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DIASTEREOSELECTIVE ADDITION OF γ-ALKYLTHIO-ALLYLBORONATES TO ALDEHYDES

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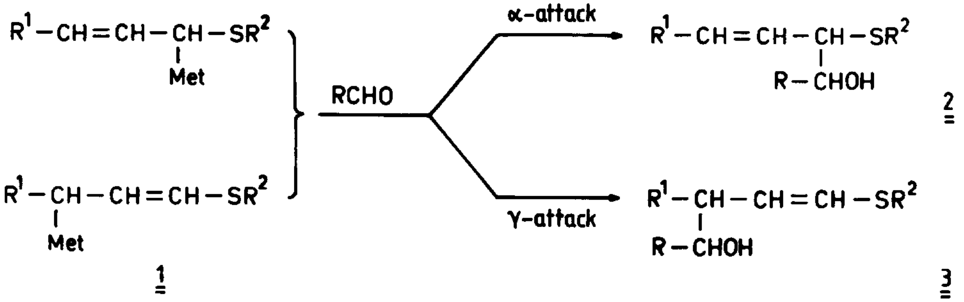
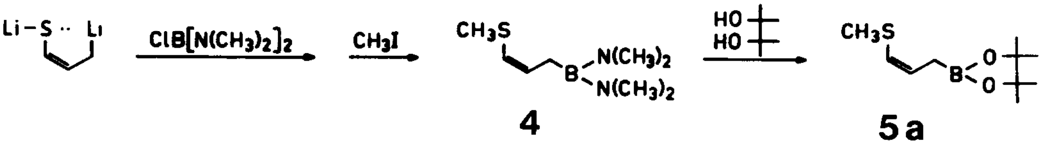
Summary: The Z- and E-γ-alkylthio-allylboronates 5 and 10 were found to add aldehydes forming diastereoselectively the adducts 7 and 6 respectively in high yield.

The alkylation and hydroxyalkylation of sulfur substituted allyllithium reagents (1, Met = Li) is of interest for various synthetic objectives. Their application[1] requires selective α- or γ-attack of the partner, which can be achieved by suitable choice of the substitutents R^2 on sulfur and the metal involved[2-5].

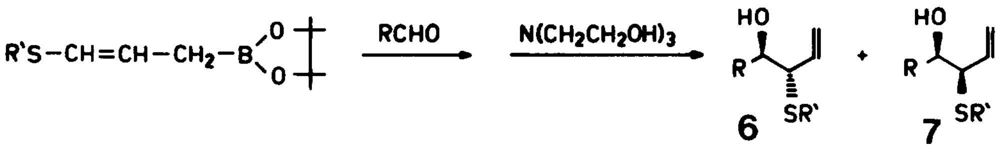


Even then, addition of the prochiral reagent 1 to a prochiral aldehyde or ketone leads to two diastereomeric adducts, be it of type 2, or type 3. When the diastereoselectivity has been determined, it has been reported to be only small[3,5,6]. We reasoned that the high diastereoselectivity observed on addition of crotylboronates to aldehydes[7] could also be extended to the reaction of heteroatom-substituted allylboronates, such as 1 (Met = $B(OR)_2$). We report here on the preparation of the γ-alkylthio-allylboronates 5 and 10 and their diastereoselective and regioselective addition to aldehydes.

In order to prepare the Z-isomer 5, allylmercaptan was metalated by n-butyllithium in THF/TMEDA2) and reacted with one equivalent of $ClB[N(CH_3)_2]_2$ 8). Subsequent addition of methyl iodide furnished 65% of 4, which was shown by ^{13}C-NMR to be >95% of Z-configuration. The diaminoborane 4 was converted in quantitative yield to the desired allylboronate 5a simply by addition of pinacol, cf.7).

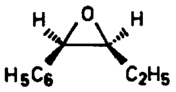


Reaction of 5 with aldehydes produced high yields of the adducts 7 with marked diastereoselectivity (cf. the table, entries 1-4). This contrasts to the diastereounselective addition of 1 (R^2, Met = Mg) to aldehydes3).



