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THE REACTION OF TRIALKYLBORANES WITH THE α-LITHIO DERIVATIVES OF BIS(PHENYLTHIO)METHANE AND OF 1,1-BIS(PHENYLTHIO)PENTANE. A CONVENIENT METHOD FOR THE PREPARATION OF ALDEHYDES AND KETONES

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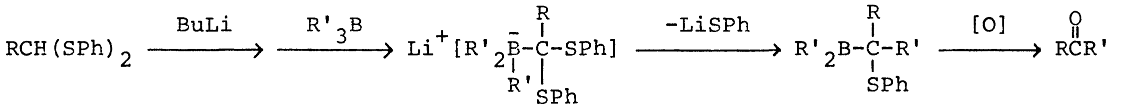
It was found that various aldehydes and ketones were readily prepared in good yields by the reactions of α-lithio derivatives of thioacetals with trialkylboranes.

In the course of the study on the reactions of trialkylboranes with carbanions, it was recently found that α-lithio derivatives of sulfides react with trialkylboranes to give alkylbenzene derivatives in good yields.$^{1)}$ This paper deals with a convenient method for the preparation of aldehydes and ketones by the use of the α-lithio derivatives of thioacetals and trialkylboranes.

The α-lithio derivatives of thioacetals (I) react with trialkylboranes to form quaternary salts (II), which in turn afford new trialkylboranes (III) by the migration of one alkyl group from the boron atom to the carbon atom in II, accompanied with elimination of lithium benzenethiolate. The new trialkylboranes are readily oxidized by usual method to give aldehydes or ketones.



$$\mathrm{RCH(SPh)_2} \xrightarrow{\mathrm{BuLi}} \xrightarrow{\mathrm{R'_3B}} \mathrm{Li^+[R'_2\underset{R'}{\overset{-}{B}}-\underset{SPh}{\overset{R}{C}}-SPh]} \xrightarrow{-\mathrm{LiSPh}} \mathrm{R'_2B-\underset{SPh}{\overset{R}{C}}-R'} \xrightarrow{[O]} \mathrm{R\overset{O}{\overset{\|}{C}}R'}$$

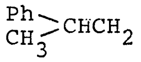
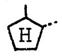
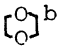
I II III IVa, R = H
b, R = n-C_4H_9

As shown in Table I, various aldehydes were synthesized in high yields by the reaction of the α-lithio derivative of bis(phenylthio)methane with trialkylboranes.

Further, various ketones were isolated by the use of the α-lithio derivative of 1,1-bis(phenylthio)pentane. In the case of tricyclohexylborane or tricyclopentylborane, the oxidation of new trialkylborane III was carried out by treating III with a solution of 1 M sodium acetate-30% hydrogen peroxide-dioxane (or -dihydropyran). On the other hand, when this trialkylborane III was treated with 3 N sodium hydroxide-30% hydrogen peroxide, the sulfide (n-C_4H_9(R')CHSPh) was obtained as the main product. The results are summarized in Table II.

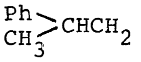
The following procedure for the conversion of bis(phenylthio)methane into cyclohexanecarbaldehyde is representative. Bis(phenylthio)methane (1.16 g, 5.0 mmol) was converted into its α-lithio derivative by the treatment with 1.1 equiv of n-butyllithium in 30 ml of dry THF at -30°C under argon, and tricyclohexylborane (1.36 g,

Table I. Preparation of Aldehydes (IVa)

R'	Conditions in oxidation step			Yield(%)^a
	Additives	Temp.(°C)	Time(hr)	
$n\text{-}C_6H_{13}$	H_2O_2(0.9 eq./B-C)-pH 7.0 buffer	r.t.	1.5	79
 $\mathrm{Ph(CH_3)CHCH_2}$	H_2O_2(1.3 eq./B-C)-pH 7.0 buffer	0	1	95
	H_2O_2(2.0 eq./B-C)-pH 7.0 buffer	< 20	1	94
	H_2O_2(2.0 eq./B-C)-pH 7.0 buffer	< 20	1	91
	H_2O_2(2.0 eq./B-C)-pH 7.0 buffer	< 20	1	75
	H_2O_2(2.0 eq./B-C)-1 M CH_3CO_2Na-  ^{b}	< 20	1	82

a. Isolated as 2,4-dinitrophenylhydrazone.
b. When it was treated with H_2O_2-pH 7.0 buffer, there was obtained in 74% yield.

Table II. Preparation of Ketones (IVb)

R'	Conditions in oxidation step			Yield(%)
	Additives	Temp.(°C)	Time(hr)	
$n\text{-}C_4H_9$	H_2O_2(5.0 eq./B-C)-3 N NaOH	r.t.	12	76
$n\text{-}C_6H_{13}$	H_2O_2(5.0 eq./B-C)-3 N NaOH	r.t.	2	95
$PhCH_2$	H_2O_2(5.0 eq./B-C)-3 N NaOH	r.t.	12	74
 $\mathrm{Ph(CH_3)CHCH_2}$	H_2O_2(5.0 eq./B-C)-3 N NaOH	r.t.	2	86
	H_2O_2(5.0 eq./B-C)-1 M CH_3CO_2Na- 	50	10	84
	H_2O_2(5.0 eq./B-C)-1 M CH_3CO_2Na- 	r.t.	12	77

6.0 mmol) dissolved in 20 ml of THF was added to the solution of the α-lithio derivative. Then, the reaction mixture was oxidized by addition of 50 ml of pH 7.0 buffer followed by dropwise addition of 3.4 ml of 30% hydrogen peroxide below 20°C. After the addition had been completed, the reaction mixture was stirred for an additional 1 hr at 15～20°C. The organic layer was treated with a methanol solution of 1.1 equiv of 2,4-dinitrophenylhydrazine and a catalytic amount of conc. hydrochloric acid. There was obtained the corresponding hydrazone (1.37 g, 94%) by silica gel column chromatography.

Seebach already reported$^{2)}$ that aldehydes and ketones were obtained from the α-lithio derivatives of thioacetals by the treatment with alkyl halides, followed by hydrolysis. Our method has some advantages to the Seebach's method in the following points: (i) alkyl groups are derived from olefins via hydroboration and (ii) the simple oxidation procedure leads to the formation of aldehydes and ketones.

In conclusion, it was established that various aldehydes and ketones were readily prepared in good yields by the use of α-lithio derivatives of thioacetals and trialkylboranes.

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2) D. Seebach, Synthesis, 1, 17 (1969).

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