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LIGAND-COUPLING THROUGH σ-SULFURANE FORMED ON TREATMENT OF SULFILIMINES WITH HYDRIDE

Kyoung Soo Kim. In Bae Jung, and Yong Hae Kim*

Department of Chemistry
Korea Advanced Institute of Science and Technology
P.O. Box 150 Cheongyang-Ni, Seoul 130-650, Korea

and Shigeru Oae*

Okayama University of Science
Ridai-cho 1-1, Okayama 700, Japan

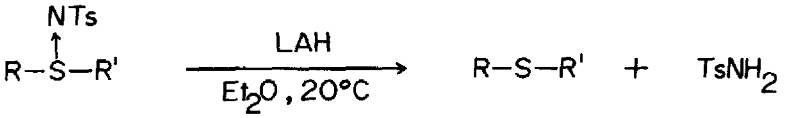
SUMMARY: The reaction of N-(4-tosyl)sulfilimines with lithium aluminum hydride was found to proceed via the ligand-coupling within the σ-sulfurane formed as an intermediate by giving the corresponding sulfides in excellent yields under mild conditions.

Tetracoordinate sulfuranes formed by the treatment of sulfilimines with nucleophiles[1], disulfides[2], and iodide[3] have recently attained to a remarkable importance as intermediates both in mechanism and in organic synthesis.

The hypervalent species named σ-sulfuranes[4] are relatively unstable and hence tend to transform. by extruding an axial ligand and an equatorial ligand with a pair of electron, to stable compounds in which the central atom resumes a normal valency.

If there is any cohesive interaction between an axial and an equatorial ligand, the two ligands would be eliminated from the central valence-shell expanded atom concertedly to afford a ligand coupling product. In previous work, we have reported that for a complex reaction mechanism where various possible pathways exist for the conversion of starting materials of tricoordinate compounds such as sulfoxides, sulfonium salts, and other tricoordinate heteroatom compounds, it is best explained by a new ligand-coupling concept.[5] We have now found a new reaction which involves both an initial pseudorotation and the subsequent ligand-coupling between nitrogen and hydrogen atom within a σ-sulfurane formed as an intermediate from sulfilimines and hydride. When sulfilimines were treated with lithium aluminum hydride in ether at 20°C, the corresponding sulfides and 4-toluenesulfonamide were obtained in excellent yields. In this communication, we wish to describe the first example of the clean-cut ligand-coupling within σ-sulfurane intermediate containing hydride ligand.

Table 1. Reaction of Sulfilimines with Lithium Aluminum Hydride.



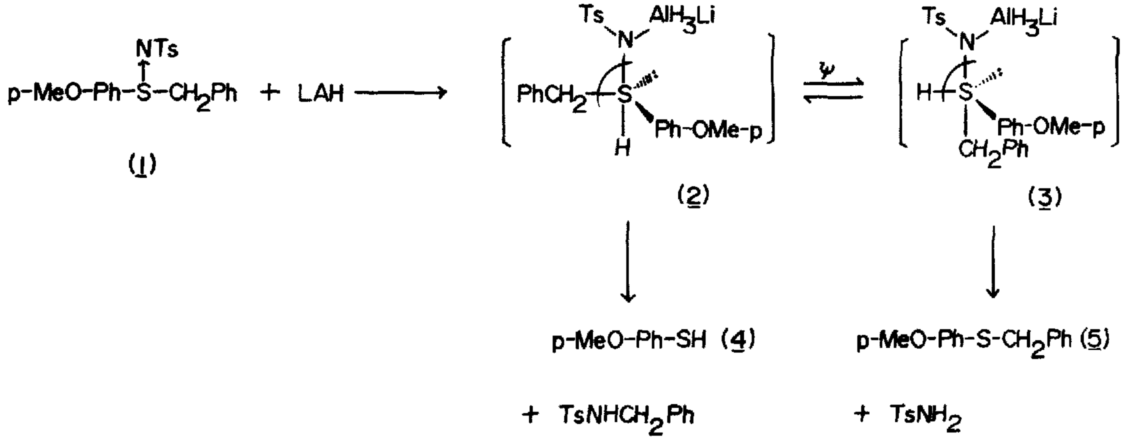
Run	Substrate R	R'	$LiAlH_4$ (eq)	Reactn. Time (h)	R-S-R' Yield (%)[a]
1	4-Br-C_6H_4	4-CH_3O-C_6H_4	4.0	1	93
2	4-Cl-C_6H_4	CH_2Ph	3.0	2	81
3	C_6H_5	C_6H_5	8.0	4	94
4	4-CH_3-C_6H_4	4-CH_3O-C_6H_4	6.0	6	92
5	4-CH_3O-C_6H_4	CH_2Ph	4.0	4	91[c]
6	C_6H_5	CH_3	4.0	4	99[b]
7	4-CH_3-C_6H_4	CH_3	4.0	4	83
8	4-CH_3O-C_6H_4	CH_3	4.0	4	86
9	4-Cl-C_6H_4	CH_3	3.0	2	96

a) Isolated yields. b) Yields by ^1H-NMR. c) 4-Methoxythiophenol (6%) was obtained

