

A Facile and Efficient Method for the Reduction of Sulfoxides into Sulfides with an Al-NiCl₂·6H₂O System

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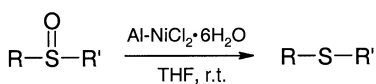
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Abstract: It has been observed that alkyl aryl and dialkyl sulfoxides can be conveniently and rapidly converted to the corresponding sulfides with an Al-NiCl₂·6H₂O system in high yields. Ketones are not affected under these reaction conditions.

Key words: sulfoxides, reduction, sulfides, aluminium, nickel chloride hexahydrate

Organosulfur compounds play an important role in organic synthesis due to the ease of incorporation of the element into complex structures, the ability to modify the valency of the atom, the variety of chemical characteristics exhibited by those varied oxidation states, and the ease of removal of sulfur as needed for the synthesis.¹ Therefore, the interconversion of one oxidation state to another is a crucial aspect of the successful use of sulfur in synthetic applications.² Reduction of sulfoxides to sulfides is one of the transformations that are of increasing importance in organic³ and biological⁴ reactions. There are various procedures for the conversion of sulfoxides to sulfides.^{3a,5} However, the reduction of sulfoxides with many reagents suffers from serious disadvantages, such as use of an expensive reagent,^{5d-5f,6} difficult work-up procedures,⁷ dry reaction conditions,⁸ harsh acidic⁹ or basic¹⁰ conditions, low yields,¹¹ very high reaction temperatures,^{3a,12} side products^{9b} and long reaction times.¹³ Metal-metal salt binary systems such as Al-NiCl₂·6H₂O-THF,¹⁵ Al-SbCl₃ or Zn-SbCl₃,¹⁶ Fe-NiCl₂·6H₂O-THF¹⁷ have long been used as reducing agents for many functional groups. In this communication, the use of the Al-NiCl₂·6H₂O system is reported for the selective reduction of sulfoxides to sulfides in very good yields under mild conditions.

In continuation of our interest in sulfur chemistry,¹⁴ we were in need of a rapid, cost effective and convenient method for the reduction of sulfoxides to sulfides. It was observed that Al-NiCl₂·6H₂O reduced sulfoxides to their corresponding sulfides within a short period of time in

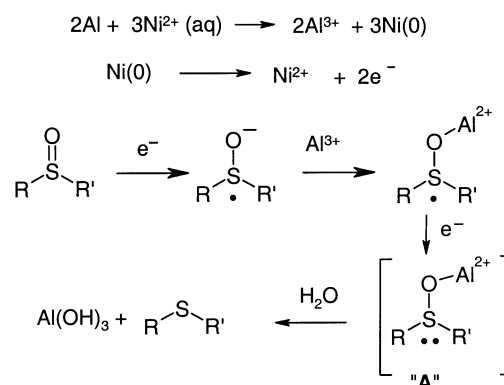


Where R = alkyl, aryl

Scheme 1

high yields¹⁸ (Scheme 1). Interestingly, ketones are not reduced under these reaction conditions (entry 9). The reaction is general, as shown in Table 1.

The probable mechanism of the reaction can be rationalized by taking account of the mechanism proposed for this type of binary system^{15,16,20} as shown in Scheme 2. The sulfoxide accepts electrons released during the oxidation of Ni(0), formed in the reaction of aluminum and NiCl₂·6H₂O,²⁰ to Ni²⁺. The radical anion reacts with aluminum chloride, which accepts another electron to give the species 'A'. The species 'A' then decomposes to give the product.



Scheme 2

It is evident from the results summarized in Table 1 that dialkyl and alkyl aryl sulfoxides are reduced to the corresponding sulfides in good to excellent yields. The reaction is complete within a short period of time. The final product can be obtained simply by filtration of the reaction mixture and subsequent column chromatography.

In summary, the use of Al-NiCl₂·6H₂O in THF provides a very rapid and effective means of reducing sulfoxides. The high yields, selectivity, mild reaction conditions, short reaction times, low cost of the reagents and the very convenient isolation process of this reaction makes this method an attractive alternative to existing methods.

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Table 1 Reduction of Sulfoxides to Sulfides

Entry	Substrates	Time (min)	Products	Yield (%) ^a
1		45		92
2		50		94
3		45		84
4		60		86
5		40		90
6		50		84
7	$C_2H_5SC_2H_4OAc$	50	$C_2H_5SC_2H_4OAc$	87
8	$C_5H_{11}SC_2H_4OH$	45	$C_5H_{11}SC_2H_4OH$	93
9		40		86
10	$C_{16}H_{33}SC_2H_5$	45	$C_{16}H_{33}SC_2H_5$	94
11	$C_8H_{17}SC_5H_{11}$	50	$C_8H_{17}SC_5H_{11}$	91
12	$C_{18}H_{37}SC_2H_5$	45	$C_{18}H_{37}SC_2H_5$	93

^a Yields refer to isolated yields. All compounds were characterized by ¹H NMR, ¹³C NMR, IR spectroscopy and elemental analysis.

