CHEMISTRY LETTERS, pp. 2087-2090, 1989.

New Reactions of a Thionitrosoarene

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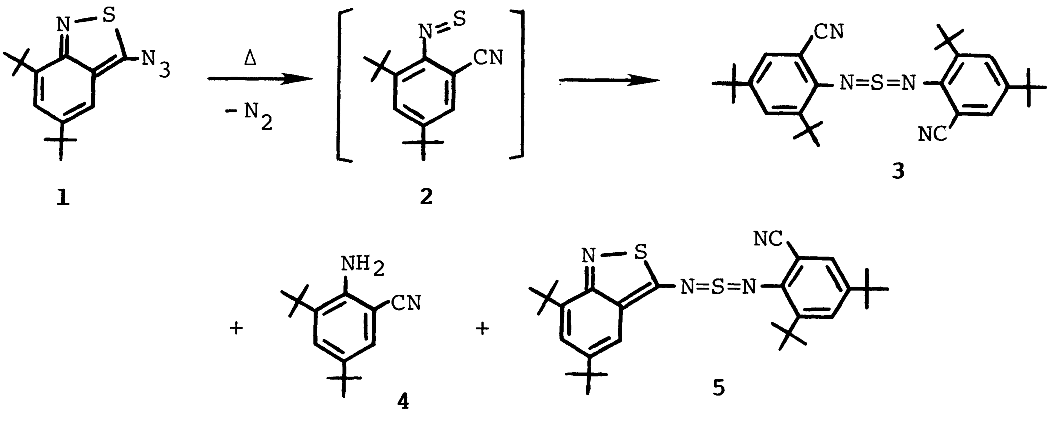
A transient thionitrosoarene was trapped by an azide, diazo compound, oxygen, and thiirane to give a sulfur diimide, thiocarbonylimine, N-sulfinylaniline, and N-thiosulfinylaniline, respectively. In the reaction with oxygen N-sulfonylaniline was also formed and underwent a novel type of intramolecular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

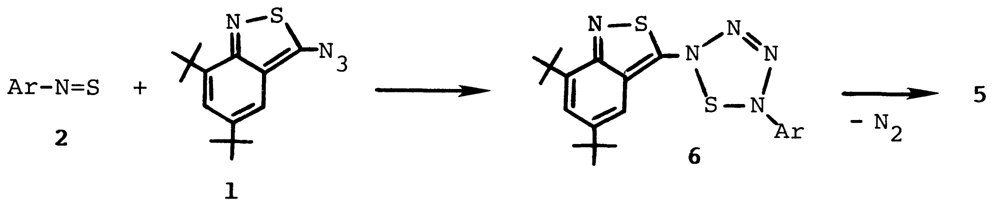
Organic compounds containing multiple bonds of heavier typical elements are of current interest.1) Although thiocarbonyl compounds have well been studied,1c) relatively few reactions have been known for thionitroso compounds (R-N=S). Reactions so far reported for thionitroso compounds are a Diels-Alder 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.



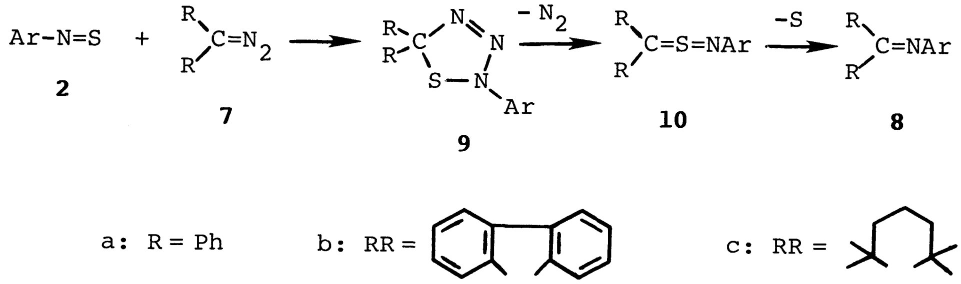
When a hexane solution of **1** was heated at 60 °C for 1 h, sulfur diimide **3**, aniline **4**, and unsymmetrical sulfur diimide **5** were obtained in 72, 14, and 11% yields, respectively.4) Azide **1** slowly (2 days) decomposed also at room temperature to give **3** (50%), **4** (40%) and **5** (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).

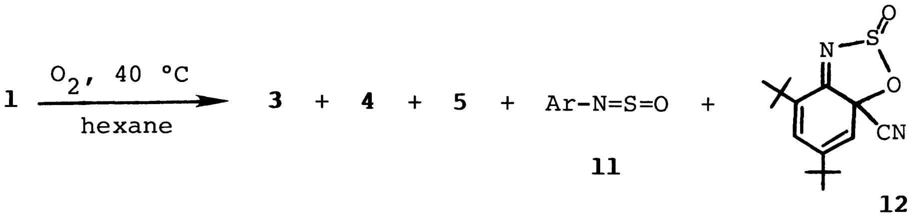


Ar: 2,4-di-t-butyl-6-cyanophenyl

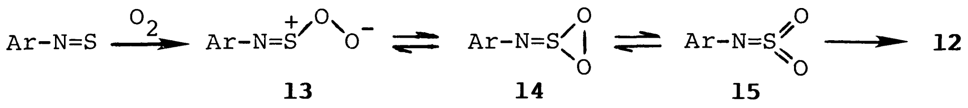
Similar cycloaddition reactions were also observed in the reaction with diazoalkanes. When **1** was allowed to react with an excess (5 equiv.) of diphenyldiazomethane (**7a**) and diazofluorene (**7b**) in hexane at room temperature, imines **8a** and **8b** were obtained in 78 and 80% yields, respectively.4) 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)



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%).

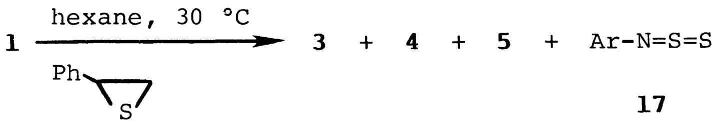


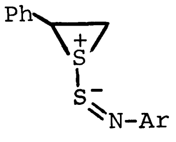
The formation of **11** and **12** in the above reaction can reasonably be interpreted in terms of intermediacy of thionitrosoarene **2** as shown in the following scheme. Although it is not certain at present whether the initial product in the reaction with oxygen is **13**, **14** or **15**, the formation 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 intramolecualr 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.



13, **14** or **15** + Ar-N=S ⟶ 2 **11**

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**.





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The reaction of thionitrosoarene **2** with thiirane **16** is similar to that of thiobenzophenone, which reportedly gives a transient thione S-sulfide $Ph_2C=S=S$,[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 ($R_2C=S=O$) 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. ($C_{30}H_{40}N_4S_2$) 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 $C_{28}H_{30}N_2$ 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 $C_{28}H_{28}N_2$ 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, $\Delta\delta$=0.14ppm, 2H); MS m/z 398(M^+, 47%), 260(100); high resolution MS 398.2755 (calcd for $C_{25}H_{38}N_2S$ 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 $C_{15}H_{20}N_2OS$ 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 $C_{15}H_{20}N_2O_2S$ 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 $C_{15}H_{20}S_2N_2$ 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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(Received September 28, 1989)