Entry	Allylboronate		Aldehyde	equiv.	Homoallylalcohols	
	R'	E : Z			% yield	6 : 7
1	CH_3	<5 : >95	C_6H_5CHO	1.0	95	2 : 98
2	CH_3	<5 : >95	$(CH_3)_2CHCHO$	1.0	90	5 : 95
3	CH_3	8 : 92	CH_3CHO	1.0	86	8 : 92
4	CH_3	8 : 92	CH_3CH_2CHO	1.0	91	9 : 91
5	CH_3CH_2	44 : 56	CH_3CH_2CHO	1.0	90	44 : 56
6	CH_3CH_2	73 : 27	CH_3CH_2CHO	1.0	94	77 : 23
7	CH_3CH_2	44 : 56	CH_3CH_2CHO	0.4	95	91 : 9
8	CH_3CH_2	44 : 56	$(CH_3)_2CHCHO$	0.4	95	95 : 5
9	CH_3CH_2	70 : 30	CH_3CHO	0.65	80	90 : 10
10	CH_3CH_2	70 : 30	C_6H_5CHO	0.65	95	95 : 5

The 3R*,4R*-structure of the benzaldehyde adduct 7 was proven by conversion to the epoxide 8 (i. reduction with diimide, ii. trimethyloxonium-tetrafluoroborate, iii. aqueous sodium hydroxide), which showed in its ^{1}H-NMR-spectrum a 4 Hz coupling constant of the two oxirane-protons, characteristic of cis-substituted epoxides[9]. It is assumed that the other adducts derived from 5 have the same stereostructure.



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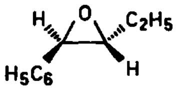

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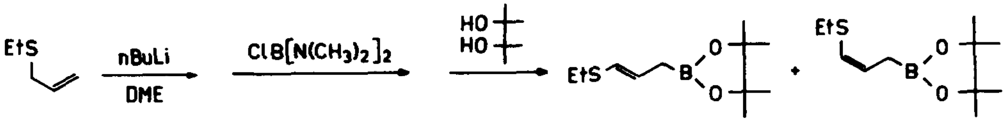
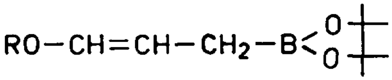
The reagent 10 with E-configuration of the double bond has so far not been obtained in pure form: metalation of allyl-ethyl-sulfide with n-butyllithium in dimethoxyethane followed by reaction with $ClB[N(CH_3)_2]_2$ gave 85% of a 70:30 mixture of E and Z products, which were quantitatively converted to the pinacol esters 10 and 5b.



Reaction of such E/Z-mixtures with one equivalent of propionaldehyde resulted in two diastereomeric adducts 6 and 7 (cf. entries 5,6 of the table). The diastereomer ratio corresponded closely to the E/Z-ratio of the reactands, demonstrating that not only 5, but also 10 added with high diastereoselectivity to aldehydes.

We noted a considerable difference in the reaction rates of 5 and 10. The higher reactivity of 10 could be used to obtain the adducts 6 in reasonable diastereomeric purity simply by adding slightly less aldehyde to the mixture of 5 and 10, than is required to react only 10; cf. entries 7-10 of the table. The structure of the benzaldehyde adduct 6 follows as 3S*,4R* from its conversion (vide supra) to 9 showing J = 2.1 Hz of the oxirane protons[9].

In summary we have been able to convert aldehydes in high yields and high diastereoselectivity to either of the adducts 6 or 7 by making use of the sulfur-substituted allylboronates 10 and 5. The corresponding oxygen-substituted allylboronates 11 are also of interest10). We have prepared the reagents 11 by similar routes. Their addition to aldehydes proceeded in high yield and diastereoselectivity, essentially as observed with 5 and 10. A detailed report of these studies will be published in the near future.



11

R	E : Z
CH_3	<5 : >95
CH_3	45 : 55
CH_3OCH_2	<5 : >95
$CH_3OC(CH_3)_2$	6 : 94

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