Stereospecific Synthesis of (*E*)-Vinyl Sulphides *via* 1-Iodoalk-1-enyldialkylboranes

Masayuki Hoshi, Yuzuru Masuda, and Akira Arase*
Department of Industrial Chemistry, Kitami Institute of Technology, Kitami 090, Japan

Isomerically pure (*E*)-vinyl sulphides were obtained by reaction of 1-iodoalk-1-enylbis(1,2-dimethylpropyl)boranes successively with alkylthiomagnesium bromides, n-butyl-lithium, and aqueous sodium hydroxide.

Vinyl sulphides are potentially useful intermediates in organic synthesis,[1] and their stereospecific synthesis has been attempted. We report a new, highly stereospecific synthesis of (*E*)-vinyl sulphides (**3**) using 1-iodoalk-1-enylbis(1,2-dimethylpropyl)boranes (**1**).

We previously found that compounds (**1**) were transformed into *S*-alkyl alkanethioates (**4**) by reaction with alkylthiomagnesium bromides followed by alkaline hydrogen peroxide.[2] The 1-alkylthioalk-1-enylbis(1,2-dimethylpropyl)boranes (**2**) which we assume are formed as intermediates would afford vinyl sulphides by protonolysis.

Preliminary g.l.c. examination of the *in situ* protonolysis of the mixtures obtained by the reaction of (**1**) with alkylthiomagnesium bromides,† using carboxylic acids, normal reagents for the protonolysis of alkenylboranes,[3] failed to

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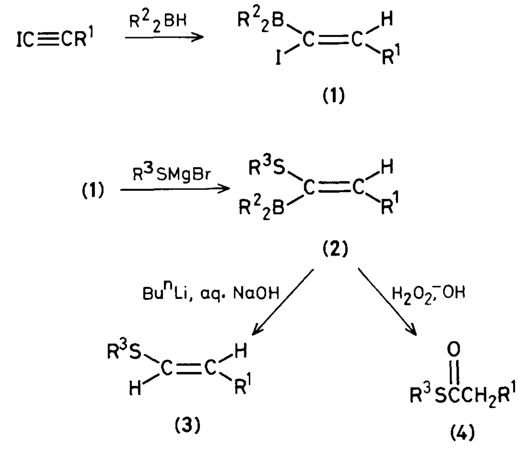
† Alkylthiomagnesium bromides were prepared by the slow addition of alkanethiols to ethylmagnesium bromide in tetrahydrofuran.



Scheme 1. $R^2 = Me_2CHCHMe$

show any detectable products. However, treatment of the same mixtures with n-butyl-lithium and then aqueous sodium hydroxide, a method reported by Negishi *et al.* for conversion of the carbon–boron bond of alk-1-enylboranes into a carbon–hydrogen bond with retention of configuration,[4] afforded (**3**) in about 50% yields based on the 1-iodoalk-1-yne precursors of (**1**). Addition of hexamethylphosphoric triamide (HMPT) as a co-solvent increased the yields markedly.

As shown in Table 1, the reaction could be applied to various organothiomagnesium bromides including alkylthio-, phenylthio-, and benzylthio-compounds. Isomerically pure compounds (**3**) were isolated following work-up by column chromatography using basic aluminium oxide coated with sodium hydroxide.‡ The configuration was assigned to all compounds (**3**) by the coupling constant (*J* 14.7—15.1 Hz) for the vinyl protons in the ^1H n.m.r. spectra. Signals resulting from the *Z* isomers were not found in any cases, indicating that the reactions were stereospecific.

Previously, Vermeer *et al.* reported a highly stereoselective synthesis of (*E*)-vinyl sulphides employing alk-1-ynyl sulphides RC≡CSR′ as the starting materials.[5]

Table 1. Yields of (*E*)-vinyl sulphides (**3**).[a]

R^1	R^3	Yield of (**3**)[b]
Bu^n	Bu^n	82 (45)
,,	Bu^t	87
,,	Ph	67
,,	$PhCH_2$	62
n-Hexyl	Bu^n	70

[a] The reactions of $R^1CH{=}CIBR^2_2$ (**1**), prepared by hydroboration of 1-iodoalk-1-ynes (10 mmol) with bis(1,2-dimethylpropyl)borane (10 mmol) in tetrahydrofuran (THF), with R^3SMgBr (10 mmol) in THF, were carried out at −50 °C for 1 h followed by warming to room temperature, addition of HMPT (5 ml), and then treatment with Bu^nLi (10 mmol) in hexane and aqueous 6 M-NaOH (10 ml). [b] Isolated yields based on starting 1-iodoalk-1-yne; yield in parentheses in the absence of HMPT.

The configurations of compounds (**2**) could not be defined directly. However, our results strongly suggest that the alkylthio groups were introduced at the α-alkenyl carbon atoms of compounds (**1**) with inversion of configuration giving the (*E*)-alkenylboranes (**2**).

The advantages of the present synthesis are that all reagents, including 1-iodoalk-1-ynes, are readily available and relatively cheap, and all reactions may be carried out without isolation of the intermediates (**2**), giving isomerically pure products (**3**).

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‡ Aluminium oxide was treated with 10% aqueous NaOH and dried at 150 °C.