References

- (1) (a) Block, E. *J. Chem. Ed.* **1971**, *48*, 814. (b) Fleming, I. *Chem. Ind. (London)* **1975**, 449. (c) Davidson, A. H.; Hodgson, P. K. G.; Howells, D.; Warren, S. *Chem. Ind. (London)* **1975**, 455.
- (2) Drabowicz, J.; Numata, T.; Oae, S. *Org. Prep. Proced. Int.* **1977**, *9*, 63.
- (3) (a) Madesclaire, M. *Tetrahedron* **1988**, *44*, 6537. (b) Drabowicz, J.; Dudzinski, B.; Mikołajczyk, M. *Synlett* **1992**, 252. (c) Mohanazadeh, F.; Momeni, A. R.; Ranjbar, Y. *Tetrahedron Lett.* **1994**, *35*, 6127. (d) Lee, G. H.; Choi, E. B.; Lee, E.; Pak, C. S. *Tetrahedron Lett.* **1994**, *35*, 2195. (e) Zhang, Y.; Yu, Y.; Bao, W. *Synth. Commun.* **1995**, *25*, 1825. (f) Wang, J. Q.; Zhang, Y. M. *Synth. Commun.* **1995**, *25*, 3545. (g) Nicolas, E.; Vilaseca, M.; Giralt, E. *Tetrahedron* **1995**, *51*, 5701. (h) Fujiki, K.; Kurita, S.; Yoshida, E. *Synth. Commun.* **1996**, *19*, 3619. (i) Wang, Y.; Koreeda, M. *Synlett* **1996**, 885.
- (4) Black, S.; Harte, E. M.; Hudson, B.; Wartofsky, L. *J. Biol. Chem.* **1960**, *235*, 2910.
- (5) (a) Drabowicz, J.; Numata, T.; Oae, S. *Org. Prep. Proced. Int.* **1977**, *9*, 63. (b) Iranppoor, N.; Firouzabadi, H.; Shaterian, H. R. *J. Org. Chem.* **2002**, *67*, 2826. (c) Miller, S. J.; Collier, T. R.; Wu, W. *Tetrahedron Lett.* **2000**, *41*,

