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ACYCLIC STEREOCONTROL IN THE ADDITION OF γ-ALKYLTHIO-ALLYLBORONATES TO ALDEHYDES[1]

REINHARD W. HOFFMANN and BRUNO KEMPER
Fachbereich Chemie der Philipps-Universität Marburg Hans-Meerwein-Strasse, D-3550 Marburg/L., Federal Republic of Germany

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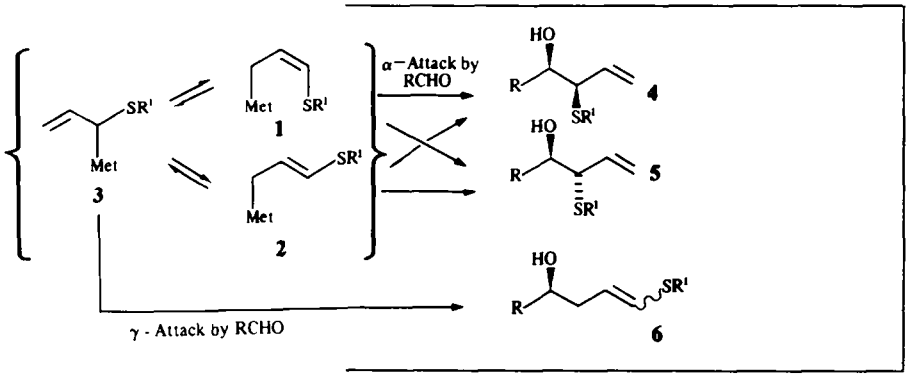
Abstract—*The* Z-isomer **10** of the γ-alkylthio-allylboronates adds to aldehydes giving the *syn*-diastereomer **4** of the product homoallyl-alcohol. The *E*-isomer **12** leads in turn to the *anti*-diastereomer **5** with a high degree of acyclic stereocontrol. Kinetic diastereoselection can be applied to obtain the *anti*-diastereomer **5** even when using *E*/*Z*-mixtures of the γ-alkylthio-allylboronates.

The complexity of the targets at which the synthetic efforts in organic chemistry are nowadays directed require that the C–C-bond forming reactions should not only create the proper functionality for further elaboration of the intermediates, but also directly the proper stereochemistry at all newly formed stereocenters. The sort of problem which has to be solved can nicely be illustrated with reference to the addition of S-substituted allyl metal derivatives **1–3** to aldehydes:



The organometallic species **1–3** may suffer either α-attack generating **4** and **5** or γ-attack generating **6**. It may be assumed that the isomer **3** leads predominantly to **6** and that the other isomers **1** or **2** produce the α-adducts **4**, **5**.

Hence, the selectivity of an equilibrating mixture of **1**⇌**2**⇌**3** may be difficult to control.[2] Not surprisingly the lithio-derivatives were reported to show little α, γ-selectivity.[3–7] Higher regioselectivity can be attained by shifting the equilibrium to either side: With metals that form more highly covalent bonds, e.g. Cd,[8] Cu,[9] $Ti(OR)_3$,[10,11] AlR_2,[7,12] BEt_3,[4] SnR_3,[7] the isomers **1**, **2** may be favoured in the equilibrium fostering the formation of the α-adducts **4** and **5**. In complement a suitable choice of the substituent R^1 on sulfur[11,13,14] allows the metal derivative **3** to be favoured leading eventually to the formation of the γ-adducts **6**.

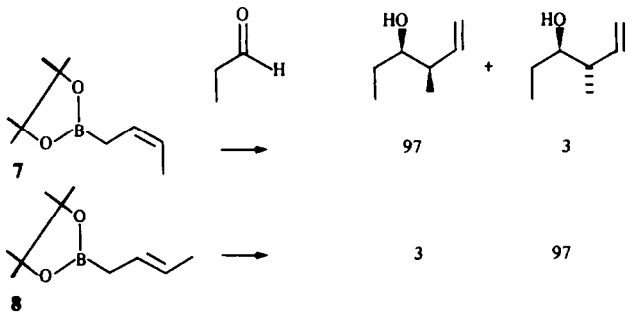
When the α-attack of an aldehyde on the metal derivatives **1**, **2** is considered, the problem of acyclic stereocontrol becomes apparent, since in this addition two prochiral C-residues are joined to form a pair of diastereomers **4** and **5**. Unfortunately low diastereoselectivity[5–7,15,16] was reported in such addition reactions.

