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REVERSIBLE ALLYLIC CONDENSATION OF METALLOALLYLS OF HETEROCYCLES: COUNTERION EFFECT.

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Summary: Metalloallyls of benzothiazole, benzoxazole and pyrimidine 2 condense with aldehydes to furnish α-regioisomers 3 and 4 or γ-regioisomer 5 depending upon the experimental conditions and the nature of the metal of 2. The allylic condensation of 2 with aldehydes appears to proceed with satisfactory to high syn diastereoselectivity as for the α-regioisomers; γ-regioisomers are of exclusive trans configuration.

In recent years much attention has been paid to the allylation of aldehydes, since the resulting allylic alcohol units constitute a characteristic structural feature of numerous macrolide and polyether antibiotics[1] and may be readily transformed into aldols,[2] homologated to δ-lactones[3] and epoxidised.[4] A number of various allylmetal reagents, such as allyllithium, allylborane, allylboronate, allyltitanium, allylaluminum, allylstannane, allylsilane are currently used to this end.[1,5] The control of α versus γ substitution as well of the stereochemistry in the C-C bond forming reaction of such allylmetals depends upon many factors among which the metal, the charge delocalisation, steric effects, solvation, the type of electrophile.[6] The control of all these parameters in order to perform the condensation in a regioselective and stereoselective fashion is highly desirable from both practical and theoretical viewpoints.

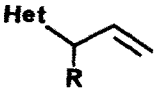
Allylmetals stabilized by heterocyclic moiety have not been studied much, particularly with reference to the regio- and stereo-chemistry of the condensation reaction with carbonyls, although the heteroatoms in the heterocyclic residue are expected to influence the regio- and the stereo-chemistry by electronic effects and coordinative assistance.

In a preliminary communication[7] we have reported that allyllithiums of benzothiazole, benzoxazole and pyrimidine condense with aldehydes in a regio- and diastereoselective manner depending upon the experimental conditions.

We have now investigated such an allylic condensation in more detail with particular reference to the counterion effect.

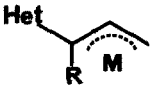
Allyllithiums 2a-c, readily accessible through lithiation of the related allyl derivatives 1a-c, add to a number of aldehydes to afford quite high yields of the homoallylic alcohols 3 and 4 when the reaction is carried out at -78°C and quenched with sat. aqueous NH_4Cl soon after mixing the reactants. The condensation proceeds with complete α-regioselectivity and

satisfactory to high syn-diastereoselectivity. Homoallylic alcohols 3 and 4 could be easily isolated and characterised by IR and ^{1}H-NMR spectroscopy. The syn and anti diastereoisomers were assigned the configuration on the basis of the coupling constants between Ha and Hb protons. Syn diastereoisomers show normally smaller coupling constants.

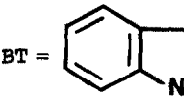


1a: Het = BT; R = H
1b: Het = BO; R = H
1c: Het = PR; R = H
1d: Het = BO; R = Me

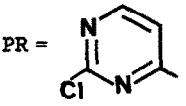
1e: Het = BT
1f: Het = PR

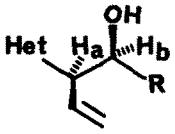


2a: Het = BT; M = Li; R = H
2b: Het = BO; M = Li; R = H
2c: Het = PR; M = Li; R = H
2d: Het = PR; M = MgBr; R = H
2e: Het = PR; M = $SiMe_3$; R = H
2f: Het = PR; M = BEt_3Li; R = H
2g: Het = PR; M = ZnBr; R = H
2h: Het = PR; M = $Sn(Et)_3$; R = H
2i: Het = PR; M = Cu; R = H
2l: Het = BT; M = MgBr; R = H
2m: Het = BT; M = $SiMe_3$; R = H
2n: Het = BT; M = BEt_3Li; R = H
2o: Het = BT; M = ZnBr; R = H
2r: Het = BT; M = Cu; R = H
2s: Het = BO; M = Li; R = Me

