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Tetrahedron Letters 48 (2007) 427–430
Tetrahedron Letters

Moderate generation of sulfenylnitrenes from novel *N*-sulfenylsulfodiimides

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Received 5 October 2006; revised 6 November 2006; accepted 10 November 2006

Abstract—*N*-Sulfenylated sulfodiimides were first prepared by the reaction of *S*,*S*-diphenyl-*N*-tosylsulfodiimide with arenesulfenyl chlorides under the basic conditions. Thermolysis of *S*,*S*-diphenyl-*N*-(2-nitrophenylsulfenyl)- and *S*,*S*-diphenyl-*N*-(2,4-dinitrophenylsulfenyl)sulfodiimides in the presence of olefins proceeded at 50–80 °C to give the corresponding deiminated *S*,*S*-diphenyl-*N*-tosylsulfimide and *N*-sulfenylaziridines in very good yields. 2,4-Dinitrophenyl-sulfenylnitrene was trapped by *trans*- and *cis*-1-phenylpropenes stereospecifically. The thermolysis temperature of the *N*-sulfenylsulfodiimides was found to be lower than *N*-sulfenylsulfoximide and higher than *N*-sulfenyliminosulfonium salt and very effective to trap the sulfenylnitrene to give the *N*-sulfenylaziridines in very good yields.

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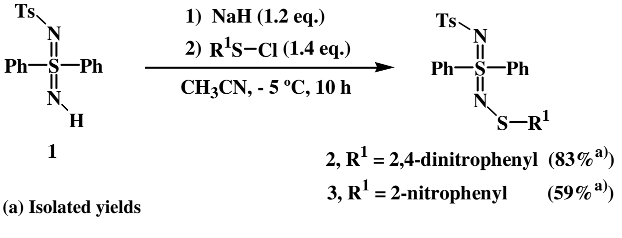
1. Introduction

Recently, we reported that *N*-sulfenylation of triphenyl-λ^6-sulfanenitrile[1] generates sulfenylnitrenes at −30 °C to give the corresponding *N*-sulfenylaziridines by trapping with olefins, though the yields of the sulfenylaziridines are not enough.[2] In this reaction *cis*- and *trans*-1-phenylpropenes afforded the corresponding stereospecific products, *cis*- and *trans*-2-methyl-3-phenyl-*N*-(2,4-dinitrophenylsulfenyl)-aziridines, respectively, though the *cis*-olefin gave the aziridine in poor yield. Sulfenylnitrenes are known to be generated by the oxidation of the corresponding sulfenamides with lead tetraacetate[3a,b] and with NBS.[3e] But these reactions have a drawback, that is, the formed sulfenylnitrenes attack the sulfenamides to lower the yield of the aziridines. Kaszynski and Young also reported the generation of propylsulfenylnitrene by thermolysis of 3,6-diphenyl-1-propanesulfenimido-1,2,4,5-tetrazine, though they did not trap the nitrene.[4] Another method involving thermolysis of *N*-arylsulfenylimino-1,4-dihydro-naphthalenes[3c,d] gives the sulfenylaziridines in very good yields. These results show that the reactivity of sulfenylnitrene is not enough high towards olefins at −30 °C and requires higher temperature. However, stereospecificity of trapping by the Atkinson's method[3a–d] is low. Therefore, milder thermolytic generation of sulfenylnitrene has been interesting. On the other side, Furukawa et al.[5] reported that the reaction of diphenylsulfoximides with *p*-toluenesulfenyl chloride gives the corresponding *N*-sulfenylsulfoximide which further undergoes thermolysis at 140 °C to give the corresponding sulfoxides, though they have not shown the evidence of the formation of the sulfenylnitrenes in this thermolysis. This result shows that the N-sulfenylation of the sulfoximide activates the S–N bond to reduce the thermolysis temperature, because the usual sulfoximide does not decompose up to 300 °C. Meanwhile, there is no example of *N*-sulfenylsulfodiimide to date except for



Scheme 1.

Keywords: Sulfenylnitrene; *N*-Sulfenylsulfodiimide; λ^4-Sulfanenitrile; DFT calculation.

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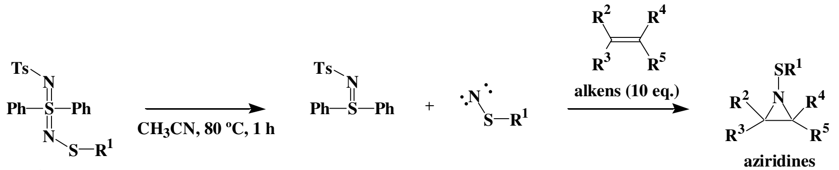
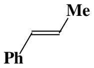
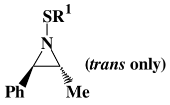
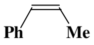
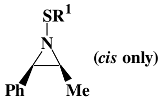
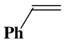
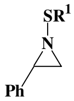
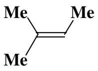
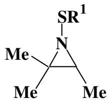
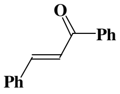
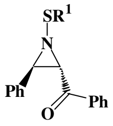
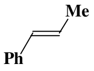
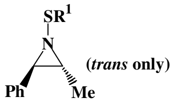
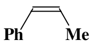
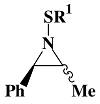
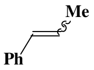
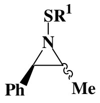
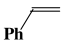
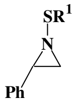
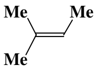
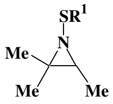
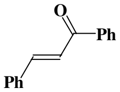
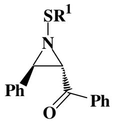
doi:10.1016/j.tetlet.2006.11.078

