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COPPER INDUCED SOLVOLYSIS OF SULFUR COMPOUNDS

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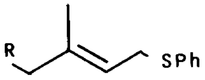
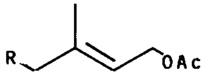
Abstract : The displacement of a phenylthio group by an acetate ion in some allylic or α-alcoxy sulfides and thioacetals was cleanly performed by treating them with a mixture of copper powder and cupric acetate in acetic acid.

The nucleophilic displacement of an aryl or alkylthio group is known to be promoted by heavy metal ions such as Hg^{2+}, Ag^{+}, Tl^{3+}, ... (1,2). We wish to report here (3b) that such substitutions can easily be performed under mild conditions without use of these expensive and/or toxic reagents.

TABLE

Substrate	Products	Yield, (%)
		
1a, R = H	2a	45
1b, R = Prenyl	2b	43
$R_1R_2R_3C$ - SPh	$R_1R_2R_3C$ - OAC	
3a, $R_1=R_2=H$; $R_3=Ph$	4a	low
3b, $R_1=R_2=H$; $R_3=O-Hexyl$	4b	63
3c, $R_1=R_2=H$; $R_3=SPh$	4c	82
3d, $R_1=H$; $R_2=Ph$; $R_3=SPh$	4d	80
3e, $R_1= H$; $R_2=-CH_2-CMe=CH_2$; R=SPh	4e	66

Some sulfides and thioketals (Table) (3a) were submitted to the following conditions : *2g of copper powder, 2g of hydrated cupric acetate and 5g of hydrated lithium acetate were heated in acetic acid (13ml) plus acetic anhydride (7ml) at reflux for an hour. To the cooled suspension the thio compound was then added and the mixture was stirred at 85-90°C under* *nitrogen for 4 to 10 hours. After dilution with methylene chloride the yellow to pale green solid was removed by filtration and the filtrate was stirred several hours with cold water, washed with cold water and dried ($MgSO_4$). Filtration on a short column of silica gel then evaporation of the solvant and distillation of the residue afforded the acetate as a colourless liquid.*

With the isoprenoid substrate 1b, some elimination products (myrcene/ocimene) were isolated (4). With 3f (R_1=Ph,R_2-R_3 as 3e) the conjugated diene was the only formed product.

A cuprous species is thought to be operative : a) the yellow precipitate led to phenylthio acetate when stirred with acetyl chloride in ether (5) ; b) without added copper powder the rate was considerably lowered and some diphenyldisulfide was formed (6,7) ; c) 3d gave 4d using preformed cuprous acetate (8).

This simple process seems to have some applicability : a) the phenylthio residue can easily be reused (5,9) ; b) a selective displacement in polythio compounds can be expected since saturated alkyl or benzyl sulfides are almost unreactive ; c) the thio acetates so obtained are easily cleaved into the corresponding keto compounds (10). This method therefore constitutes a mild deblocking procedure for thioketals.

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