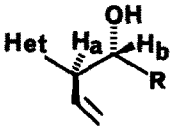


BO = " ; X = O



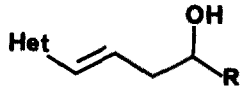


3a: Het = BT; R = Ph
3b: Het = BO; R = Ph
3c: Het = PR; R = Ph
3d: Het = BT; R = 2,6-$Cl_2C_6H_3$
3e: Het = BO; R = "
3f: Het = PR; R = 4-ClC_6H_4
3g: Het = BT; R = Me
3h: Het = PR; R = $PhCH_2$
3i: Het = BT; R = 4-ClC_6H_4
3l: Het = PR; R = CH_3

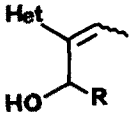


4a: Het = BT; R = Ph
4b: Het = BO; R = Ph
4c: Het = PR; R = Ph
4d: Het = BT; R =2,6-$Cl_2C_6H_3$
4e: Het = BO; R = "
4f: Het = PR; R = 4-ClC_6H_4

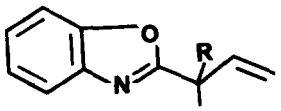
4h: Het = PR; R = $PhCH_2$
4i: Het = BT; R = 4-Cl-C_6H_4
4l: Het = PR; R = CH_3



5a: Het = BT; R = Ph
5b: Het = BO; R = Ph
5c: Het = PR; R = Ph
5d: Het = BT; R = 2,6-$Cl_2C_6H_3$
5e: Het = BO; R = "
5f: Het = BT; R = 4-Cl-C_6H_4



6a: Het = BT; R = Me



7a: R = CH_3
7b: R = CH_2Ph
7c: R = $CH_2CH=CH_2$

In contrast, γ-regioisomers 5 were exclusively obtained upon addition of aromatic aldehydes to 2a-c at -78°C followed by quenching with NH_4Cl after 2-3 h at RT. ^{1}H-NMR data show compounds 5 possess a trans geometry, as indicated by the high coupling constants between the vinylic hydrogens of 5[8] and as found for γ-regioisomers obtained in the alkylation of other stabilised allylmetals.[9,10] Under the same experimental conditions, no γ-regioisomer could be obtained upon treatment of 2a, 2c and 2d with aliphatic aldehydes. Indeed, the reaction of 2a with CH_3CHO at -78°C followed by addition of NH_4Cl after 3 h at RT gave a mixture of the allylic alcohol 6a and the allylbenzothiazole 1a, partly isomerised to the vinylbenzothiazole 1e. Similarly, the reaction of 2c with $PhCH_2CHO$ led to the homoallylic alcohols 3h and 4h mixed with 1f, on quenching the reaction mixture soon after mixing the reactants, while quenching after 2 h at RT gave the vinyl pyrimidine 1f and the reaction of 2d with CH_3CHO led to the α-regioisomers 3l and 4l, whatever the experimental conditions.

We could then conclude that the condensation of allyllithiums 2a-c with aldehydes, except with the aliphatic ones, for which only α-regioisomers could be obtained, may be kept under control in order to get either α-regioisomers 3 and 4 or γ-regioisomers 5, just choosing the appropriate experimental conditions.

It is worth noting that the allylic condensation of 2 turns out to be markedly sensitive to the solvent effect: indeed, 2a does not react with PhCHO when carried out in ether at least under the conditions where it does in THF. The weaker base character of ether with respect to THF must be taken into consideration.

In order to evaluate the counterion effect on both the regiochemistry and the stereochemistry of the allylic condensation of 2, we prepared a number of allylmetals of benzothiazole and pyrimidine and reacted them with aldehydes under the experimental conditions described for allyllithiums 2a-c. Allylmetals 2d-r, prepared through metal exchange of allyllithiums 2a and 2c with $MgBr_2$, $ZnBr_2$, Me_3SiCl, BEt_3, CuI, $Sn(Et)_3Br$, were used in situ without isolation. The important data are summarized in the Table.