Table 1. Thermolysis of *N*-sulfenylated sulfodiimides

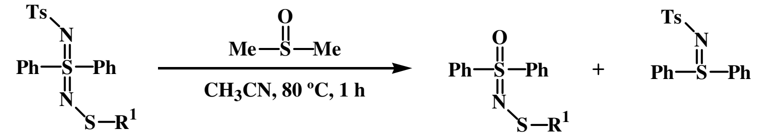


2; R^1 = 2,4-dinitrophenyl
3; R^1 = 2-nitrophenyl

Entry	Substrate	Alkenes	Products	Products yields (%)	
				Aziridines (%)	Sulfimides
1	2	None	Unidentified products	—	Quant
2				98[a]	Quant
3				97[a]	Quant
4				99[a]	Quant
5				99[a]	Quant
6				38[b]	Quant
7	3			85[b]	Quant
8				70[b] (*trans*:*cis* = 64:36)	Quant
9				77[b] (*trans*:*cis* = 99:1)	Quant
10				90[b]	Quant
11				65[b]	Quant
12				60[b]	Quant

[a] Isolated yields.

[b] ^{1}H NMR yields.



2, R^1 = 2,4-dinitrophenyl 96%$^{a)}$ Quant

3, R^1 = 2-nitrophenyl 85%$^{b)}$ Quant

(a) Isolated yield, (b) ^{1}H NMR yield.

Scheme 2.

dimethyl-*N*-thiocyanosullfodiimide.[6] The reaction of diphenylsulfodiimide with *p*-toluenesulfenyl chloride is known to give the reduction products, sulfide and sulfimide,[5] and thus the thermolysis temperature of some *N*-sulfenysulfodiimides can be expected to be lower than that of the sulfoximides. This letter will report that *N*-sulfenylsulfodiimides were first isolated and their thermolysis was carried out in the presence of alkenes.

S,*S*-Diphenyl-*N*-(substituted)-*N*′-sulfenylsulfodiimides (**2**–**3**)[7] were obtained in 50–90% yields by treating the corresponding sulfodiimides **1** with 2,4-dinitro- or 2-nitrobenzenesulfenyl chloride[8] in the presence of NaH in anhydrous CH_3CN under Ar atmosphere at −5 °C (Scheme 1), though the reaction at room temperature gave a mixture with decomposed product *N*-tosylsulfimide like the results of Furukawa and co-workers.[5] The structure of these compounds was assigned based on the analysis of ^{1}H, ^{13}C NMR, IR spectra and elemental analysis.[9] This is the first examples of *N*-sulfenylated sulfodiimides except for *N*-thiocyanosulfodiimide.[6]

Thermolysis of *N*-sulfenylsulfodiimides was carried out at 80 °C in CH_3CN in the presence of various alkenes, and the sulfenylnitrenes were trapped very efficiently by olefins to afford *N*-sulfenylaziridines as shown in Table 1. The sulfenylnitrenes were also trapped effectively by DMSO to give the corresponding *N*-sulfenylsulfoximides as shown in Scheme 2. The thermolysis temperature at 80 °C is lower than that of Atkinson's results. However this temperature is higher than that of our previous experimental results and gave the *N*-sulfenylaziridines in very good yields to show enough activation of the low reactive sulfenylnitrenes. 2,4-Dinitrophenylsulfenylnitrene was trapped by *trans*- and *cis*-1-phenylpropenes to give the corresponding *trans*- and *cis*-*N*-sulfenylaziridines, respectively, without any other isomer (entries 1 and 2). The stereospecificity is very high inconsistently with that of Atkinson's results.[3a–d] The reason for this conflict is not clear. But 2-nitrophenyl-sulfenyl derivative with *cis*-1-phenylpropene gave a mixture of *cis*- and *trans*-aziridines (entries 7 and 8). Though the reason for this less stereospecificity is not clear, 10% *cis*–*trans* isomerization of the 1-phenylpropene was observed after the reaction. The *trans*-aziridines may be mainly formed by the reaction with the *trans*-olefins, because the reaction with 50/50 mixed olefins (*cis*/*trans* = 50/50) gave the *trans*-aziridines exclusively (*cis*/*trans* = 1/99) (entry 9). The *cis*-olefins and the formed *cis*-aziridines did not isomerize under these reaction conditions without **3**. Compared to the trapping of 2,4-dinitrophenylsulfenylnitrene, that of 2-nitrophenyl-sulfenylnitrene with electron rich alkenes such as 1-phenylpropenes and 2-methyl-2-butene reduced the yields of the aziridines, but the trapping with electron-deficient benzalacetophenone gave a better yield than that for 2,4-dinitro derivative. These electronic effects suggest that the character of the sulfenylnitrene changes from the electrophilic one (nitrene) to the less electrophilic one (λ^4-sulfanenitrile) as shown in Figure 1. Furthermore, the presence of the alkenes did not affect the rate of the thermolysis and thus the reaction is not bimolecular.