Achieving stereocontrol implies not only to be able to obtain one of, e.g. two stereoisomers selectively, but to be able to obtain each stereoisomer in high yield uncontaminated by its diastereomer. A highly pleasing solution would be, to use two stable stereoisomeric reagents, each of which would lead to only one of the stereoisomeric products. Of course this approach does not avoid the problem of stereoselectivity, but rather shifts it to an earlier stage in the synthetic scheme. This is reasonable, if the reagents, e.g. **1** and **2** are a sort of stereoisomers, that can more readily be obtained selectively, viz *E*/*Z*-isomers, than the stereoisomers of the ultimate product, e.g. the diastereomers **4** and **5**.

The reagents of interest should fulfill the following requirements:[17] 1. The stereoisomeric reagents should not equilibrate under the reaction conditions required; 2. each of the stereoisomeric reagents should be conveniently available; 3. each of the reagents should add to aldehydes in a specific manner forming only one of the adducts **4** or **5**; 4. the addition of these reagents to aldehydes should be irreversible.

Actually only few allylmetal derivatives are known for which both geometric isomers *E* and *Z* are configurationally stable, such as the Sn, Si and some B derivatives.[18]

The crotylboronates **7** and **8** for instance were found to add the aldehydes with the desired high degree of acyclic stereocontrol.[17] In view of the manifold refunctionalisation schemes originating from



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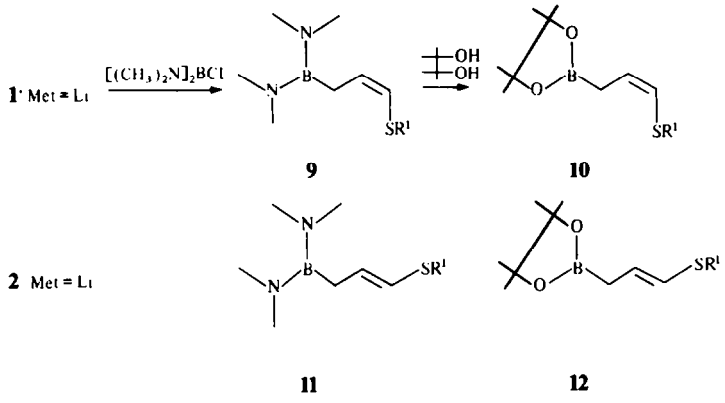
allylsulfur compounds the generation of **4** and **5** by reaction of the corresponding S-substituted allylboronates **10** and **12** appeared to be a highly worthwhile objective. Our results, previously communicated in short,[19] are reported here in full detail.

Syntheses of the γ-alkylthio-allylboronates

Borylation of the lithio-derivatives **1**, **2** could constitute a straightforward synthesis of **10** and **12**, provided the borylation proceeds with high γ-selectivity. Moreover, to arrive at either **9** or **11** requires stereohomogeneous allyl–lithium–derivatives **1** or **2**, which are known[20] to equilibrate.

Therefore one has to regard the factors (substituent R^1 and solvent) that favour either isomers **1** or **2** in such equilibria: In the case of the lithio-derivatives **1a**, **2a** the equilibrium lies on the side of **1a**.[3,22] Hence **1a** generated by metalation of allylmercaptan with two equivalents of n-BuLi in THF/TMEDA[3] was reacted to give **9a** which was converted by addition of methyl iodide into **9b** in 65% overall yield. The allylboronate **10b** was simply obtained by addition of pinacol in 96% yield. Both **9b** and **10b** were found to be stereohomogeneous to >90%, as judged from their ^{13}C-NMR spectra.

