

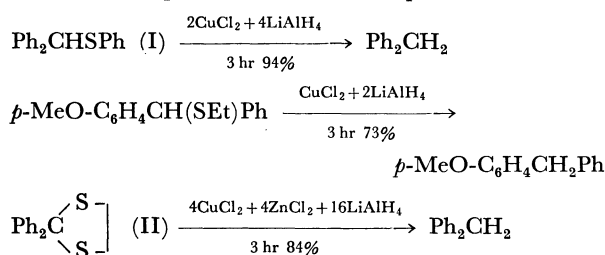
A Useful Method for Reductive Fission of Sulfides and Its Application to Carbon-Carbon Bond Formation

Teruaki MUKAIYAMA, Koichi NARASAKA, Kazuo MAEKAWA, and Masayasu FURUSATO

Laboratory of Organic Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received June 11, 1971)

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 use²⁾ 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.



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.

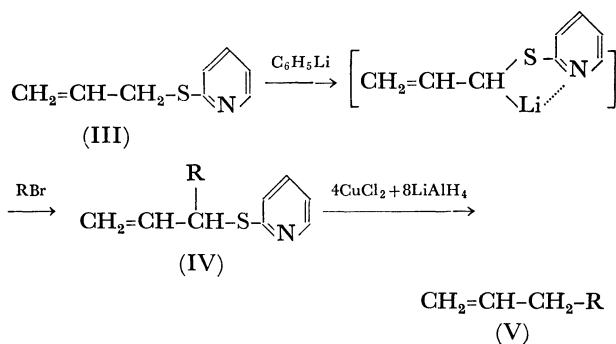
1) T. Mukaiyama, K. Narasaka, and H. Hokonoki, *J. Amer. Chem. Soc.*, **91**, 4315 (1969); T. Mukaiyama, K. Narasaka, K. Maekawa, and H. Hokonoki, *This Bulletin*, **43**, 2549 (1970); T. Mukaiyama, K. Maekawa, and K. Narasaka, *Tetrahedron Lett.*, **1970**, 4669.

2) It is well known that the reductive fission of sulfides does not proceed with LiAlH_4 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).

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 $\text{C}_6\text{H}_5\text{Li}$ 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.



R	Yield %, (purity of IV or V %)			
	IV	bp($^\circ\text{C}/\text{mmHg}$)	V	bp($^\circ\text{C}/\text{mmHg}$)
Et	95 (93)	67—72/1.7		
PhCH ₂	82 (92)	141—143/1.5	53 (93)	65/15
PhCH ₂ CH ₂	82 (95)	144—148/0.27	80 (93)	91—92/20

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