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A CONVENIENT METHOD FOR THE PREPARATION OF 1-PHENYLTHIO-1,3-BUTADIENE DERIVATIVES

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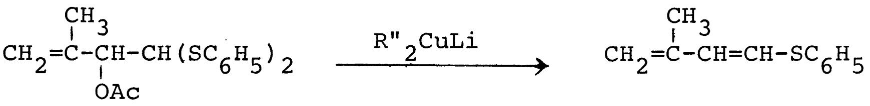
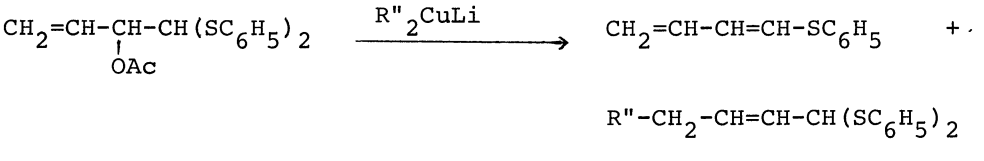
1-Phenylthio-1,3-butadiene derivatives were prepared in good yield via 1,2-elimination reaction of acetoxy and phenylthio group by treating the corresponding 1-[bis(phenylthio)-methyl] allyl acetate with dialkylcopper lithium.

We have recently reported that the corresponding olefinic compounds are obtained from β-hydroxy sulfoxides[1] or β-hydroxy sulfides[2] through 1,2-elimination reaction of hydroxy and sulfur-containing groups by treating them with o-phenylene phosphorochloridite. In connection with the studies of olefin formation reaction involving removal of sulfur-containing group, we have examined the reaction of 1-[bis(phenylthio)methyl] allyl acetate with dialkylcopper lithium and it was found that the corresponding 1-phenylthio-1,3-butadiene derivatives were obtained in good yield via 1,2-elimination of acetoxy and phenylthio groups under mild reaction conditions. For example, treatment of 1-[bis(phenylthio)-methyl]-2-methylallyl acetate, prepared by the reaction of methacrylaldehyde with bis(phenylthio)methyllithium followed by acetylation, with di-n-butylcopper lithium in ether at -30°C for 1 hr under argon atmosphere led to the formation of 1-phenylthio-3-methyl-1,3-butadiene in 71% yield. The results obtained are shown in Table 1.



$$CH_2=\overset{\overset{CH_3}{|}}{C}-\underset{\underset{OAc}{|}}{CH}-CH(SC_6H_5)_2 \xrightarrow{R''_2CuLi} CH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH-SC_6H_5$$

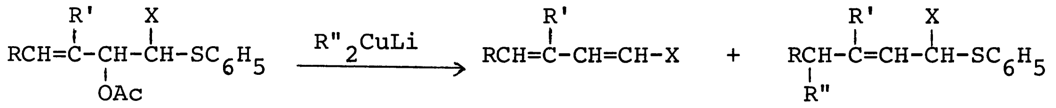
In the case of the reaction with 1-[bis(phenylthio)methyl] allyl acetate, the alkylation product was also formed as a minor one[3] along with the 1,2-elimination product, 1-phenylthio-1,3-butadiene.



$$CH_2=CH-\underset{\underset{OAc}{|}}{CH}-CH(SC_6H_5)_2 \xrightarrow{R''_2CuLi} CH_2=CH-CH=CH-SC_6H_5 \ + \ R''-CH_2-CH=CH-CH(SC_6H_5)_2$$

Similar results were obtained in the reactions of 1-(α-phenylthio)benzylallyl acetates with dialkylcopper lithium (see Table 1).

Table 1. The Reaction of (I) with Dialkylcopper Lithium.



$$\mathrm{RCH{=}\underset{OAc}{\overset{R'}{C}}{-}CH{-}\overset{X}{C}H{-}SC_6H_5 \xrightarrow{R''_2CuLi} RCH{=}\overset{R'}{C}{-}CH{=}CH{-}X \; + \; R\underset{R''}{C}H{-}\overset{R'}{C}{=}CH{-}\overset{X}{C}H{-}SC_6H_5}$$

(I) (II) (III)

(I)				Reaction Conditions		Yield (%)	
R	R'	X	R''	Temp. (^{o}C)	Time (hr)	(II)	(III)
C_6H_5	H	C_6H_5S	CH_3	0	1	70	---
C_6H_5	H	C_6H_5S	n-C_4H_9	-30	1	75	---
H	CH_3	C_6H_5S	n-C_4H_9	-30	1	71	---
CH_3	H	C_6H_5S	n-C_4H_9	-30	1	63	---
H	H	C_6H_5S	CH_3	0	1	40	33
H	H	C_6H_5S	n-C_4H_9	-30	1	62	14
C_6H_5	H	C_6H_5	n-C_4H_9	-35	1.5	80	---
H	H	C_6H_5	n-C_4H_9	-35	1	23	45

In contrast to the facile formation of 1,3-butadiene system from the allyl acetate described above, dialkylcopper lithium was shown to be inert toward the non-allylic acetate. For example, 1-[bis(phenylthio)methyl] propyl acetate or 1,4-diphenyl-2-phenylthio-3-butenyl acetate were recovered almost quantitatively after treating them with dimethyl- or di-n-butylcopper lithium under similar reaction conditions. Thus, the 1,2-elimination reaction described above is considered to be specific for the allylic acetate having leaving groups such as phenylthio group.

Further works on the scope and utility of the reactions are now in progress.

References

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