With a phenyl substituent on S the equilibrium



	R^1
a	Li
b	CH_3-
c	CH_3CH_2-
d	$(CH_3)_2CH$-
e	$(CH_3)_3C$-
f	C_6H_5-

Table 1. Reaction of the allylboronates **10** and **12** with stoichiometric amounts of aldehydes

Aldehyde R =	Allylboronate	Homoallyl alcohols % yield	4 : 5
CH_3-	10c : 12c = 92 : 8	86	92 : 8
CH_3-CH_2-	= 92 : 8	91	91 : 9
$(CH_3)_2CH$-	= >95 :<5	90	95 : 5
C_6H_5-	= >95 :<5	95	98 : 2
CH_3-CH_2-	10d : 12d = 56 : 44	90	56 : 44
CH_3-CH_2-	= 27 : 73	94	23 : 77

between the Li-compounds **1f**⇌**2f** does not markedly favour either side.[5,22,24] A slight preference for the *Z*-derivative is found for the lithio compounds **1b**, **2b** with a Me-substituent on S,[6] whereas the *E*-isomer is favoured in the case of **2d**[9] and **2e**[6] carrying more bulky substituents on S. It seems likely that stereohomogeneous **11d,e** and **12d,e** could be obtained from the latter. In order to avoid usage of the more expensive t-BuLi, we studied the metalation of ethyl allyl sulfide: n-BuLi in THF was found to give 57% of a 44:56 mixture of **11c** and **9c** after quenching with chlorobisdimethylamino-borane. Changing to a more polar solvent was expected to favour the formation of the *E*-isomer **2**;[22] metalation of ethyl allyl sufide in dimethoxyethane by n-BuLi resulted in a 70:30 ratio of **11c** and **9c** in 85% yield. Conversion of the aminoborane derivatives to the mixture of the allylboronates **12c** and **10c** proceeded in quantitative yield.

Addition to aldehydes

The allylboronate **10b** added to aldehydes much more slowly than the crotylboronates **7**.[17] Nevertheless one day at room temperature or several hours refluxing in petroleum ether sufficed to give a quantitative conversion of the allylboronate **10b** to the borates **13**. Their subsequent cleavage provided the homoallyl alcohols **4b** in high yield and >90% diastereomeric purity, *cf* Table 1.

A similar reaction of an *Z*/*E*-mixture of **10c/12c** provided mixtures of the homoallyl alcohols **4c** and **5c** in high yield. The ratio of the homoallyl alcohols formed corresponded closely to the ratio of the starting materials **10c/12c**, *cf* Table 1. These results demonstrate that each of the stereoisomeric boronates **10** or **12** led selectively to only one of the diastereomeric products **4** or **5**. It is this stereoselectivity that is sought for achieving acyclic stereocontrol, but that unfortunately can not generally be taken for granted.[25,26]

A general application of these results in stereoselective syntheses appears to be hampered as long as the *E*-isomer **12** is not also available as a stereohomogeneous material (*vide supra*). There is, however, the alternative option of using *kinetic diastereoselection*. This is based on the fact that **10c** and **12c** react at different rates with an aldehyde and that the faster reacting one will react preferentially with a deficiency of an aldehyde. The extent of diastereomeric enrichment in the products depends on both the ratio of reaction rates for **10** vs **12** and the deficiency of the aldehyde applied.[27] We found that the *E*-isomer **12** added considerably faster to aldehydes than its *Z*-counterpart **10**.[28] Hence reaction of a 44:56 mixture of **12c/10c** with 0.4 equivs of aldehydes resulted in the homoallyl alcohols **5c** and **4c** in a >90:<10 ratio. The remaining allylboronate could be recovered by chromatography and was shown to be enriched in the *Z*-isomer **10c**. Further examples of this kinetic diastereoselection are shown in Table 2. Of course, even higher diastereomeric purities could be achieved by using a smaller relative amount of an aldehyde.

