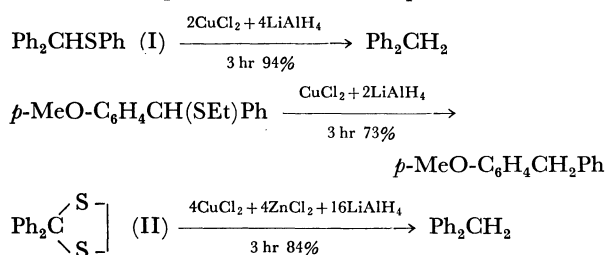# A Useful Method for Reductive Fission of Sulfides and Its Application to Carbon-Carbon Bond Formation

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In connection with the activation of bivalent sulfur compounds with $CuCl_2$,[1] we report useful methods for both reductive fission of sulfides with $CuCl_2$-$LiAlH_4$ and carbon-carbon bond forming reaction with the use of allyl 2-pyridyl sulfide. The present work was investigated anticipating that the reductive fission of sulfides would proceed in the presence of $CuCl_2$ by an attack of a hydride generated from metal hydrides. As expected, the reduction proceeded effectively by the combined use[2] of $CuCl_2$ and $LiAlH_4$ as follows. First, 2 mol of $CuCl_2$ and 4 mol of $LiAlH_4$ were stirred for 1 hr in tetrahydrofuran under argon atmosphere (black precipitate appeared immediately), then diphenylmethyl phenyl sulfide(I) was added and the reaction mixture was refluxed for 3 hr. After successive hydrolysis, diphenylmethane was obtained in 73% yield. Similarly, benzophenone ethylene-mercaptole (II) was reduced with 4 mol of $CuCl_2$ and 8 mol of $LiAlH_4$ under the same conditions to give diphenylmethane in 42% yield. The yield of diphenylmethane was increased to 84% when II was reduced with 4 mol of $CuCl_2$, 4 mol of $ZnCl_2$ and 16 mol of $LiAlH_4$ in the above experiment.

$$Ph_2CHSPh \ (I) \ \xrightarrow[\text{3 hr 94\%}]{2CuCl_2+4LiAlH_4} \ Ph_2CH_2$$

$$p\text{-MeO-}C_6H_4CH(SEt)Ph \ \xrightarrow[\text{3 hr 73\%}]{CuCl_2+2LiAlH_4}$$

$$p\text{-MeO-}C_6H_4CH_2Ph$$

$$Ph_2C\begin{matrix}S\\ \\S\end{matrix}\bigg] \ (II) \ \xrightarrow[\text{3 hr 84\%}]{4CuCl_2+4ZnCl_2+16LiAlH_4} \ Ph_2CH_2$$

For the reductive fission of sulfides, some methods have been noted.[3] However, unfavorable side reactions such as reduction of aromatic ring or carbon-carbon double bond generally accompany the desired reductive fission of carbon-sulfur bond. With the $CuCl_2$-$LiAlH_4$ method, the reductive fission of sulfides proceeded selectively with no such side reactions.

A new synthetic route for carbon-carbon bond formation involving the alkylation of allyl 2-pyridyl sulfide and a subsequent reductive fission of 2-thiopyridyl group from the alkylated products by the above mentioned reduction, was established. Selective alkylation of allyl 2-pyridyl sulfide was tried starting from the lithium salt. The alkylation of allylic phenylsulfides was reported by Biellmann and Ducep.[4] By introduction of 2-pyridyl group instead of phenyl group, it was expected that side reactions, such as a migration of double bond and a *cis-trans* isomerization, would be minimized by the effect of the stable five membered chelate ring formation of the carbanion. Actually, allyl 2-pyridyl sulfide (III) was easily converted into their carbanion with C_6H_5Li in tetrahydrofuran at -25——$15°C$. Subsequent alkylation with alkyl halides afforded the alkylated products in good yields after purification by silica gel column chromatography and distillation as shown in the Table. Analysis by vpc indicated that the products selectively contained α-alkylated products (IV) in 92—95% as shown in parentheses.

Reductive fission of 2-pyridyl group from the alkylated product (IV) proceeds successfully according to the following procedure with the use of $CuCl_2$-$LiAlH_4$; Treatment of IV with 4 mol of $CuCl_2$ and 8 mol of $LiAlH_4$ in tetrahydrofuran for 4 hr at room temperature, followed by distillation gave α-olefins (V), estimated to be 93% pure by vpc, in good yields.

$$CH_2=CH-CH_2-S-\!\!\bigcirc\!\!_N \ \xrightarrow{C_6H_5Li} \ \bigg[CH_2=CH-CH\!\!\begin{matrix}S-\bigcirc_N\\Li\end{matrix}\bigg]$$

(III)

$$\xrightarrow{RBr} \ CH_2=CH-\overset{R}{\underset{|}{CH}}-S-\!\!\bigcirc\!\!_N \ \xrightarrow{4CuCl_2+8LiAlH_4}$$

(IV)

$$CH_2=CH-CH_2-R$$

(V)

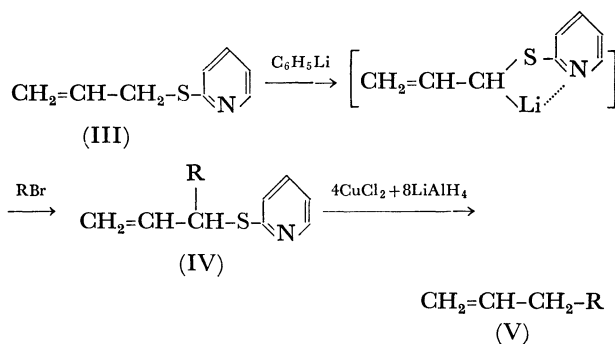| R	Yield %, (purity of IV or V %)			
	IV	bp(°C/mmHg)	V	bp(°C/mmHg)
Et	95 (93)	67—72/1.7		
PhCH₂	82 (92)	141—143/1.5	53 (93)	65/15
PhCH₂CH₂	82 (95)	144—148/0.27	80 (93)	91—92/20

1) T. Mukaiyama, K. Narasaka, and H. Hokonoki, *J. Amer. Chem. Soc.*, **91**, 4315 (1969); T. Mukaiyama, K. Narasaka, K. Maekawa, and H. Hokonoki, This Bulletin, **43**, 2549 (1970); T. Mukaiyama, K. Maekawa, and K. Narasaka, *Tetrahedron Lett.*, **1970**, 4669.

2) It is well known that the reductive fission of sulfides does not proceed with LiAlH₄ etc.; H. C. Brown, P. M. Weissman, and N. M. Yoon, *J. Amer. Chem. Soc.*, **88**, 1458, 1464 (1964).

3) A. R. Pinder and H. Smith, *J. Chem. Soc.*, **1954**, 113; N. S. Crossley and H. B. Henbest, *ibid.*, **1960**, 4413; R. Mazingo, D. E. Wolf, S. A. Harris, and K. Folkers, *J. Amer. Chem. Soc.*, **65**, 1013 (1943).

4) J. F. Biellman and J. B. Ducep, *Tetrahedron Lett.*, **1969**, 3707.