As can be seen, whatever the experimental conditions, allylmagnesium 2d reacted with benzaldehyde to give exclusively the α regioisomers 3c and 4c. Similarly, allylsilane 2e treated with benzaldehyde and 4-chlorobenzaldehyde produced the α-regioisomers 3c/4c and 3f/4f respectively in a rather pronounced syn-diastereoselectivity. Moreover, allylzincbromide 2o and allylborate 2f reacted with PhCHO giving the α-regioisomers 3a/4a and 3c/4c respectively upon quenching the reaction mixture with NH_4Cl at -78°C after 10 min, while quenching after 3 h at RT led to the γ-regioisomers 5a and 5c exclusively. On the other hand, allylzinc 2g, allyltin 2h and allylcopper 2i gave rise to 5c either on quenching at -78°C or at RT. Comparable results were obtained with the allylmetals of benzothiazole 2l-r.

A way to explain the results above must start considering that allyl-

TABLE - Reactions of allylmetals 2 with aldehydes.

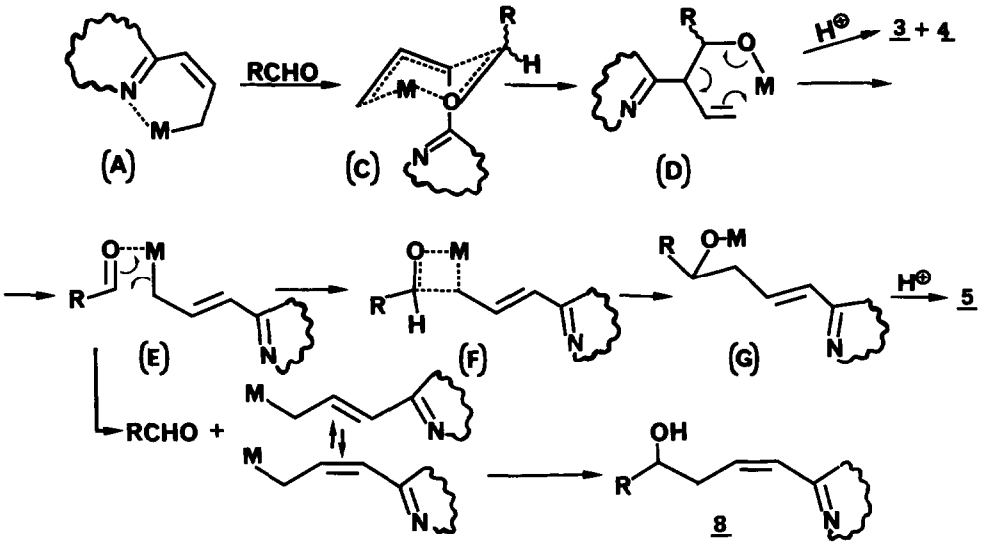
allyl-metal	R-CHO	Reaction products (%)[d,f]				Global yield (%)[e]
2a	Ph-[a]	3a (67)	4a (33)			>95
2a	Ph-[b]			5a (100)		100
2b	Ph-[a]	3b (30)	4b (55)	5b (15)		66
2b	Ph-[b]			5b (>95)		56
2c	Ph-[a]	3c (63)	4c (37)			>84
2c	Ph-[b]			5c (100)		>74
2a	$2,6\text{-Cl}_2C_6H_3$-[a]	3d (89)	4d (11)			90
2a	$2,6\text{-Cl}_2C_6H_3$-[b]			5d (>95)		>95
2b	$2,6\text{-Cl}_2C_6H_3$-[a]	3e (71)	4e (16)	5e (13)		62
2b	$2,6\text{-Cl}_2C_6H_3$-[b]			5e (100)		>95
2c	$PhCH_2$-[a,b]	3h (70)	4h (30)			70
2a	CH_3-[a]	3g (100)				>95
2a	CH_3-[b]	6a (100)				56
2d	Ph-[a,b]	3c (47)	4c (53)			40
2d	CH_3-[a,b]	3l (69)	4l (31)			>95
2l	Ph-[a,b]	3a (58)	4a (42)			48
2g	Ph-[a,b]			5c (100)		28
2o	Ph-[a]	3a (82)	4a (18)			70
2o	Ph-[b]			5a (100)		33
2e	Ph-[a,b]	3c (>95)	4c (<5)			86
2m	Ph-[a,b]	3a (40)	4a (60)			52
2e	4-ClC_6H_4-[a,b]	3f (85)	4f (15)			60
2f	Ph-[a]	3c (44)	4c (56)			57
2f	Ph-[b]			5c (100)		63
2n	Ph-[b]			5a (100)		54
2i	Ph-[a,b]			5c (100)		43
2r	Ph-[a,b]			2a (100)		20
2h	Ph-[a,b,c]			5c (100)		45