The stereochemistry of the addition

The addition of allylboronates to aldehydes is assumed in analogy to the reaction of the corresponding crotylboronates,[17] to proceed via a cyclic 6-membered transition state,[18,29] such that the *E*-isomer **12** leads to the *anti*-diastereomer[30] **5** and the

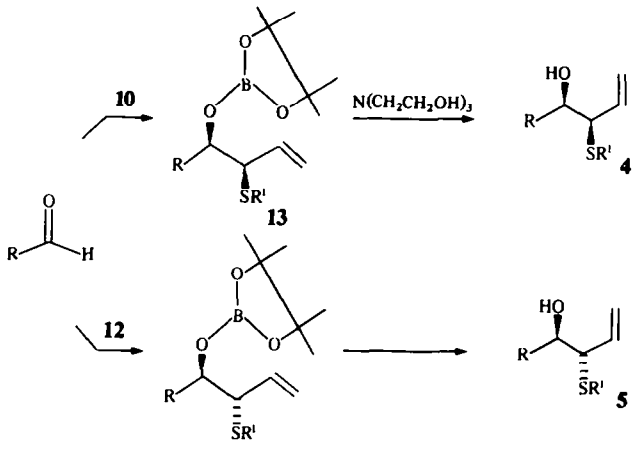
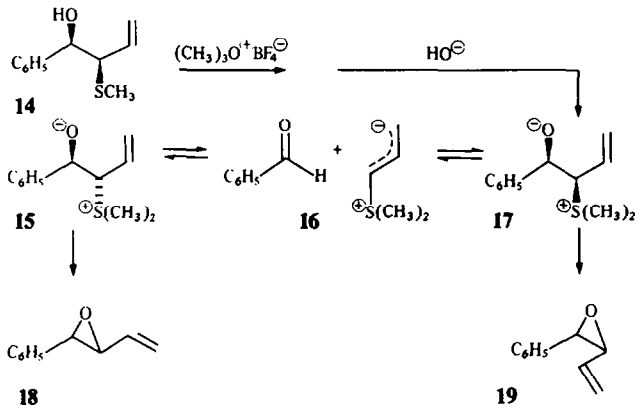


Table 2. Reaction of the allylboronates **10** and **12** with a deficiency of aldehydes resulting in kinetic diastereoselection

Aldehyde R=	equiv.	Allylboronate	Homoallyl alcohols % yield	4 : 5
CH_3-	0.65	10d : 12d = 30 : 70	80 %	10 : 90
CH_3-CH_2-	0.40	= 56 : 44	95 %	9 : 91
$(CH_3)_2CH$-	0.40	= 56 : 44	95 %	5 : 95
C_6H_5-	0.65	= 30 : 70	95 %	5 : 95



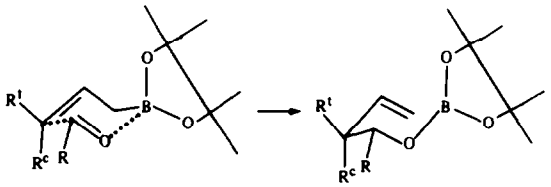
Z-isomer **10** to the *syn*-diastereomer **4**. In order to verify this hypothesis the relative configuration of the new chiral centers in the benzaldehyde adducts **14** and **21** was established by conversion to the epoxides **20** and **22**.

After alkylating the stereohomogeneous adduct **14** with trimethyloxonium tetrafluoroborate and subsequent treatment with aqueous sodium hydroxide[31] we obtained unexpectedly a mixture of epimeric vinyl oxiranes **18** and **19**.

We suspected that the zwitterion **17** dissociated reversibily into the sulfur ylide **16**[15,32] under the conditions applied allowing equilibration between the zwitterions **15** and **17**. It can be expected on steric grounds that the cyclisation **15**→**18** occurs more readily than the process **17**→**19**. Hence, the *syn*-isomer **17** should suffer extensive equilibration with **15** leading to both oxiranes **18** and **19**. In contrast little leakage, if at all,[32] should affect the transformation of the *anti*-isomer **21** via **15** to **18**. While this would explain the absence of isomerisation in related reactions involving the conversions of **5** to *E*-vinylepoxides,[10] it may be fortuitous that this held for more highly substituted cases as well.[10]