3781. (d) Yoo, B. W.; Choi, K. H.; Lee, S. J.; Yoon, C. M.; Kim, S. H.; Kim, J. H. *Synth. Commun.* **2002**, *32*, 63. (e) Somasundaran, N.; Srinivasan, C. *Ind. J. Chem., Sect. B* **2002**, *41*, 1523. (f) Yoo, B.; Choi, K. H.; Kim, D. Y.; Choi Kyung, II.; Kim, J. H. *Synth. Commun.* **2003**, *33*, 53.
- (6) (a) Drabowicz, J.; Togo, H.; Mikolajczyk, M.; Oae, S. *Org. Prep. Proced. Int.* **1984**, *16*, 171. (b) Nuzzo, R. G.; Simon, H. J.; Filippo, J. S. Jr. *J. Org. Chem.* **1977**, *42*, 568. (c) Chasar, D. W. *J. Org. Chem.* **1971**, *36*, 613.
- (7) Amos, R. A. *J. Org. Chem.* **1985**, *50*, 1311; and references cited therein.
- (8) (a) Lee, G. H.; Choi, E. B.; Lee, E.; Pak, C. S. *Tetrahedron Lett.* **1994**, *35*, 2195. (b) Hepworth, H.; Clapham, H. N. *J. Chem. Soc.* **1921**, *119*, 1188.
- (9) (a) Gazder, M.; Smiles, S. *J. Chem. Soc.* **1910**, *97*, 2248. (b) Kobayashi, K.; Kubota, Y.; Furukawa, N. *Chem. Lett.* **2000**, 400.
- (10) (a) Dyer, J. C.; Evans, S. A. Jr. *J. Org. Chem.* **1980**, *45*, 5350. (b) Dilajan, H. S.; Weber, W. P. *Tetrahedron Lett.* **1970**, 969.
- (11) Johnson, C. R.; Bacon, C. C.; Rigau, J. J. *J. Org. Chem.* **1972**, *37*, 919.
- (12) Oae, S.; Kawamura, S. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 163.
- (13) Nagata, T.; Yoshimura, T.; Fujimori, K.; Oae, S. *Tetrahedron Lett.* **1984**, *25*, 341.
- (14) (a) Saikia, A. K.; Tsuboi, S. *J. Org. Chem.* **2001**, *66*, 643. (b) Kar, G.; Saikia, A. K.; Bora, U.; Dehury, S. K.; Chaudhuri, M. K. *Tetrahedron Lett.* **2003**, *44*, 4503.
- (15) (a) Sarmah, B. K.; Barua, N. C. *Tetrahedron* **1991**, *47*, 8587. (b) Bezbarua, M. S.; Bez, G.; Barua, N. C. *Chem. Lett.* **1999**, 325.
- (16) Wang, W. B.; Shi, L. L.; Huang, Y. Z. *Tetrahedron Lett.* **1990**, *31*, 1185.
- (17) Barua, M.; Boruah, A.; Prajapati, D.; Sandhu, J. S. *Tetrahedron Lett.* **1996**, *37*, 4559.
- (18) **General Procedure:**
In a typical procedure, NiCl₂·6H₂O (10 mmol) and aluminum powder (10 mmol) were added to an ice-cooled solution of the substrate (1.0 mmol) in freshly distilled THF. An exothermic reaction took place immediately and stirring was continued for a specified period of time. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with EtOAc and filtered. The residue was washed with EtOAc several times, and the combined filtrate and washings were dried (Na₂SO₄) and evaporated to dryness. Finally, the crude product thus obtained was purified by column chromatography using EtOAc and hexane as eluent and characterized by IR, NMR and elemental analysis.¹⁹
- (19) **Ethyl Octadecyl Sulfide:** ¹H NMR (300 MHz): δ = 0.88 (t, *J* = 6.0 Hz, 3 H, -CH₃), 1.35 (m, 33 H, CH₂-, -CH₃), 1.55 (m, 2 H, -CH₂-), 2.53 (m, 4 H, -CH₂SCH₂-). IR: 2925, 2863, 1465, 723 cm⁻¹. Anal. Calcd for C₂₀H₄₂S: C, 76.35; H, 13.46; S, 10.19. Found: C, 76.52; H, 13.17; S, 10.38.
n-Pentyl-2-hydroxyethyl Sulfide: ¹H NMR (300 MHz): δ = 0.88 (t, *J* = 6.0 Hz, 3 H, -CH₃), 1.34 (m, 4 H, 2-CH₂-), 1.57 (m, 2 H, -CH₂-), 2.50 (t, *J* = 7.2 Hz, 2 H, -SCH₂-), 2.70 (t, *J* = 6.0 Hz, 2 H, -SCH₂-), 3.69 (t, *J* = 6.0 Hz, 2 H, -CH₂-O-). IR: 3391, 2960, 2935, 2858, 1465, 1050, 1015, 774 cm⁻¹. Anal. Calcd for C₉H₁₈O₂S: C, 56.80; H, 9.53; S, 16.85. Found: C, 57.12; H, 9.36; S, 17.14.
n-Pentyl Phenyl Sulfide: ¹H NMR (300 MHz): δ = 0.87 (t, *J* = 7.0 Hz, 3 H, -CH₃), 1.37 (m, 4 H, 2-CH₂-), 1.65 (m, 2 H, -CH₂-), 2.8 (t, *J* = 7.11 Hz, 2 H, -S-CH₂-), 7.54 (m, 5 H, aromatic). IR: 2930, 2858, 1588, 1486, 1107, 1025, 748 cm⁻¹. Anal. Calcd for C₁₁H₁₆S: C, 73.27; H, 8.94; S, 17.78. Found: C, 73.43; H, 9.18; S, 17.52.
2-Ethylsulfanyl Ethyl Acetate: ¹H NMR (300 MHz): δ = 1.38 (t, *J* = 7.38 Hz, 3 H, -CH₃), 2.07 (s, 3 H, CH₃CO-), 2.55 (t, *J* = 7.50 Hz, 2 H, -CH₂S-), 2.74 (t, *J* = 7.50 Hz, 2 H, -CH₂S-), 4.22 (t, *J* = 6.90 Hz, 2 H, -CH₂-OAc). IR: 2965, 2924, 1741, 1460, 1229, 1034, 748 cm⁻¹.
Phenylsulfanylacetone: ¹H NMR (400 MHz): δ = 2.27 (s, 3 H, -CH₃), 3.66 (s, 2 H, -SOCH₂CO-), 7.21 (m, 2 H, ArH), 7.32 (m, 3 H, ArH). ¹³C NMR (100 MHz): δ = 28.42, 45.06, 127.10, 129.35, 129.70, 134.84, 203.56. IR: 3073, 2935, 1711, 1358, 1235, 1163, 1025, 743 cm⁻¹.
- (20) (a) Shiota and co-workers prepared precipitated nickel by adding wet NiCl₂·6H₂O and hot zinc powder. See: Ishige, M.; Shiota, M. *Can. J. Chem.* **1975**, *53*, 1700. (b) When added to NiCl₂·6H₂O, aluminum powder reacts vigorously without heating. The reaction must be cooled for the heat to subside.