SHORT COMMUNICATIONS

Formation of Ethylenic Compounds by the Decomposition of Cuprated Sulfur Compounds

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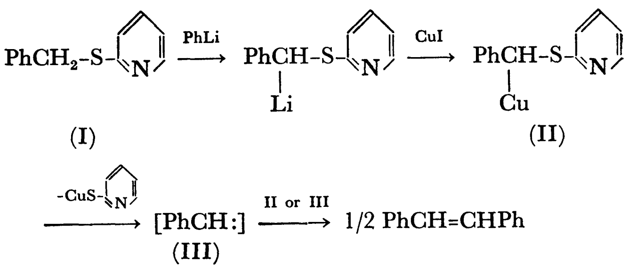
It was found in our laboratory that bivalent sulfur compounds react easily with some nucleophiles in the presence of $CuCl_2$ to give the corresponding condensation products along with copper mercaptide.[1] A study of the decomposition of α-cuprated sulfides was thus initiated with the expectation that carbenes would be generated by the elimination of copper mercaptide from the α-cuprated sulfides.

α-Cuprated sulfides were prepared according to Gilman's method by the reaction of CuI with α-lithio derivatives of sulfides in tetrahydrofuran at −70°C.[2] Decomposition of the α-cuprated sulfides was then carried out by raising the temperature of the resulting mixtures to room temperature. As an example, a tetrahydrofuran solution of 0.01 mol of benzyl 2-pyridyl sulfide (I) was treated with 0.011 mol of phenyllithium in ether under nitrogen atmosphere at −30°C for 1 hr. After the addition of 0.01 mole of CuI at −70°C, the solution was slowly warmed up to room temperature and allowed to stand for 2 hr with stirring. After hydrolysis, the organic layer was chromatographed on silica gel to afford *trans*-stilbene in 86% yield. The result is explained as shown in Scheme 1; Carbene (III) is initially produced by the elimination of copper mercaptide from the α-cuprated sulfide (II), which changed to stilbene either by dimerization or reaction with the precursor (II).



Scheme 1

Similarly, diphenylmethyl and cinnamyl 2-pyridyl sulfides gave tetraphenylethylene and 1,6-diphenylhexatriene in 33% and 10% yields, respectively.

In the cases of sulfide, mercaptals and orthothioformates (IV) with phenylthio or ethylthio group, the reactions also proceeded easily as in the case of 2-pyridyl sulfides. *n*-Butyllithium was used instead of phenyllithium in order to facilitate the formation of lithium salts of IV. The corresponding ethylenic derivatives (V) were obtained in good yields by treatment of the lithium salts with CuI in the same manner as mentioned above (Table 1).

Table 1

$$\underset{(IV)}{R^1R^2CHSR^3} \xrightarrow{\text{BuLi, CuI}} \underset{(V)}{1/2\ R^1R^2C{=}CR^1R^2}$$

IV	R^1	R^2	R^3	V Yield (%)
a	H	Ph	Ph	45 (*trans*)
b	H	PhS	Ph	82 (*trans*+*cis*)
c	Ph	PhS	Ph	76 (*trans*+*cis*)
d	PhS	PhS	Ph	61[3]
e	EtS	EtS	Et	54

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[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] H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952).

[3] Vd was previously formed by carbene route from the lithium salt of IVd; D. Seebach, *Angew. Chem.*, **79**, 468, 469 (1967).