Probably the tendendy of **17** to dissociate is enhanced by the delocalization of charge in the ylide **16**. We therefore expected that these problems should be overcome by saturation of the double bond in **14** and **21** respectively. This was accomplished by reduction with diimide. The subsequent reaction with trimethyloxonium tetrafluoroborate followed by base treatment cleanly furnished the stereohomogeneous epoxides **20** and **22**, identified with reference to their characteristic ^{1}H-NMR-spectra.[33]

Since we have thus firmly established the structures of adducts **14** and **21**, we have no doubt that the structures of the other adducts **4** and **5** are correctly assigned in analogy. These results thus enlarge the body of evidence,[18] the allylboronates tend to react with aldehydes via cyclic 6-membered transition states,[29] in which the residue R of the aldehyde prefers an equatorial disposition, *cf* **23**.

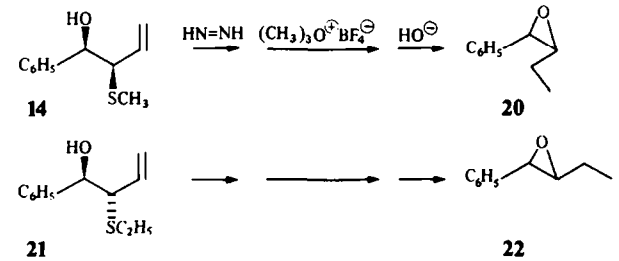


23

DISCUSSION

There are at least two principal approaches to achieve acyclic stereocontrol: The one is to use two stereoisomeric educts reacting via the same type of transition state, e.g. **23** leading individually to either of the stereoisomeric products. Our conversion of either **10b** into **4** or **12c** into **5** provides examples of this approach.

An alternative approach to acyclic stereocontrol uses only one stereoisomer of the educt. In this case two reaction modes must be available which lead via different types of transition states to each of the stereoisomeric products.[34] The viability of this approach has most recently been demonstrated by the groups of Y. and of H. Yamamoto,[7,10] with the same system of S-substituted allyl-metal compounds **2**, that form the subject of this paper. The realization of the latter concept depended on the proper choice of the key metal, so that addition of the allylmetal compound **2** to an aldehyde proceeded by either a cyclic or an open transition state. It is known[35] that both the *E*- and *Z*-isomer of crotyl–tin-compounds react with aldehydes under BF_3-catalysis to give in a stereo-



convergent fashion predominantly the *syn*-adducts. This seems to be characteristic for reactions via open transition states.[18,35]. In line with these experiments, treatmment of the *E*-allyllithium derivative **2d** with tributyltin chloride, followed by addition to benzaldehyde in the presence of BF_3 led to **4d** and **5d** in a 9:1 ratio, the *syn*-isomer predominating.[7]

In complement, it is known that *E*-crotyl-titanium-alkoxides add to aldehydes forming the *anti*-adducts selectively,[11,36] probably via cyclic transition states similar to **23**. Hence, reaction of the *E*-allyllithium derivative **2e**, with $Ti(OiPr)_4$ followed by addition to benzaldehyde gave a 9:1 ratio of the adducts **5e** and **4e**, the *anti*-isomer predominating.[10,37] With other aldehydes even higher selectivities were recorded.[10] A similar result is obtained by converting **2d** to the Cp_2ZrCl-derivative, which reacted with benzaldehyde probably also via a cyclic transition state[26] to give the *anti*-product **5d** with a 9:1 selectivity.[7]

Hence, both approaches to achieve acyclic stereocontrol have been demonstrated to be successful in the addition of S-substituted allylmetal derivatives **1**, **2** to aldehydes forming the homoallyl alcohols **4** and **5**.

EXPERIMENTAL

^{1}H-NMR spectra were recorded with Varian T-60 and HA-100 spectrometers. ^{13}C-NMR spectra were recorded with Varian CFT-20 and XL-100 spectrometers. Diastereomer ratios were determined by analytical gaschromatography using a Perkin–Elmer gaschromatograph F-900 with a 10 ft × 1/8 in. column with 3% OV 225 on Gas-Chrom Q, (100–120 mesh). Preparative purifications were achieved with a Wilkens Aerograph A-90 P-3 gaschromatograph with a 5 ft × 1/4 in. column with 5% SE-30 on Chromosorb G, AW-DMCS (60–80 mesh) 120 ml He/min. Elemental analyses were performed by the department. All temps quoted are non corrected.

