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Generation of sulfenylnitrenes by *N*-sulfenylation of triphenyl-λ^6-sulfanenitrile

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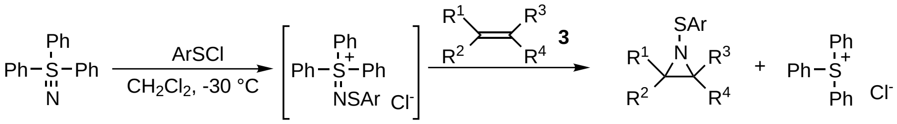
Abstract—The sulfenylation of triphenyl-λ^6-sulfanenitrile (**1**) with 2,4-dinitrobenzenesulfenyl chloride in the presence of alkenes affords aziridines together with triphenylsulfonium salt. The reaction of **1** with sulfur dichloride also generates ClSN which is trapped by 2,5-diphenylfuran to give 5-benzoylisothiazole. © 2002 Elsevier Science Ltd. All rights reserved.

The development of new methodologies for the generation of reactive species is an important goal in organic chemistry. The highly reactive transient species, sulfenylnitrenes, have received considerable interest from the structural and synthetical points of view.[1,2] Nitroarylsulfenylnitrenes generated from the oxidation of the corresponding sulfenamides with lead tetraacetate were trapped by several alkenes to give *N*-sulfenylaziridines.[1c,d] Thermolysis of *N*-arylsulfenylimino-1,4-dihydronaphthalenes also gave the sulfenylnitrenes, which were trapped by alkenes to give the corresponding aziridines.[1e]

Recently, we prepared triphenyl-λ^6-sulfanenitrile (**1**) bearing a sulfur–nitrogen triple bond from fluorodiphenyl-λ^6-sulfanenitrile with phenyllithium and found it easily reacts with several electrophiles such as alkyl halides, tosyl chloride, acid anhydrides, NO_2BF_4, to give the corresponding *N*-substituted iminosulfonium salts.[3] We have now examined *N*-sulfenylation of **1** with arenesulfenyl chloride. This work led us to the finding that the resulting *N*-arylsulfenyliminosulfonium chloride readily undergoes S^{VI}–N cleavage to generate the sulfenylnitrenes. In addition, we also found that the reaction of **1** with sulfur dichloride generates ClSN, which was confirmed by converting 2,5-diphenylfuran into 5-benzoylisothiazole.

The reaction of triphenyl-λ^6-sulfanenitrile (**1**) with 2,4-dinitrobenzenesulfenyl chloride[4] was first examined. When 1 equiv. of 2,4-dinitrobenzenesulfenyl chloride was added to a solution of **1** in CD_2Cl_2 at −80°C in an NMR tube, **1** immediately disappeared and the peaks due to the *N*-(2,4-dinitrophenylsulfenyl)iminosulfonium



1 **2** **4** **5**

3a: $R^1 = R^2 = R^3 = H, R^4 = Ph$ **4a** (15%[a)])
3b: $R^1 = Me, R^2 = R^3 = H, R^4 = Ph$ **4b** (71%[a)])
3c: $R^1 = H, R^2 = Me, R^3 = H, R^4 = Ph$ **4c** (7%[a)])
3d: $R^1 = R^2 = H, R^3 = Me, R^4 = (Me)C{=}CH_2$ **4d** (61%[a)])

Scheme 1. Ar = 2,4-dinitrophenyl; (a) isolated yield.

Keywords: λ^6-sulfanenitrile; sulfenylnitrene; aziridines; sulfenylation; thiazyl chloride.

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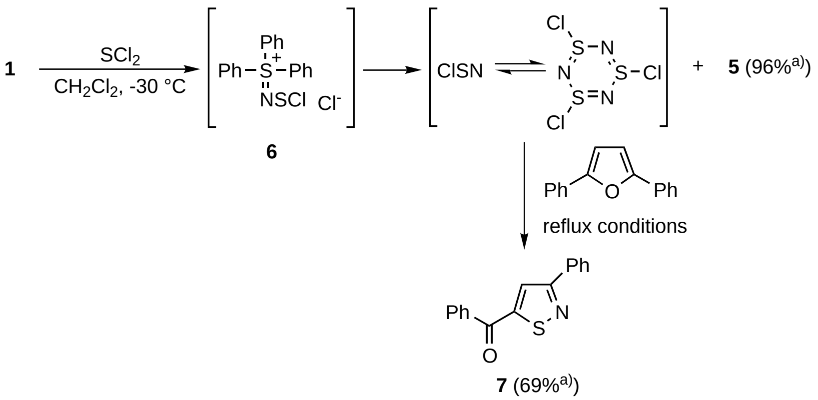

