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REGIOSELECTIVE 1,5-ENYNE SYNTHESIS FROM ORGANOBORANES

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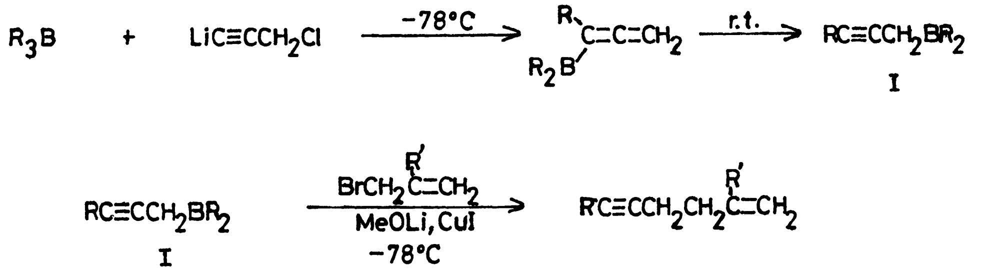
2-Alkynylboranes prepared from 2-propynyl chloride and trialkylboranes react readily with allylic halides in the presence of cuprous iodide to give 1,5-enynes regioselectively.

Although allyl-allyl or 2-propynyl-allyl coupling reaction is one of the most direct and convenient methods to construct the 1,5-diene or 1,5-enyne unit present in natural terpenoids,[1] there are many difficulties to obtain the desired stereo- and regioselectivity in those methods.[2] We have recently reported that allylic boranes prepared from allyl phenyl ether and trialkylboranes react with allyl bromide at the terminal position to give 1,5-dienes regioselectively.[3] We now wish to report that 1,5-enynes are obtained regioselectively by the coupling reaction between 2-alkynylboranes (I)[4] and allylic halides (Eq. 1).



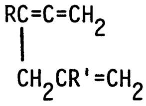
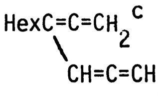
$$R_3B + LiC{\equiv}CCH_2Cl \xrightarrow{-78\,°C} \overset{R}{}\!\!\!\underset{R_2B}{}\!\!C{=}C{=}CH_2 \xrightarrow{r.t.} \underset{\text{I}}{RC{\equiv}CCH_2BR_2} \qquad (1)$$

$$\underset{\text{I}}{RC{\equiv}CCH_2BR_2} \xrightarrow[\text{MeOLi, CuI}\ -78\,°C]{BrCH_2\overset{R'}{C}{=}CH_2} RC{\equiv}CCH_2CH_2\overset{R'}{C}{=}CH_2$$

The starting 2-alkynylboranes (I) are readily prepared as a THF solution by the Zweifel's procedure,[5] and subsequent addition of lithium methoxide, cuprous iodide and allylic bromides at -78 °C gave 1,5-enynes as the major products with a small amount of their allenic isomers. The ratio of the products slightly depends upon the allylic halides and alkyl groups of organoboranes used, but the major products are always straight-chain 1,5-enynes (Table 1). 2-Propynyl bromide reacted via S_N2' mechanism to give the allenic product, and 2,3-dibromo-1-propene reacted only at the allylic position.

The following procedure for the preparation of 1-undecen-5-yne is representative. To a stirring solution of 2-propynyl chloride (0.145 ml, 2.00 mmol) in 5 ml of THF was added 1.11 ml of butyllithium in ether (1.80 M, 2.00 mmol) slowly at -78 °C followed by dropwise introduction of 0.82 ml of trihexylborane (2.45 M in THF, 2.00 mmol). The resulting clear yellow solution was allowed to warm to room temperature and stirred for 30 min. further. Then the reaction mixture was again cooled to -78 °C and 2 mmol of lithium methoxide suspended in 5 ml of THF[6] was added. After 5 min. at -78 °C, 0.381 g of CuI (2 mmol) was added and the mixture was stirred for 30 min. Finally 0.173 ml of allyl bromide(2 mmol) was added and the reaction mixture was stirred at -78 °C for 1 h and then at room temperature overnight. During the stirring at room temperature, the initial suspension changed into a deep orange solution. After alkaline hydrogen peroxide oxidation, glc analysis revealed that 1-undecen-5-yne was obtained in 62 % yield with a small amount of the allenic product (6 %).

Table 1. Reactions of 2-Alkynylboranes with Allylic and 2-Propynyl Halides.

R_3B, R	Halide	Yield (%)[a]	Product distribution (%)[b]	
			$RC{\equiv}CCH_2CH_2CR'{=}CH$	 $RC(CH_2CR'{=}CH_2){=}C{=}CH_2$
Hexyl	$CH_2{=}CHCH_2Br$	68	91	9
Butyl	"	68	84	16
Isobutyl	"	72	96	4
Cyclopentyl	"	70	86	14
sec-Butyl	"	82	91	9
Hexyl	$CH_2{=}C(Me)CH_2Br$	68	84	16
Butyl	$CH_2{=}C(Br)CH_2Br$	65	95	5
Hexyl	$HC{\equiv}CCH_2Br$	85	$HexC{\equiv}CCH_2CH{=}C{=}CH_2$[c]	 $HexC(CH{=}C{=}CH_2){=}C{=}CH_2$[c]
			91	9

a) Glc yield, based on organoborane used.

b) Determined by glc. The structures were determined by NMR and IR spectra, and elemental analyses.

c) Terminal acetylenic products could not be obtained.

References

1. For the recent selective synthesis of 1,5-dienes and 1,5-enynes, see H. Matsushita and E. Negishi, J. Am. Chem. Soc., 103, 2882 (1981); E. Negishi, C. L. Rand, and K. P. Jadhav, J. Org. Chem., 46, 5041 (1981).
2. For the recent selective coupling reaction between allylic metals and allylic halides, see Y. Yamamoto and K. Maruyama, J. Am. Chem. Soc., 100, 6282 (1978).
3. S.Hara, S. Imai, T. Hara, and A. Suzuki, Synth. Commun., in press.
4. We have failed to determine the structures of intermediates, but Zweifel et al. proposed that allenic boranes initially produced isomerize to 2-alkynyl forms upon warming to room temperature.[5)]
5. G. Zweifel, S. J. Backlund, and T. Leung, J. Am. Chem. Soc., 100, 5561 (1978).
6. Prepared as follows. To 64 mg of methanol (2 mmol) in 5 ml of dry THF was added at 0 °C, 1.11 ml of butyllithium in ether (1.80 M, 2 mmol) and the mixture was stirred for 10 min.

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