1. 2-(3-*Methylthio*-*Z*-2-*propenyl*-1)-4,4,5,5-*tetramethyl*-1,3,2-*dioxaborolane* (**10b**)

Allylmercaptan, FLUKA (6.4 ml, 80 mmol) and tetramethylethylenediamine (18.56 g, 160 mmol) were dissolved in dry THF (100 ml). To this soln was added dropwise at 0° n-BuLi (100.8 ml of a 1.6 n soln in n-hexane). The orange coloured soln was stirred 4 hr at 0° and cooled to −78°. Chloro-bis(dimethylamino)-borane (10.80 g, 80 mmol) in 10 ml THF was added at once resulting in a exothermic decolourisation of the soln. The temp was allowed to attain 0° during 2 hr. After stirring for 1 hr MeI (5.6 ml, 90 mmol) was added. After refluxing for 2 hr the solvents were distilled off and the residue was bulb to bulb distilled at 10^{-2} torr to give 9.6 g (65%) **9b** b.p. 64°/0.1 torr. ^{1}H-NMR (δ, $CDCl_3$) 1.75 (d, 2H), 2.2 (s, 3H), 2.65 (s, 12H), 5.2–5.9 (m, 2H). ^{13}C-NMR (δ, $CDCl_3$): 16.8, 40.2, 123.5, 127.9, displaying an *E*/*Z*-ratio of < 10 : > 90.

To the soln of **9b** (8.0 g, 43 mmol) in 40 ml ether were added 2,3-dimethylbutanediol-2,3 (5.1 g, 43 mmol). After stirring for 3 hr the solvents were removed i.vac. and the residue was filtered with CH_2Cl_2 over silica gel (30 g). Elution with CH_2Cl_2 (750 ml) yielded **10b** (8.8 g, 96%) as colourless liquid. A small sample was purified by preparative VPC. at 120°. ^{1}H-NMR (δ, $CDCl_3$): 1.15 (s, 12H), 1.55 (broad d, 2H), 2.1 (s, 3H), 5.18–5.8 (m, 2H). ^{13}C-NMR (δ, $CDCl_3$): 16.7, 24.5, 83.1, 124.2, 126.2, displaying an *E*/*Z*-ratio of < 10 : > 90. (Found: C, 55.78; H, 9.24. Calc for $C_{10}H_{19}BO_2S$: C, 56.09; H, 8.94%.)

2. 2-(3-*Ethylthio*-E/Z-2-*propenyl*-1)-4,4,5,5,-*tetramethyl*-1,3,2-*dioxaborolane* (**12c/10c**)

To 3-ethylthiopropene (3.06 g, 30 mmol) in THF (20 ml) were added dropwise at −40° n-BuLi (18.6 ml of a 1.6 n soln in n-hexane). After stirring for 1 hr at −40° the soln was cooled to −78°. Chloro-bis(dimethylamino)-borane (4.2 g, 30 mmol) in THF (5 ml) were added at once. The soln was allowed to attain room temp during 2 hr. The solvents were removed at 20 torr and the residue was bulb to bulb distilled at 10^{-2} torr. The condensate was fractionated to give **11c/9c** (3.4 g, 57%) as colourless liquid; b.p. 61°/10^{-2} torr. ^{1}H-NMR (δ, $CDCl_3$): 1.3 (t, 3H), 1.75 (d, 2H), 2.65 (q and s, 14H), 5.3–5.9 (m, 2H). ^{13}C-NMR (δ, $CDCl_3$): E: 14.5, 27.2, 40.0, 119.6, 132.4; Z: 15.3, 27.6, 40.0, 121.5, 128.7, displaying an *E*/*Z*-ratio of 44:56.

