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REGIOSELECTIVE CARBON-CARBON BOND FORMATION AT THE α-POSITION OF A SULFUR STABILIZED ALLYL CARBANION VIA AN ALKYLTHIOALLYLBORON "ATE" COMPLEX

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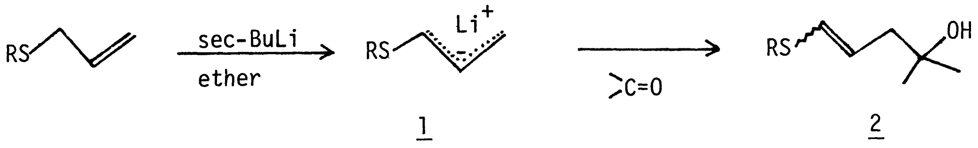
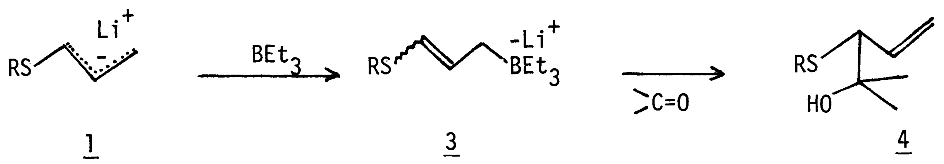
Reaction of lithium alkylthioallylboron "ate" complexes (3), prepared from alkylthioallyllithium (1) and triethylborane at -78°C in ether, with carbonyl compounds proceeds via the attack at the α-position to produce the corresponding α-alkylated derivatives (4) in good yields.

In general, the reactions of sulfur stabilized allyl carbanions (1) with carbonyl compounds lead via γ-substitution to the vinyl sulfides (2) (eq 1).[1] However, this tendency of the regiochemistry is system dependent and the influencing factors are: the nature of R,[2-4] the counterion,[5] and the solvent system and/or additives.[6]



(1)

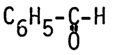
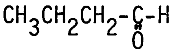
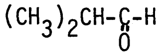
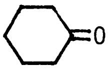
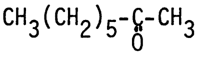
On the other hand, the reactions of 1 with organic halides proceed predominantly via α-substitution and the various methods for directing the halides to the α-position are established.[7] It is highly desirable to develop a new methodology which enables to direct carbonyl compounds to the α-position, since the resulting α-substituted allyl sulfides are useful for the organic synthesis.[7a] We now wish to report a new procedure for such a transformation via lithium alkylthioallylboron "ate" complexes (3) (eq 2).



(2)

The results are summarized in Table 1. Very high regioselectivity can be realized in the reaction of aldehydes. Unfortunately, however, the reaction of cyclohexanone proceeds through preferential α-attack, though not exclusive, presumably owing to the steric factor of the carbonyl group. The following procedure for the reaction of benzaldehyde is representative. To a solution of allyl isopropyl sulfide (1 mmol) in dry ether (3 ml) was added sec-butyllithium in

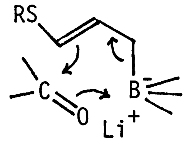
Table 1. Reaction of 3 (R = iso-Pr) with carbonyl compounds[a]

Carbonyl Compound	Borane	α-Product (4), %[b]	γ-Product (2), %[b]	Total yield, %[c]
 $C_6H_5\text{-}\underset{O}{\overset{\parallel}{C}}\text{-}H$	Et_3B	98	2	82
	n-Bu-9-BBN	>99	<1	70
	None[d]	28	72	e
 $CH_3CH_2CH_2\text{-}\underset{O}{\overset{\parallel}{C}}\text{-}H$	Et_3B	94	6	76
	None[d]	43	57	e
 $(CH_3)_2CH\text{-}\underset{O}{\overset{\parallel}{C}}\text{-}H$	Et_3B	94	6	75
	None[d]	44	56	e
	Et_3B	72	28	80
	None[d]	42	58	e
 $CH_3(CH_2)_5\text{-}\underset{O}{\overset{\parallel}{C}}\text{-}CH_3$	Et_3B	47	53	70
	None[d]	32	68	e

[a] All reactions were performed on a 1 mmol scale with the same procedure as described in the text. [b] Identified by I.R., Mass, and N.M.R. spectroscopy, elemental analysis, and/or comparison with authentic materials. Product ratio was determined by g.l.c. [c] Isolated yield. [d] The normal reaction of 1 with the electrophile at -78°C. [e] Not determined precisely, but it seemed to be good. n-Bu-9-BBN = 9-n-Butyl-9-borabicyclo[3.3.1]nonane.

pentane (1.04M, 1 mmol) at -78°C under N_2. After 30 min at -35°C, the solution was again cooled to -78°C. Addition of Et_3B (1 mmol) caused the formation of a white suspension. Benzaldehyde (1 mmol) was slowly added and the resulting mixture was allowed to warm slowly to 0°C (1 - 2hr). The normal oxidation of Et_3B with H_2O_2-NaOH at 0°C, separation of the organic layer, drying, and distillation by Kugelrohr gave the desired α-alkylated allyl sulfide: 82 %, b.p.140-145°C(2 mmHg).

Although the structure of the "ate complex" is not fully characterized, we assume that the allylic boron "ate" complex such as 3 is involved.[8] In fact, the related "ate" complex is isolated from the reaction of an allylic lithium with triphenylborane.[9] The present high regioselectivity is presumably a reflection of the coordinative effect such as 5. While further studies are required before the mechanism can be fully understood, the present development clearly provides a new method to control the regiochemistry of allyl carbanions.



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