

New Reactions of a Thionitrosoarene

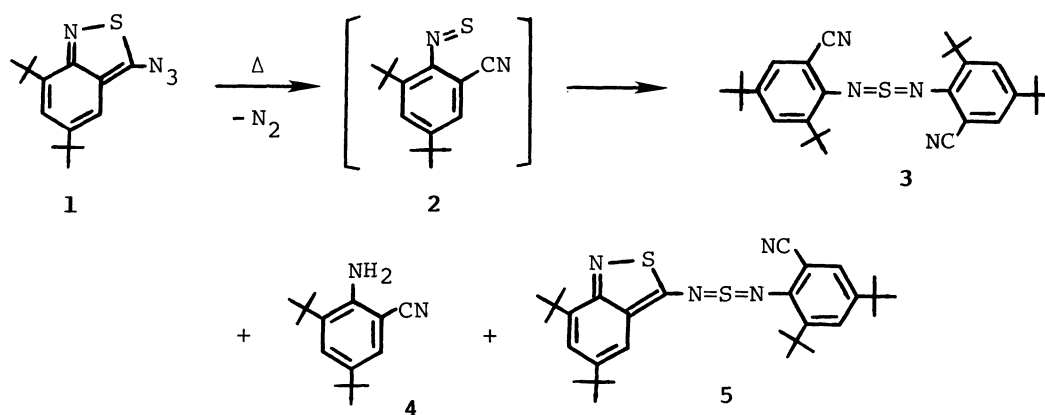
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A transient thionitrosoarene was trapped by an azide, diazo compound, oxygen, and thiirane to give a sulfur diimide, thio-carbonylimine, N-sulfinylaniline, and N-thiosulfinylaniline, respectively. In the reaction with oxygen N-sulfonylaniline was also formed and underwent a novel type of intramolecular cyclization.

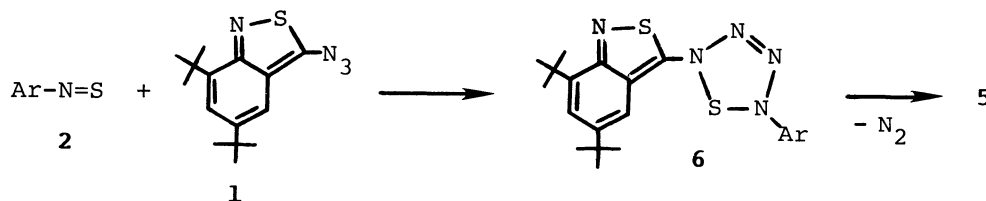
Organic compounds containing multiple bonds of heavier typical elements are of current interest.¹⁾ Although thiocarbonyl compounds have well been studied,^{1c)} relatively few reactions have been known for thionitroso compounds ($R-N=S$). Reactions so far reported for thionitroso compounds are a Diels-Alder type cycloaddition with dienes, ene reaction, and dimerization resulting in the formation of sulfur diimide after the loss of one sulfur.²⁾

We have recently reported the photoreaction of 3-azido-2,1-benzisothiazole (1) leading to thionitrosoarene 2, which is detected in low temperature matrices by electronic and IR spectroscopies.³⁾ We delineate here that the thermal reaction of 1 also results in the formation of thionitrosoarene 2 and that 2 can be trapped by some new types of reactions for thionitroso compounds.



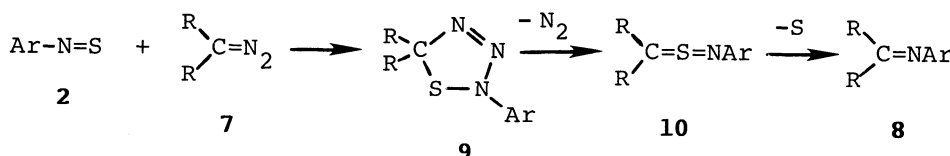
When a hexane solution of 1 was heated at 60 °C for 1 h, sulfur diimide 3, aniline 4, and unsymmetrical sulfur diimide 5 were obtained in 72, 14, and 11% yields, respectively.⁴⁾ Azide 1 slowly (2 days) decomposed also at room temperature to give 3 (50%), 4 (40%) and 5 (7%). The unsymmetrical sulfur diimide 5 was also produced in 8% yield in the photoreaction of an ethanol solution of 1 at -78 °C, the major products being 3 (43%) and 4 (33%).

The formation of **5** can most reasonably be explained by 1,3-dipolar cycloaddition of thionitrosoarene **2** with the starting azide **1** followed by loss of molecular nitrogen from intermediary thiatetrazole **6** which is a yet unknown type of heterocycle and considered to be very unstable (Ar denotes 2,4-di-*t*-butyl-6-cyanophenyl hereafter in this paper).