To a soln of 1.0 g (5.0 mmol) of the above mixture in ether (5 ml) was added 2,3-dimethylbutanediol-2,3 (0.59 g, 5 mmol). After stirring for 3 hr the solvents were removed i.vac. leaving **12c/10c** as a colourless liquid (1.14 g, 100%). A small sample was purified by VPC at 150°. ^{1}H-NMR (δ, $CDCl_3$): 1.25 (s, 12H and t, 3H), 1.75 (d, 2H), 2.6 (q, 2H), 5.3–6.1 (m, 2H). ^{13}C-NMR (δ, $CDCl_3$): *E*: 14.3, 24.5, 26.6, 82.9, 121.9, 126.7; *Z*: 15.2, 24.5, 27.6, 82.9, 124.0, 125.0, displaying an *E*/*Z*-ratio of 44:56. (Found: C, 58.31; H, 9.60. Calc for $C_{11}H_{21}BO_2S$: C, 57.91; H, 9.28%.) When the metalation of 3-ethylthiopropene was run similarly in 1,2-dimethoxyethane **11c/9c** and **12c/10c** were obtained in a 70:30 ratio.

3. *Preparation of the homoallyl alcohols* **4**, **5**,

General procedure. The allylboronate (**10**, **12**) and the aldehyde were reacted either neat or in petroleumether for the time given. The solvents were removed i.vac. and the crude product was taken up in CH_2Cl_2. After adding one equiv of triethanolamine the mixture was stirred for 3 hr at room temp. The crude product was filtered with CH_2Cl_2 over silica gel (20 g) yielding pure samples.

R*,R*-3-*Methylthio*-1-*pentenol*-4: **10b** (10.0 mmol), acetaldehyde (10.0 mmol), in petroleumether (5 ml), 24 h, 20°. ^{1}H-NMR (δ, $CDCl_3$): 1.25 (d, 3H), 2.05 (s, 3H), 2.6 (broad s, 1H), 3.05 (t, J = 8.0 Hz, 1H), 3.5–4.1 (m, 1H), 5.0–6.1 (m, 3H). (Found: C, 54.41; H, 9.04. Calc for $C_6H_{12}OS$: C, 54.50; H, 9.15%.)

R*,R*-3-*Methylthio*-1-*hexenol*-4: As above using propanal: ^{1}H-NMR (δ, $CDCl_3$): 0.9 (t, 3H), 1.2–1.7 (m, 2H), 2.0 (s, 3H), 2.3 (broad s, 1H), 3.0 (t, J = 8.0 Hz, 1H), 3.45 (m, 1H), 4.8–5.8 (m, 3H), *cf* lit[15]. (Found: C, 57.94; H, 9.74. Calc for $C_7H_{14}OS$: C 57.49; H, 9.65%.)

R*,R*-3-Methylthio-5-methyl-1-hexenol-4: As above using 2-methylpropanal and refluxing for 8 h. ^{1}H-NMR (δ, $CDCl_3$): 0.8 (d, 3H), 0.95 (d, 3H), 1.5–1.9 (m, 1H), 1.9 (s, 3H), 2.25 (broad s, 1H), 3.05 (t, J = 9.0 Hz, 1H), 3.3 (m, 1H), 4.8–5.8 (m, 3H), *cf* lit[15]. (Found: C, 59.58; H, 10.10. Calc for $C_8H_{16}OS$: C, 59.95; H, 10.065%.)

R*,R*-3-*Methylthio*-4-*phenyl*-1-*butenol*-4 (**14**): As above using benzaldehyde and refluxing for 4 hr. ^{1}H-NMR (δ, $CDCl_3$): 2.0 (s, 3H), 3.1 (broad s, 1H), 3.3 (t, J = 8.0 Hz, 1H), 4.6 (d, J = 8.0 Hz, 1H), 4.8–5.8 (m, 3H), 7.3 (s, 5H). (Found: C, 68.20; H, 7.27. Calc for $C_{11}H_{14}OS$: C, 68.00; H, 7.26%.)