a) Reaction carried out at -78°C and quenched with sat aqueous NH_4Cl a few minutes after mixing the reactants. b) Reaction carried out at -78°C and quenched with NH_4Cl after 3 h at RT. c) Reaction carried out in hexane. d) Products ratio has been determined on isolated diastereoisomers or by ^{1}H-NMR or by HPLC. e) Yields based on either isolated products or on HPLC and ^{1}H-NMR analysis. f) Compounds 3a, 4a, 3c, 4c, 3d, 4d, 3e, 4e, 3g, 5a, 5c, 5d, 5e, and 6a were described in the Ref. 7.

metals likely exist as an equilibrium of the two forms (A) and (B), the former being the more predominant.

(A) (B)

We suggest that the intramolecularly chelated form A adds to the aldehyde with allylic rearrangment likely through the cyclic six-membered transition state (C) affording the α-regioisomeric alkoxide (D), that then reverses with time into the allylmetal-aldehyde complex (E), which then collapses, possibly via a four-membered transition state (F) to form the thermodinamically more stable γ-regioisomeric alkoxide (G). Our suggestion that the intramolecularly chelated form (A) acts as the reactive species to produce through allylic rearrangement the α-regioisomers is also supported by the fact that alkylation of allyllitium 2s with methyl iodide, benzyl chloride and allyl bromide has been found to give exclusively and irreversibly the α-cross-coupled products 7a, 7b and 7c respectively notwithstanding the substitution at the α position of 2s. This result appears somewhat contrasting with the rather common view that alkylation of stabilized allyl metals leads to a mixture of α- and γ-regioisomers, at least with alkylating agents other than methyl iodide.[11]

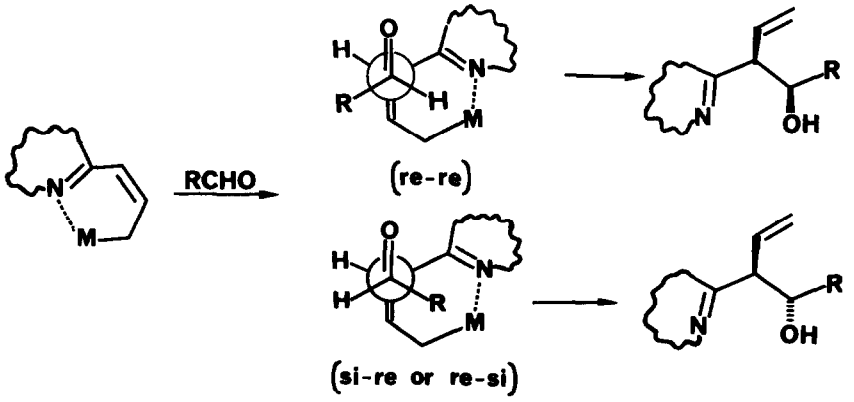


The fact that γ-regioisomers 5 have the trans geometry seems to exclude the complete dissociation of complex (E) into the aldehyde and the trans γ-allylmetal since the latter before recombination with the aldehyde might isomerize to the cis γ-allylmetal that is expected to generate the cis γ-regioisomeric homoallylic alcohol 8.