In a typical experimental procedure, lithium aluminum hydride (22.8mg, 0.6mmol) was slowly added to a solution of S-(4-chlorophenyl)-S-methyl-N-(4-tosyl)sulfilimine (178.5mg, 0.6mmol; ether, 10ml) at ca. 20°C under dry argon atmosphere. After being stirred for 3h at 20°C with good stirring, the reaction mixture was cautiously poured into 30ml of cold water, and then extracted with methylene chloride (3 x 30ml). Drying over anhydrous $MgSO_4$ and concentration under reduced pressure gave crude 4-chlorophenyl methyl sulfide (94.1mg 99%) which was purified by preparative TLC (silica gel, 10cm x 10cm x 1mm, n-Hexane) to give pure 4-chlorophenyl methyl sulfide (91.3mg, 96%). 4-Toluenesulfonamide was isolated from the aqueous layer after acidifying the solution with hydrochloric acid. The products were identified by comparing their IR, ^1H-NMR and GC with those of the authentic samples.

The products obtained are summarized in Table 1. Various N-(4-tosyl)-sulfilimines, such as S-alkyl-S-aryl- and S,S-diaryl-N-(4-tosyl)sulfilimines were readily reduced into the corresponding sulfides in excellent yields under mild conditions by lithium aluminum hydride.

In order to see the effects of 4-substituted group on the ligand-coupling, competitive reaction of various methyl 4-substituted phenyl sulfilimines with lithium aluminum hydride was carried out. The reaction appears apparently to be initiated via nucleophilic attack of the hydride on the trivalent sulfur to form a sulfurane (2) (Hammett's σ value +1.5, γ=0.993).[6] The rate-determining step appears to be the nucleophilic attack of the hydride on the central sulfur atom as the case of the reaction of the sulfilimines with phosphine.[5] The most plausible mechanism is thus shown below. In the reduction of S-benzyl-S-(4-methoxyphenyl)-N-(4-tosyl)sulfilimine (1), the hydride ion may initially attack the sulfinylsulfur atom from the back side of the sulfinylnitrogen atom, to form the σ-sulfurane (2) containing axial hydride ligand.



σ-Sulfuranes which contain highly electronegative axial ligands are relatively stable.[7] Thus, interconversion of the ligands takes place by pseudorotation to form the preferred sulfurane (3) in which the hydride is placed at an equatorial position and the apicophilic benzyl group becomes an axial ligand,[8] keeping an angle between the two ligand of ca. 90° in the incipient σ-sulfurane. Then, the ligand coupling reaction within the preferred σ-sulfurane intermediate (3) gives benzyl 4-methoxyphenyl sulfide (5) in excellent yield. However if the ligand coupling takes place within 2, 4-methoxythiophenol (4) can be formed. When S-benzyl-S-(4-methoxyphenyl)-N-(4-tosyl)sulfilimine was reacted with lithium aluminum hydride, 4-methoxythiophenol was actually obtained in 6% yield as a minor product together with benzyl 4-methoxyphenyl sulfide (91%). This fact shows that σ-sulfurane, 3 is more stable than **2** intermediate. Since the ligand-coupling of **3** is clean-cut reaction, the mechanistic study is interesting and it is also promising procedure for the reduction of sulfilimines to the sulfides. The detailed mechanism is under investigation.

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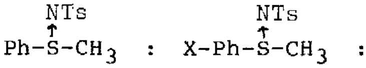
6. Relative reaction rates were determined by the competitive reduction of two sulfilimines with lithium aluminum hydride i.e., methyl phenyl sulfilimines and each of the 4-substituted sulfilimines R=Me, R'=4-Tol, R=Me, R'=4-MeOC_6H_4; R=Me, R'=4-ClC_6H_4. Molar ratio of competitive reduction:  $Ph-\overset{\overset{NTs}{\uparrow}}{S}-CH_3 : X-Ph-\overset{\overset{NTs}{\uparrow}}{S}-CH_3 : LiAlH_4 = 1.0 : 1.0 : 1.25$. The relative yields of sulfides were determined by GC analyses.
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