Synthesis of *S*-Alkyl Alkanethioates *via* 1-Iodoalk-1-enyldialkylboranes

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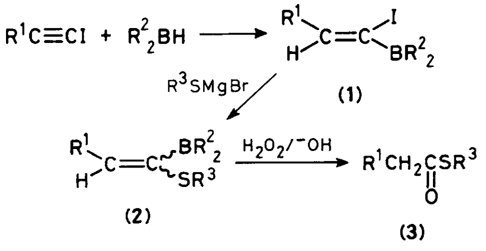
S-Alkyl alkanethioates were formed in high yields by successive reactions of 1-iodoalk-1-enylbis(1,2-dimethylpropyl)boranes with alkylthiomagnesium bromides and alkaline hydrogen peroxide.

There have been few studies on the synthesis of substituted alkenylboranes by the introduction of a substituent onto the α-alkenyl carbon atom of alk-1-enylboranes.[1] In the course of studies to modify the alkenyl moiety of alkenylboranes, we found that *S*-alkyl alkanethioates (**3**) were formed by successive reactions of 1-iodoalk-1-enylbis(1,2-dimethylpropyl)boranes (**1**) with alkylthiomagnesium bromides and alkaline hydrogen peroxide.

The reactions were carried out at −50 °C using equimolar amounts of (**1**), prepared by hydroboration of 1-iodoalk-1-ynes (10 mmol) with bis(1,2-dimethylpropyl)borane (10 mmol) in tetrahydrofuran (THF), and alkylthiomagnesium bromides, prepared by the reaction of alkanethiols (10 mmol) with ethylmagnesium bromide (10 mmol).† The reaction mixtures were oxidized with alkaline hydrogen peroxide at 0 °C.

In most cases examined, compounds (**3**) were formed in about 60% yields based on starting 1-iodoalk-1-ynes, precursors of (**1**). Addition of hexamethylphosphoric



Scheme 1. $R^2 = Me_2CHCMeH$

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† Alkylthiomagnesium bromides were prepared by the slow addition of alkanethiol to ethylmagnesium bromide in THF.

Table 1. Yields of *S*-alkyl alkanethioates (**3**).[a]

R^1	R^3	Co-solvent	Yield of (**3**)/%[b]
Bu^n	Bu^n	None	58
"	"	HMPT	83
"	"	TMEDA	100 (92)
"	Bu^s		100 (93)
"	Bu^t		72 (64)
"	$n-C_6H_{13}$		95 (91)
"	$c-C_6H_{11}$	TMEDA	85 (80)
$n-C_6H_{13}$	Bu^n		93
Bu^n	$PhCH_2$		98 (94)
Bu^n	Ph		88

[a] The reactions of $R^1CH{=}CIBR^2_2$ (**1**) with R^3SMgBr were carried out at −50 °C for 1 h and then warmed to room temperature, followed by treatment with alkaline hydrogen peroxide. [b] G.l.c. yields based on starting 1-iodoalk-1-yne (column chromatography).

triamide (HMPT) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as co-solvent, increased the yields of (**3**). Particularly, TMEDA showed a marked effect.

As shown in Table 1, the reaction could be applied to several types of organothiomagnesium bromides, including alkylthio-, phenylthio-, and benzylthio- compounds. In most cases, the yields are high and comparable or superior to those obtained by other methods.[2]

The above results show that the iodine atom of (**1**) was successfully replaced by the alkylthio group to give intermediates (**2**), and it has been shown that alkenyl groups attached to boron are transformed to carbonyl groups by alkaline hydrogen peroxide oxidation.[3] Intermediates (**2**) were not isolated from the reaction mixtures and their configurations have not been clarified. However, they may be expected to undergo reactions characteristic of alkenylboranes.[4]

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