaki, and N. Inamoto, ibid., 52, 2002 (1979); c) S. Nakamura, M. Takahashi, R. Okazaki, and K. Morokuma, J. Am. Chem. Soc., 109, 4142 (1987); d) R. Okazaki, M. Unno, and N. Inamoto, Chem. Lett., 1987, 2293.

3) K. Nishiyama and N. Tanaka, J. Chem. Soc., Chem. Commun., 1983, 1322.

4) **1**: mp 77-79 °C(dec); ^{1}H NMR($CDCl_3$) δ 1.21(s, 9H), 1.44(s, 9H), 7.17(ABq, 2H, $\Delta\delta$=0.08, J=1.9 Hz); UV-VIS(hexane) λ_{max} 228 nm (ε 18400), 255(sh, 6890), 297(4280), 312(4260), 356(7720); high MS 288.1403(calcd for $C_{15}H_{20}N_4S$ 288.1408). **3**: mp 175.0-175.5 °C; ^{1}H NMR($CDCl_3$) δ 1.17(s, 36H), 7.38(ABq, $\Delta\delta$=0.15, J=2.4 Hz); UV-VIS(pentane) λ_{max} 284 nm (ε 10300), 416(5400); high MS 488.2954(calcd for $C_{30}H_{40}N_4S$ 488.2972). **4**: mp 80.0-80.5 °C; ^{1}H NMR($CDCl_3$) δ 1.13(s, 9H), 1.28(s, 9H), 4.33(bs, 2H), 7.15(ABq, 2H, $\Delta\delta$=0.19, J=2.0 Hz); UV-VIS(pentane) λ_{max} 246 nm (ε 6300), 319(4000); high MS 230.1773(calcd for $C_{15}H_{22}N_2$ 230.1781).

5) Products **3** and **4** were isolated by silica gel chromatography (hexane-ether 5:1) and recrystallization.

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7) A. Mehlhorn, J. Sauer, J. Fabian, and R. Mayer, Phosphorus and Sulfur, 11, 325 (1981).

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