Stereoselective Synthesis of 1,4-Dienes and Mono-olefins by Methylcopper-induced Cross-coupling of Dialkenylchloroboranes with Organic Halides

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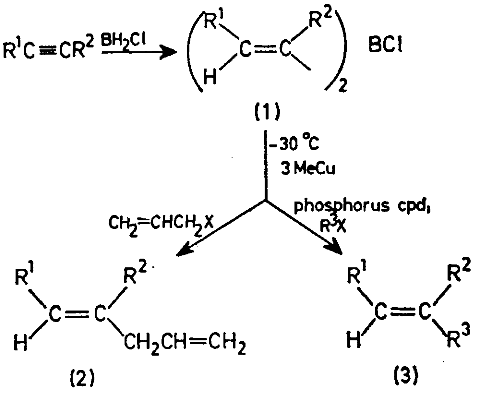
Summary Mono-olefins and 1,4-dienes have been synthesised with >99% stereochemical purity by the methylcopper-induced cross-coupling of dialkenylchloroboranes, formed from alkynes, with organic halides.

WE recently reported that dialkenylchloroboranes (**1**) dimerized in the presence of methylcopper at 0 °C to yield isomerically pure (*E*,*E*)-1,3-dienes.[1] This result suggested the formation of vinyl organocopper intermediates, and it appeared possible that treatment of (**1**) with methylcopper at lower temperatures followed by addition of organic halides might provide the cross-coupling products.



SCHEME

Treatment of (**1**) with 3 mol. equiv. of methylcopper at −30 to −40 °C followed by addition of allyl halides produces (4*E*)-1,4-dienes (**2**). For simple alkyl halides, the cross-coupling products (**3**) are obtained with the aid of phosphines or phosphites (Scheme). The stereochemical purity of the product is >99%. This procedure, therefore, provides a new stereoselective transformation of acetylenes into olefin derivatives. The results are summarized in the Table.

In contrast to the reaction of boranes derived from terminal acetylenes with allyl halides (entries 1—3 and 5), in the reaction of the non-terminal acetylene dimerization competed with the desired cross-coupling reaction (entry 4). Cross-coupling with simple alkyl halides required 6 mol. equiv. of a phosphorus compound such as $P(OEt)_3$ or PPh_3. Use of a phosphorus compound, however, created substantial difficulties in product isolation, and it was found that the use of PhSLi was more convenient. Presumably, the vinyl organocopper intermediate can react with PhSLi to produce a mixed heterocuprate-type intermediate.[2] Although both alkenyl groups of the borane (**1**) can be utilized in the reaction with allyl bromide, in the reaction with simple alkyl halides only one alkenyl group participates.

TABLE. Methylcopper-induced cross-coupling of (**1**) with organic halides[a]

Entry	Alkyne $R^1C\equiv CR^2$ R^1	R^2	Halide R^3X	Yield (%)[b] of (**2**) or (**3**) (isolated yield)
1	Bu^n	H	$CH_2{=}CHCH_2Br$	95 (72)
2	Bu^n	H	$CH_2{=}CHCH_2Cl$	91
3	$Cl[CH_2]_3$	H	$CH_2{=}CHCH_2Br$	(48)
4	Bu^n	Bu^n	$CH_2{=}CHCH_2Br$	70[c]
5	Bu^n	H	$PhCH{=}CHCH_2Br$	(42)[d]
6	Bu^n	H	Bu^nI	47[e]
7	Bu^n	H	MeI	43[e]

[a] All reactions were performed on a 2-mmol scale with the same procedure as described in the text. Isolation was carried out on a 10 mmol scale. [b] Identified by i.r. and n.m.r. spectroscopy, elemental analysis, and/or comparison with authentic materials. Yields were determined by g.l.c., and are based on the alkenyl group of (**1**); they are not necessarily optimum. [c] Accompanied by the dimerization product (14%). [d] An 84:16 mixture of $Bu^nCH{=}CHCHPhCH{=}CH_2$ and $Bu^nCH{=}CHCH_2CH{=}CHPh$ was obtained. [e] $P(OEt)_3$ was used.

The preparation of (4*E*)-nona-1,4-diene is representative. MeLi (1·1 M; 30 mmol) in ether was slowly added to a stirred mixture of CuI (30 mmol) and dry ether at 0 °C under argon. The mixture was cooled to −30 to −40 °C, bis(hex-1-enyl)chloroborane (10 mmol), prepared from hex-1-yne and chloroborane in ether,[3] was added, and the mixture was stirred for 1 h at −30 to −40 °C. The colour changed from yellow to dark blue. Allyl bromide (20 mmol) was added and the mixture was allowed to come to room temperature, when it became colourless. After oxidation with alkaline H_2O_2 the ether layer was separated off. Distillation yielded the desired (4*E*)-1,4-diene: 1·78 g, 72%, b.p. 128 °C (at 760 mmHg), n_D^{25} 1·4301. A modified procedure was used for the preparation of mono-olefins. Triethyl phosphite (60 mmol) and $HCONMe_2$ (30 ml) were added to the dark blue mixture at −30 to −40 °C before addition of the alkyl halides.

Recently various procedures for the stereoselective synthesis of olefins *via* boranes or borates have been developed,[4] all of which proceed with migration of the alkyl groups from boron to carbon. Consequently, the present development not only provides a new stereoselective route to olefins from acetylenes, but also introduces a new field of borane reactions.[5]

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[1] Y. Yamamoto, H. Yatagai, and I. Moritani, *J. Amer. Chem. Soc.*, 1975, **97**, 5606.

[2] G. H. Posner, C. E. Whitten, and J. J. Sterling, *J. Amer. Chem. Soc.*, 1973, **95**, 7788. Normally, heterocuprates are prepared by the reaction of PhSCu with RLi. However, it seems that they are also preparable through the reaction of PhSLi with RCu.

[3] H. C. Brown and N. Ravindran, *J. Org. Chem.*, 1973, **38**, 1617.

[4] For the most recent references see: K. Utimoto, T. Furabayashi, and H. Nozaki, *Chem. Letters*, 1975, 397; A. Pelter, C. Subrahmanyan, R. J. Laub, K. J. Gould, and C. R. Harrison, *Tetrahedron Letters*, 1975, 1633; A. Pelter, K. J. Gould, and C. R. Harrison, *ibid.*, p. 3327; K. Yamada, N. Miyaura, M. Itoh, and A. Suzuki, *ibid.*, p. 1961; G. Zweifel and R. P. Fisher, *Synthesis*, 1975, 376.

[5] During the present work the allylation of vinylalanes was reported. (R. A. Lynd and G. Zweifel, *Synthesis*, 1974, 658).