

THE REACTION OF LITHIUM TRIALKYLALKYNYLBORATE
WITH METHANESULPHINYL CHLORIDE.
A NOVEL ROUTE TO INTERNAL ACETYLENES

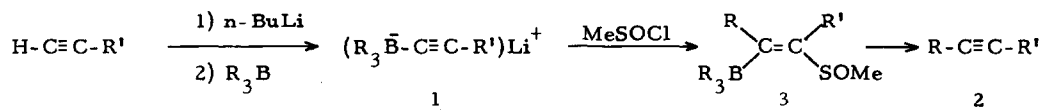
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In continuation of the synthetic studies with trialkylalkynylborates,¹ this paper describes the reaction of these borates with methanesulphinyl chloride affording disubstituted acetylenes.

To a stirred solution of phenylacetylene (0.51 g, 5.0 mmol) in THF (5 ml) at 0° maintained under nitrogen, n-butyllithium (5.0 mmol) dissolved in hexane (5 ml) was added. Stirring was continued at room temperature for 30 min, then tri-sec-butylborane (0.91 g, 5.0 mmol) was added to the solution at 0°, and the solution was stirred at room temperature for 1 hr. Methanesulphinyl chloride (0.59 g, 6.0 mmol) was then added, giving rise to a vigorous exothermic reaction. The reaction mixture was stirred for an additional 3 hr at room temperature, filtered, and distilled under reduced pressure. Chromatography on silica gel column with benzene as the eluant gave 0.50 g (63% yield) of 1-phenyl-3-methyl-1-pentyne (2g), bp 101-107° (30 mm).



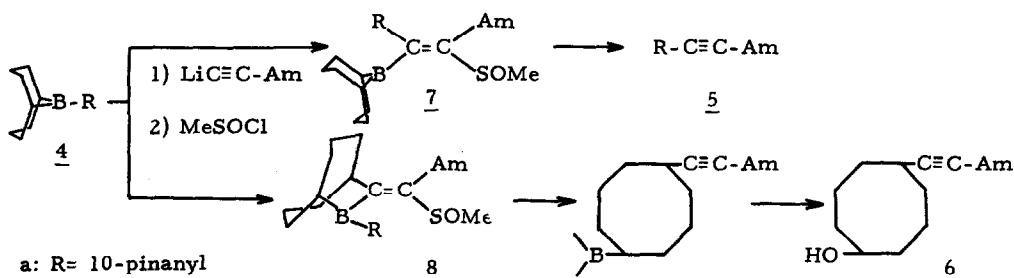
Combination of the substituents (R and R') and disubstituted acetylenes prepared in this way are listed in Table I. As the R₃B is prepared by hydroboration of an olefin, >C=C< , the present sequence of reactions produces an internal acetylene, $\text{>CH-C}\equiv\text{C-R}'$, thereby making possible the anti-Markovnikov-reductive alkynylation of the olefin.

Although 2g was also prepared by the reaction of 1g with methanesulphonyl chloride in THF-hexane (1:1), the yield was only 28% even when the mixture was refluxed for 10 hr.

Table I. Disubstituted Acetylenes (2)

	R	R'	Yield (%)	bp °C (mm)	MS (M ⁺) m/e, %	Ref.
<u>a</u>	n-Bu	n-Am	55 ^a	—	152, 4	2
<u>b</u>	sec-Bu	"	72 ^b	83- 88 (15)	152, 2	3
<u>c</u>	cyclohexyl	"	62 ^b	117-119 (24)	178, 8	3
<u>d</u>	10-pinanyl	"	61 ^b	116-120 (7)	232, 1	3
<u>e</u>	i-Pr	Ph	82 ^a	101-104 (35)	144, 44	3
<u>f</u>	n-Bu	"	63 ^a	—	158, 33	4
<u>g</u>	sec-Bu	"	62 ^b	101-107 (30)	158, 46	3

a) Glic yield, b) isolated yield.



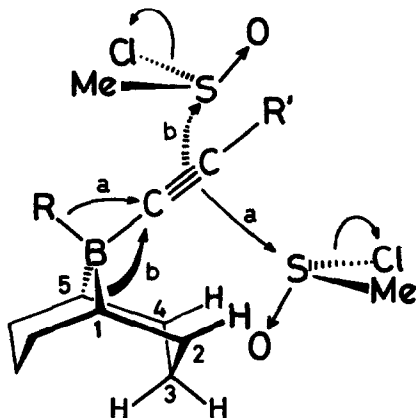
a: R= 10-pinanyl

b: R= hexyl

Although 3 was not isolated, it is a probable

intermediate in the transformation of 1 to 2.