Ar: 2,4-di-*t*-butyl-6-cyanophenyl

Similar cycloaddition reactions were also observed in the reaction with diazoalkanes. When **1** was allowed to react with an excess (5 equiv.) of diphenyldiazomethane (**7a**) and diazofluorene (**7b**) in hexane at room temperature, imines **8a** and **8b** were obtained in 78 and 80% yields, respectively.⁴⁾ This result is explicable also in terms of 1,3-dipolar cycloaddition of **2**. Intermediary thiatriazole **9** is again an unknown heterocycle and probably unstable to give **8a** and **8b** via thiocarbonylimine **10**.^{5a)} Indeed the reaction of **1** with sterically bulky diazomethane **7c** under similar conditions resulted in the formation of thiocarbonylimine **10c** (98%),⁴⁾ which is stable toward desulfurization by steric protection. This represents a new mode of the formation of thiocarbonylimines.^{5b)}

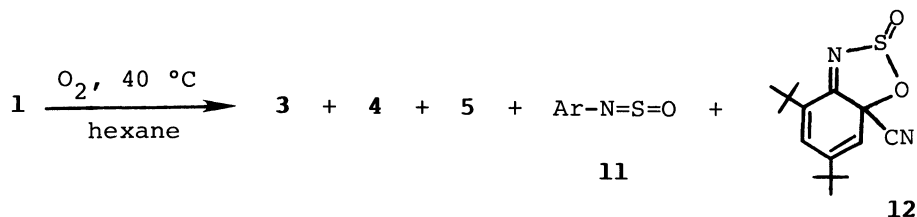


a: R = Ph

b: RR =

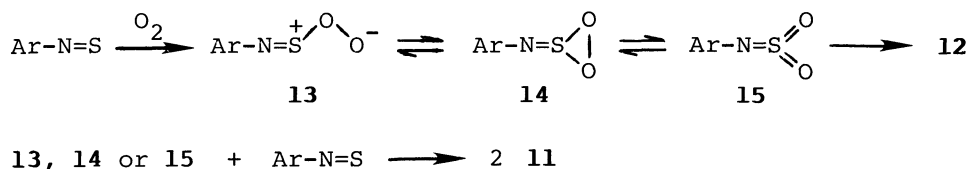
c: RR =

The thionitroso intermediate **2** also reacted with molecular oxygen to afford N-sulfinylaniline **11** and oxathiazole **12**. Thus, when a hexane solution of **1** stood for 6 h at 40 °C while oxygen was bubbled into the solution, **11** (11%) and **12** (30%)⁴⁾ were obtained in addition to **3** (14%), **4** (15%), and **5** (14%).

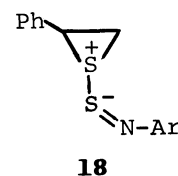
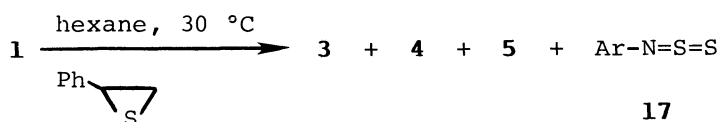


The formation of **11** and **12** in the above reaction can reasonably be interpreted in terms of intermediacy of thionitrosoarene **2** as shown in the following

scheme. Although it is not certain at present whether the initial product in the reaction with oxygen is **13**, **14** or **15**, the formation of **12** is best explained by the intramolecular cyclization of **15** since we have previously found a similar type of cyclization for N-thiosulfinylamines.⁶⁾ The cyclization of **15** can be regarded as intramolecular 1,3-dipolar cycloaddition and represents the first example of 1,3-dipolar behavior of N-sulfonylamines ($RN=SO_2$).⁷⁾ It is noteworthy that **15** undergoes the cyclization at the sacrifice of aromatic stabilization.



The thermal reaction of **1** with thiirane **16** in hexane at 30 °C afforded N-thiosulfinylaniline **17**⁴⁾ (31%) along with **3** (13%), **4** (22%), and **5** (5%). The reaction most likely proceeds via ylide **18**.



The reaction of thionitrosoarene **2** with thiirane **16** is similar to that of thiobenzophenone, which reportedly gives a transient thione S-sulfide $\text{Ph}_2\text{C}=\text{S}=\text{S}$,⁸⁾ although the reactivity of **2** is definitely much higher than that of the thioketone if one considers the low concentration of the transient species **2**. The higher reactivity of the thionitrosoarene is obvious also in the oxidation reaction. An oxidation reaction of a thione to a thione S-oxide ($\text{R}_2\text{C}=\text{S}=\text{O}$) does not proceed with molecular oxygen and needs a stronger oxidizing reagent such as a peracid.