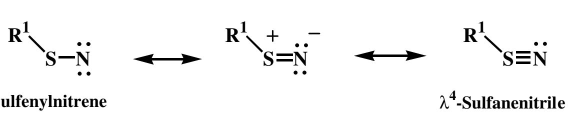
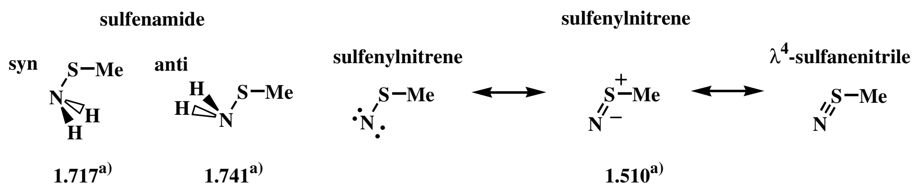


Figure 1. Resonance extreme structure.

Sulfenylnitrenes can be expected to have a character of λ^4-sulfanenitriles like examples of thiazyl halide, and perfluoroalkyl R–S≡N as a resonance extreme shown in Figure 1. Unlike these electrophilic λ^4-sulfanenitriles, present aromatic sulfenylnitrenes are considered to reduce its electrophilicity.

The electronic structure of sulfenylnitrenes was investigated by DFT calculation using a model compound (MeS–N) as shown in Figure 2.[10] The SN bond length



(a) SN bond length (Å)

Figure 2. Calculated SN bond lengths (Å) of sulfenamide and sulfenylnitrene at B3LYP/6-31G* level.

of the sulfenylnitrene (MeS–N 1.510 Å) was found to be shorter than that of sulfenamides ($MeSNH_2$ *syn*: 1.717 Å, *anti*: 1.741 Å) to suggest that the electronic structure of the sulfenylnitrene has a character of λ^4-sulfanenitriles. These results suggest that the lower reactivity of the present sulfenylnitrenes is due mainly to the electronic structure of the λ^4-sulfanenitrile and the character of the electrophilic nitrene is probably contributed by the electron withdrawing nitro group.

2. Summary

We have demonstrated the convenient generation of sulfenylnitrenes with *N*-sulfenylsulfodiimides. Furthermore, 2,4-dinitrophenylsulfenylnitrene was trapped by *trans*- and *cis*-1-phenylpropenes stereospecifically.

References and notes

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7. *S*,*S*-Diphenyl-*N*-(2,4-dinitrophenylsulfenyl)-*N*′-tosylsulfodiimide **2**. Mp 138 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 6.94 (d, 2H), 7.54–7.70 (m, 8H), 8.12 (d, $J = 8.8$ Hz, 4H), 8.30 (dd, $J_1 = 9.2$ Hz, $J_2 = 2.4$ Hz, 1H), 8.51 (d, $J = 9.2$ Hz, 1H), 8.97 (d, $J = 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 120.5, 126.0, 127.0, 127.25, 127.33, 128.3, 128.7, 130.0, 134.2, 138.2, 140.5, 140.8, 142.8, 144.0; IR (KBr) 1343, 1300 cm^{-1} (O=S=O), 1157, 1110, 1080, 1063 cm^{-1} (N=S=N), 987 cm^{-1} (S=N); Anal. Calcd for $C_{25}H_{20}N_4O_6S_3$: C, 52.80; H, 3.55; N, 9.85. Found: C, 52.94; H, 3.65; N, 9.65.
   S,*S*-diphenyl-*N*-(2-nitrophenylsulfenyl)-*N*′-tosylsulfodiimide **3**. Mp 98 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H), 6.90 (d, $J = 8.0$ Hz, 2H), 7.19 (td, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H) 7.54–7.65 (m, 9H), 8.13–8.17 (m, 5H), 8.28 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 124.1, 124.9, 125.8, 126.1, 128.3, 128.6, 129.8, 133.76, 133.85, 138.9, 140.6, 141.4, 142.4, 144.0; IR (KBr) 1333, 1300 cm^{-1} (O=S=O), 1184, 1143, 1083, 1047 cm^{-1} (N=S=N), 985 cm^{-1} (S=N).
8. The sulfenylating reagents, 2,4-dinitro- and 2-nitrobenzenesulfenyl chlorides, used are relatively stable and commercially available.
9. *N*-Sulfenylated sulfodiimide was unable to see the parent peek by EI and FAB mass spectrum.
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