Regiocontrolled Head-to-tail Coupling of Alkylthioallyl Carbanions with Allylic Halides *via* Lithium Alkylthioallyl Borates

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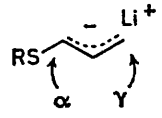
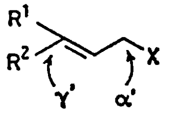
Summary Reaction of lithium alkylthioallyl borates (**3**), prepared from alkylthioallyl-lithium (**1**) and trialkylboranes at −78 °C, with allylic halides (**2**) gives head-to-tail 1,5-dienes (**4**) in good yields.

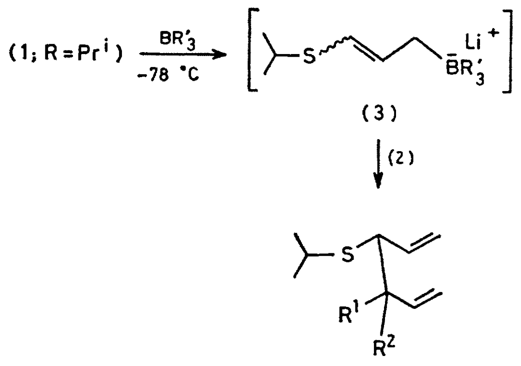
THE regiochemistry of reactions of heterosubstituted allyl carbanions is well recognized.[1] The alkylthio group generally directs electrophiles to the α-position (**1**). Reaction of the alkylthioallyl-lithium (**1**) with allylic halides (**2**) proceeds mainly *via* α–α′ (head-to-head) coupling.[2] Reaction of alkylthioallylcopper compounds with (**2**) affords γ–γ′ coupling products.[3] We report a regiocontrolled head-to-tail (α–γ′) coupling *via* lithium alkylthioallyl borates, probably (**3**).



(**1**)



(**2**)



(**4**)

We recently reported that lithium allylic borates, prepared from allylic lithium compounds with trialkylboranes, undergo regiocontrolled head-to-tail coupling with allylic halides and that regiocontrolled, electronically unimpeded coupling[4] is achieved *via* lithium alkoxyallyl borates.[5] Consequently, we have now examined the reaction of alkylthio-substituted allyl carbanions in the presence of trialkylboranes. The results are summarized in the Table.

TABLE. Reaction of (**3**) with (**2**)[a]

	Allylic halide (2)			Borane	Product/%[b]				Yield/%[c]
Entry	R^1	R^2	X	BR'_3	α–γ′	α–α′	γ–γ′	γ–α′	(isolated)
1	Me	Me	Cl	$\mathrm{Bu^n}$-9-BBN[d]	93	7	—	—	79 (68)
2	Me	Me	Cl	$\mathrm{Bu^n_3B}$	92	8	—	—	48
3	Me	Me	Br	$\mathrm{Bu^n_3B}$	96	4	—	trace	78
4	Me	Me	Br	None[e]	—	55	—	45	70
5	Me	H	Br[f]	$\mathrm{Bu^n}$-9-BBN[d]	>99	—	—	—	90 (77)
6	Me	H	Br[f]	$\mathrm{Bu^n_3B}$	59	2	18	21	85
7	Me	H	Cl	$\mathrm{Bu^n_3B}$	51	3	15	31	55
8	H	H	Br	$\mathrm{Bu^n}$-9-BBN[d]	89		11		60 (52)

[a] All reactions were performed on a 1 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., mass, and n.m.r. spectroscopy, elemental analysis, and/or comparison with authentic materials. Yields and product ratio were determined by g.l.c. The term α or γ indicates the coupling position. [c] Total yield of 1,5-dienes. [d] $\mathrm{Bu^n}$-9-BBN = 9-n-butyl-9-borabicyclo[3.3.1]nonane. [e] The normal reaction of (**1**) with prenyl bromide. [f] Contaminated with 3-bromobut-1-ene (16%).

The regioselectivity and the yield of (**4**) are both higher with the 9-BBN ate complexes than those with the tri-n-butylborates (entries 1 and 5 compared with 2 and 6). Generally, the bromides give better results than the chlorides (entries 3 and 6 compared with 2 and 7). The regiochemical difference between the ate complex and the simple allyl-lithium complex is clearly indicated in entries 3 and 4.

The preparation of 3-isopropylthio-4,4-dimethylhexa-1,5-diene is representative. To a solution of allyl isopropyl sulphide (*ca.* 10 mmol) in dry ether (30 ml) was added s-butyl-lithium in pentane (1·04 M, 10 mmol) at −78 °C under N_2. After 30 min at −35 °C, the solution was again cooled to −78 °C. Addition of $\mathrm{Bu^n}$-9-BBN (10 mmol) caused the formation of a white suspension. After 10 min at −78 °C, prenyl bromide (10 mmol) was slowly added, and the mixture was stirred overnight at room temperature. Water (5 ml) was added and the borane was oxidized with a slow stream of air. The organic layer was separated, dried, and condensed. Filtration through a silica column using hexane as eluant, followed by distillation, gave the desired 1,5-diene: 77%, b.p. 70—72 °C (10 mmHg).

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