Scheme 2. (a) Isolated yield.

chloride **2** appeared.[5] Up to −50°C, compound **2** gradually decomposed to triphenylsulfonium chloride (**5**) along with some unidentified products. This result indicates the S^{VI}–N bond cleavage of **2**, although **2** was not isolated. We investigated the potential of **2** to act as a source of sulfenylnitrene in trapping experiments with alkenes. The reaction of **1** with 2,4-dinitrobenzenesulfenyl chloride in CH_2Cl_2 at −30°C was carried out in the presence of alkenes **3a**–**d** (10 equiv.) as a trapping regent. The results are summarized in Scheme 1. From alkenes **3a**–**c**, *N*-(2,4-dinitrophenylsulfenyl)azridines **4a**–**c** were obtained in 15, 71, and 7% respective yields, and from 2,3-dimethyl-1,3-butadiene (**3d**), *N*-(2,4-dinitrophenylsulfenyl)-2-isopropenyl-2-methylaziridine (**4d**) was obtained in 61% yield.[6–9] In all reactions, triphenylsulfonium chloride (**5**) was produced almost quantitatively. Thus, the formation of **4** suggests the generation of 2,4-dinitrophenylsulfenylnitrene in the course of the reaction of **1** with 2,4-dinitrobenezenesulfenyl chloride.

Further, the generation of thiazyl chloride[2a] (ClSN) by the reaction of λ^6-sulfanenitrile **1** with sulfur dichloride was examined (Scheme 2). ClSN is in thermal equilibrium with its trimer $(ClSN)_3$ and these species are useful for the synthesis of heterocyclic compounds with N–S, N–S–N, and S–N–S units.[10] After the reaction of **1** with sulfur dichloride in CH_2Cl_2 at −30°C for 30 min, 5 equiv. of a trapping reagent, 2,5-diphenylfuran, was added to the reaction mixture. On boiling this mixture for 1 h, the expected 5-benzoyl-3-phenylisothiazole (**7**)[10b] was obtained together with **5**. This reaction is assumed to involve the initial sulfenylation to provide **6**, followed by fission of the S^{VI}–N bond to afford ClSN together with **5**. Finally, this reactive species, its monomer or trimer, will be converted 2,5-diphenylfuran into isothiazole **7**.[10b,c]

In summary, we have demonstrated the generation of a reactive species with a sulfur–nitrogen bond through the reaction of λ^6-sulfanenitrile **1** with arenesulfenyl chloride and sulfur dichloride. Our current efforts include elucidation of the mechanism for the fission of the S^{VI}–N bond and application of this reaction system to the generation of other reactive species.

Acknowledgements

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4. The sulfenylation reagent used is 2,4-dinitrobenzenesulfenyl chlorides, which is relatively stable and commercially available.
5. ^1H NMR (400 MHz, CD_2Cl_2, −80°C) δ 7.83–8.02 (m, 17H), 8.98 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, −80°C) δ 121.1, 124.7, 125.4, 127.6, 129.6, 131.3, 137.6, 140.4, 143.9, 148.9.
6. All aziridines gave satisfactory spectral data (NMR, IR, and MS). The side products were mainly 2,4-dinitrobenzenesulfenamide (5–18% yields) and a complex mixture including some unidentified products.

7. The aziridination of *trans*- and *cis*-1-phenylpropene (**3b** and **3c**) proceeded stereospecifically to give the corresponding aziridine **4b** and **4c**, but the yield of the *cis*-aziridine **4c** was very low. On the other hand, the addition of 2,4-dinitrophenylsulfenylnitrene from the oxidation and thermolysis of sulfenamides to *cis*-1-phenylpropene gave a mixture of *cis*- and *trans*-aziridine in the ratio of ca. 3:1 (see Refs. 1c,e).
8. The formation of **4d** from 2,4-dinitrophenylsulfenylnitrene with butadiene **3b** is in contrast to the formation of [4+2] adduct, 1λ^4,2-thiazacyclohexa-1,4-diene from FSN (Bludssus, W.; Mews, R. *J. Chem. Soc.*, *Chem. Commun.* **1979**, 35–36).
9. No azridination products were obtained using alkyl substituted alkenes such as cyclohexene and 1-decene.
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