R*,S*-3-Ethylthio-1-pentenol-4: Using **12c/10c** and a deficiency of acetaldehyde, *cf* Table 2, reacting 2 weeks at −30°. ^{1}H-NMR (δ, $CDCl_3$): 1.3 (t, 3H), 1.3 (d, 3H), 2.2 (d, 1H), 2.55 (q, 2H), 3.25 (dd, 1H), 3.9 (m, 1H), 4.9–6.1 (m, 3H). (Found: C, 57.73; H, 9.88; S, 21.83. Calc for $C_7H_{14}OS$: C, 57.49; H, 9.65; S, 21.92%.)

R*,S*-3-*Ethylthio*-1-*hexenol*-4: As above using a deficiency of propanal, *cf* Table 2. ^{1}H-NMR (δ, $CDCl_3$): 0.8–1.7 (m, 5H), 1.2 (t, 3H), 2.1 (broad s, 1H), 2.45 (q, 2H), 3.3 (dd, 1H), 3.5 (m, 1H), 4.8–6.0 (m, 3H). (Found: C, 60.19; H, 10.38; S, 19.97. Calc for $C_8H_{16}OS$: C, 59.95; H, 10.06; S, 20.00%.)

R*,S*-3-*Ethylthio*-5-*methyl*-1-*hexenol*-4: As above using a deficiency of 2-methylpropanal, *cf* Table 2. ^{1}H-NMR (δ, $CDCl_3$): 0.9 (d, 3H), 1.05 (d, 3H), 1.3 (t, 3H), 1.8 (m, 1H), 2.2 (broad s, 1H), 2.6 (q, 2H), 3.4 (m, 2H), 5.0–6.1 (m, 3H). (Found: C, 61.85; H, 10.52; S, 18.04. Calc for $C_9H_{18}OS$: C, 62.02; H, 10.41; S, 18.39%.)

R*,S*-3-*Ethylthio*-4-*phenyl*-1-*butenol*-4 (**21**): As above using a deficiency of benzaldehyde, *cf* Table 2. ^{1}H-NMR (δ, $CDCl_3$): 1.3 (t, 3H), 2.45 (q, 2H), 2.6 (broad s, 1H), 3.55 (dd, 1H), 4.6–6.2 (m, 4H), 7.2 (s, 5H). (Found: C, 68.86; H, 7.93; S, 15.26. Calc for $C_{12}H_{16}OS$: C, 69.19; H, 7.74; S, 15.39%.)

4. 2-*Ethenyl*-3-*phenyl*-*oxirane* (**18, 19**)

To a soln of **14** (0.97 g, 5.0 mmol) in 10 ml CH_2Cl_2 was added trimethyloxonium tetrafluoroborate (0.89 g, 6.0 mmol). After stirring for 1 hr at room temp, 2n NaOH (10 ml) was added. The mixture was stirred overnight, the organic phase was separated and washed twice with water (10 ml each) and twice with sat NaCl aq (10 ml each). The combined aqueous extracts were extracted twice with CH_2Cl_2 (20 ml). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue (0.44 g, 60%) was shown by its ^{1}H-NMR spectrum to be a 44:56 mixture of **18** and **19**.

5. cis-2-*Ethyl*-3-*phenyl*-*oxirane* (**20**)

To a stirred soln of **14** (1.5 g, 7.5 mmol) and potassium azodicarboxylate (4.0 g, 20 mmol) in dry MeOH (10 ml) was added dropwise during 30 min AcOH (2.4 g, 40 mmol). After stirring for 2 hr the mixture was neutralized with sat $NaHCO_3$ aq and extracted four times with petroleum ether (30 ml each). The combined extracts were dried (Na_2SO_4) and concentrated giving R*,R*-2-methylthio-1-phenyl-butanol-1 (1.2 g, 85%). 0.78 g (3.8 mmol) of the above product were converted into **20** (0.35 g, 62%) by the procedure given under 4. The product was identified by comparison of its ^{1}H-NMR spectrum with the data reported.[33]

6. trans-2-*Ethyl*-3-*phenyl*-*oxirane* (**22**)

The conversion of **21** was carried out as above giving 96% *R**,*S**-2-ethylthio-1-phenyl-butanol-1 and subsequently 75% **22** identified by comparison of its ^{1}H-NMR spectrum with the data published.[33]

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