The interaction of the sulphonyl chloride to the acetylenic π -system⁵ of 1 induces alkyl migration from the negatively charged, tetravalent boron atom. This kind of alkyl migration is commonly observed in a series of reactions of organoboranes, e. g., with carbon monoxide⁶ and α -bromo esters.⁷ Cis elimination⁸ of the methanesulphonyl and dialkylboron groups from 3 leads to the formation of 2.



Scheme 1

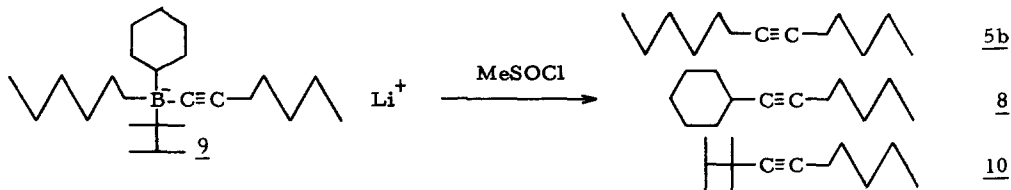
Certain substituents on boron are known to have a negligible migratory aptitude. For example, alkylation with B-alkyl-9-borabicyclo[3.3.1]nonane (B-alkyl-9-BBN, 4) was shown

to be selective, to transfer of the B-alkyl group occurring exclusively.¹⁰ Similar selectivity is apparently exhibited by a thexyldialkylborane as the thexyl group does not migrate.¹¹ We wish to point out that, unexpectedly, neither of these boron reagents exhibited this type of selectivity in the present reaction.

A solution of B-(10-pinanyl)-9-BBN (4a) in THF (10 mmol in 10 ml) was prepared in situ by Brown's method.¹² The solution was maintained at room temperature while 1-lithio-1-heptyne, prepared from 1-heptyne (0.96 g, 10 mmol) and n-butyllithium (10 mmol in 20 ml hexane), was added. The mixture was stirred for 2 hr and then methanesulphonyl chloride (1.18 g, 12 mmol) was added. After being stirred for an additional 2 hr at room temperature, this resulting mixture was treated with alkaline hydrogen peroxide and extracted with hexane. The extract was dried (Na_2SO_4) and the solvents were removed by evaporation. Chromatography on silica gel column with benzene as the eluant gave 2d (0.093 g, 4%) and 1-(5-hydroxycyclooctyl)-1-heptyne (6),³ bp 112-114° (6 mm),¹³ (0.53 g, 24%).¹⁴ Similarly, the reaction of B-hexyl-9-BBN (4b) gave 5-tridecyne (5b),³ bp 104-107° (15 mm)¹³ (2%), and 6 (23%). The predominant migration of the cyclooctyl moiety affording the intermediate 8 is accounted for on the assumption that R migrated to the neighbouring acetylenic carbon while the other acetylenic carbon underwent S_N attack at sulphur, both occurring in the trans manner,¹⁵ either concertedly or stepwise as shown in the Scheme 1. Pathway a gives rise to R migration under considerable steric inhibition of C(2) and C(4) hydrogens. Pathway b is devoid of such nonbonded interactions and apparently results in the preferential migration of the cyclooctyl moiety.

Cyclohexylhexylthexylborane (10 mmol), prepared by the successive addition of equimolar amounts of cyclohexene and 1-hexene to a solution of thexylborane in THF, was treated first with an equivalent amount of 1-lithio-1-heptyne and then with 1.2 equivalents of methanesulphonyl chloride. Three isomeric acetylenes (65%) were obtained: 2,3,3-trimethyl-4-decyne (10),³ bp 95-97° (15 mm),¹³ 1-cyclohexyl-1-heptyne (8), and 5-tridecyne (5b) in a ratio of 12:50:38. The structures of these new compounds were determined by nmr, ir and ms. The migration of the thexyl group is without precedent, but is probably enforced here by

the heavy congestion around the boron atom in intermediate 9.



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