In conclusion, we have found that thionitrosoarene **2** thermally generated from **1** undergoes 1,3-dipolar cycloaddition, oxygenation, and sulfurization which represent new types of reactions for thionitroso compounds.

References

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- 4) All new compounds were identified by spectroscopic and analytical data (NMR spectra were taken in CDCl_3 and expressed in δ). **5**: ^1H NMR 1.36(s, 9H), 1.44(s, 18H), 1.65(s, 9H), 7.53(m, 2H), 7.86(ABq, $J=2.0$ Hz, $\Delta\delta=0.19$ ppm, 2H); ^{13}C NMR 30.3, 30.9, 31.05, 31.13, 34.9, 35.5, 36.1, 36.3, 105.5, 114.1, 116.2, 124.5, 127.9, 129.2, 130.4, 142.5, 143.1, 143.5, 149.1, 149.3, 156.4, 162.3; MS m/z 520(M^+ , 57%), 213(100); Anal. ($\text{C}_{30}\text{H}_{40}\text{N}_4\text{S}_2$) C, H, N, S. **8a**: ^1H NMR 1.25(s, 9H), 1.47(s, 9H), 7.36(ABq, $J=2.0$ Hz, $\Delta\delta=0.44$ ppm, 2H), 7.37(m, 10H); ^{13}C NMR 29.9, 31.1, 34.5, 36.3, 101.2, 119.0, 127.1, 127.8, 128.2, 130.3, 141.4, 146.0, 150.1, 168.0; MS m/z 394(M^+ , 35%), 317 (100); high resolution MS 394.2392 (calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2$ 394.2407). **8b**: ^1H NMR 1.24(s, 9H), 1.29(s, 9H), 7.45(m, 8H), 7.52(ABq, $J=2.2$ Hz, $\Delta\delta=0.22$ ppm, 2H); ^{13}C NMR 29.4, 31.3, 34.7, 35.9, 101.5, 118.1, 127.6, 128.6, 132.4, 139.6, 146.9, 150.8, 164.7; MS m/z 392(M^+ , 81%), 377(100); high resolution MS 392.2266 (calcd for $\text{C}_{28}\text{H}_{28}\text{N}_2$ 392.2253). **10c**: ^1H NMR 1.29(s, 9H), 1.39(s, 9H), 1.40(s, 6H), 1.57-1.66(m, 4H), 1.63(s, 6H), 1.68-1.74(m, 2H), 7.43(ABq, $J=2.3$ Hz, $\Delta\delta=0.14$ ppm, 2H); MS m/z 398(M^+ , 47%), 260(100); high resolution MS 398.2755 (calcd for $\text{C}_{25}\text{H}_{38}\text{N}_2\text{S}$ 398.2755). **11**: ^1H NMR 1.33(s, 9H), 1.43(s, 9H), 7.64(ABq, $J=2.0$ Hz, $\Delta\delta=0.14$ ppm, 2H); ^{13}C NMR 17.0, 26.4, 29.7, 31.2, 33.1, 34.4, 36.0, 39.2, 40.3, 41.1, 41.6, 104.1, 120.5, 128.0, 143.9, 144.3, 152.4, 183.5; MS m/z 276(M^+ , 12%), 57(100); high resolution MS 276.1299 (calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{OS}$ 276.1297). **12**: ^1H NMR 1.13(s, 9H), 1.39(s, 9H), 5.99(d, $J=1.85$ Hz, 1H), 6.62(d, $J=1.85$ Hz, 1H); ^{13}C NMR 28.9, 29.0, 35.1, 35.6, 87.6, 113.7, 117.9, 133.8, 143.2, 149.1, 176.5; MS m/z 292(M^+ , 13%), 57(100); high resolution MS 292.1241 (calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ 292.1244). **17**: ^1H NMR 1.37(s, 18H), 7.64(ABq, $J=2.4$ Hz, $\Delta\delta=0.18$ ppm, 2H); MS m/z 292 (M^+ , 4%), 236 (100); high resolution MS 292.1036 (calcd for $\text{C}_{15}\text{H}_{20}\text{S}_2\text{N}_2$ 292.1067).
- 5) a) Although some stable thiocarbonylimines with special structures are known, they undergo photochemical or thermal desulfurization to give imines. See, for example, S. Tamagaki, K. Sakai, and S. Oae, *Bull. Chem. Soc. Jpn.*, 46, 2608 (1973); b) For reviews on thiocarbonylimines, see: Y. Inagaki and R. Okazaki, *Yuki Gosei Kagaku Kyokai Shi*, 36, 1 (1978); S. Motoki and T. Saito, *Sulfur Reports*, 4, 31 (1984).
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