It is worth noting that allyllithiums 2a-c add reversibly to aldehydes contrary to what is reported for other allylorganolithiums.[9]

The result that aliphatic aldehydes lead only to α-regioisomers upon treatment with 2a, 2c or 2d is not unprecedented.[5] In the reaction of 2a with CH_3CHO a fast irreversible isomerisation of the homoallylic alcohols 3g to the allylic isomer 6a might be responsible for not observing the retro-aldol type reaction that would lead then to the γ-regioisomers. Moreover, removal by enolisation of $PhCH_2CHO$ derived from the retro-aldol reaction of 3h may explain the recovery of the vinylbenzothiazole 1e and vinylpyrimidine 1f observed in the reaction of 2a and 2d with CH_3CHO and originated by isomerisation of the allyllithiums 2a and 2d in the reaction medium.

The observed syn stereoselection might be explained by considering the transition state energy. In the reaction between the allylmetals 2 with an aldehyde, the syn transition state arising from the re/re face matching is favored over the anti transition state (si/re or re/si face matching) which experiences a larger steric compression.



The observed syn stereoselection is in agreement with the general observations that the diastereoselectivity of unsymmetrical allylic organometallic re-

agents is dictated by the allylic geometry so that Z-allylmetals lead to syn products, while E-allylmetals lead to anti adducts.

The α regioselective allylic condensation of allylmagnesium (2d and 2l) and allylsilanes (2e and 2m) and the γ regioselectivity occurring with allylzinc (2g), allyltins (2h and 2p) and allylcoppers (2i and 2r) as well as the α or the γ regioselection taking place with allyllithiums 2a-c, allyllithiumborate 2f and the allylzinc 2o might be accounted for by considering that allylic organometallics may add to carbonyls reversibly. The aldol-type condensation of 2 will proceed with α or γ regioselectivity depending upon the rate of the retro-aldol type reaction (D)→(E): the lower the (D)→(E) reaction rate the higher the α regioselectivity. The rate of the (D)→(E) reaction should be determined by the balance of factors such as the metal-oxygen bond polarity of (D), the solvent coordinating ability, the Lewis acid character of metal halides eventually present in the reaction medium ($MgBr_2$, $ZnBr_2$, CuI, etc.). The higher the M-O bond polarity, the Lewis acid character of MX, the higher will be rate of the retro-aldol reaction and consequently the regioselectivity. For example the greater tendency of zinc alkoxide of 3a (or 4a) to convert to the γ-regioisomers with respect to lithium counterparts might be ascribed to the higher Lewis acid affinity of zinc (II) than lithium ion for the aldehyde component.[12]

It was interesting to find that titanium tetrachloride catalysed reactions of 1a with benzaldehyde and p-chlorobenzaldehyde carried out in CH_2Cl_2 in the presence of triethylamine and using long reaction times gave predominantly the α-regioisomers of anti configuration 4a and 4i respectively. Actually syn α-regioisomers 3a and 3i formed first but during the time converted to the diastereomers 4a and 4i. The formation of γ-regioisomers 5a and 5f was also observed.

In conclusion the results presented in this paper clearly indicate that in the allylic condensation of metalloallyl derivatives of benzothiazole, benzoxazole and pyrimidine with aldehydes experimental conditions and the nature of the counterion play a major role in determining the relative regio and stereochemistry. This appears to be useful from the synthetic viewpoint as homoallylic alcohols 3, 4 and 5 may have application in organic synthesis as precursors of unsaturated hydroxy carbonyls, upon deblocking of the heterocyclic moiety. Work is in progress to this end and results will be reported in due course.

EXPERIMENTAL

^{1}H-NMR spectra were recorded on a Varian EM 360A or Varian XL 200 spectrometer and chemical shifts are reported in parts per million (δ) from internal Me_4Si. Melting points were determined on a Electrothermal apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 598 spectrophotometer. A Beckman (HPLC) apparatus equipped with 25-cm Ultrasphere ODS column and UV detector (λ 254 nm) with 55:45 methanol/water as the eluent at a flow rate of 1 ml/min was used for HPLC measurements. Thin layer chromatography (TLC) was performed on a silica gel sheet with fluorescent indicator (DC-Alufolien Kieselgel 60 F_{254}, Merck). Column chromatogarphy was carried out by using 70-230 mesh silica gel from Merck. Flash chromatographs were done with Merck 230-400 mesh silica gel.

Materials: - Tetrahydrofuran (THF) from commercial grade (RS, Carlo Erba) was purified by distillation (twice) from sodium wire in a N_2 atmosphere. Petroleum ether (RS, C.E.) refers to the 40-60° boiling fraction. Dichloromethane (RS, C.E.) was purified by distillation. 2-Allylbenzothiazole 1a and 2-allylbenzoxazole 1b were prepared by reaction of allylmagnesium bromide with 2-chlorobenzothiazole and 2-chlorobenzoxazole.[12,13] 2-Allylpyrimidine 1c was obtained by addition of allylmagnesium bromide to commercial 2-chloropyrimidine and dehydrogenation with 2,3-dichloro-5,6-dicyano-

-1,4-benzoquinone (DDQ).[7]
$MgBr_2$, Me_3SiCl, BEt_3, $ZnBr_2$, $SnEt_3Br$ and CuI were commercial grade and used without further purification.
Reaction of allyllithiums 2a-c with aldehydes. - As described in Ref. 7.
Preparation of metalloallyls 2d-r. - The metalloallyls 2d-r were prepared in situ without isolation from the allyllithiums 2a and 2c (1 mole) through metal exchange with $MgBr_2$, Me_3SiCl, BEt_3, $ZnBr_2$, $SnEt_3Br$ and CuI respectively (1.2 mole).
Reaction of allylmagnesium bromides 2d and 2l with benzaldehyde. - The reaction of allylmagnesium bromide 2d with benzaldehyde is described as an example. To a THF (10 ml) solution of 2c (6.5 mmole) prepared as described in ref. 7, a solution of $MgBr_2$ Et_2O (6.8 mmole) in 10 ml of THF was added dropwise with stirring at -78°C under nitrogen. After 10 min a solution of benzaldehyde (7.76 mmole) in 10 ml of THF was added dropwise and the stirring continued for 30 min at -78°C. Then the reaction mixture was allowed to warm to RT, kept there for 3 h and then quenched with sat aqueous NH_4Cl. Extraction with ether (3x25 ml), drying over $MgSO_4$ and solvent removal under reduced pressure yielded the α regioisomers 3c and 4c which could be separed by flash chromatography and characterised spectroscopically. Data are given below. The same results were obtained on quenching the reaction mixture above at -78°C 15 min after mixing the reactants.
Reaction of allylzinc bromides 2g and 2o with benzaldehyde. - The reaction of 2g is here described. To a stirred THF (15 ml) solution of 2c (3.23 mmole) at -78°C and under nitrogen $ZnBr_2$ (3.87 mmole) was added portionwise. After 10 min a solution of benzaldehyde (3.87 mmole) in 5 ml of THF was added. Stirring at -78°C was maintained for 3 h. Then the reaction mixture was allowed to warm to RT, kept there overnight, quenched with sat aqueous NH_4Cl and worked up as usual to give almost pure γ-regioisomer 5c further purified by flash chromatography. The same result was obtained on quenching the reaction mixture above at -78°C with NH_4Cl 15 min after mixing the reactants. The reaction of 2o with PhCHO carried out as above gave a mixture of the α-regioisomers 3a and 4a on quenching the reaction mixture with sat aqueous NH_4Cl after 30 min at -78°C, while quenching after 36 h at RT afforded the γ-regioisomer 5c.
Reaction of allyltrimethylsilanes 2e and 2m with benzaldehyde. - The reaction of 2e is here described. To a stirred THF (20 ml) of 2c (1.94 mmole) under nitrogen at -78°C a solution of Me_3SiCl (2.33 mmole) in 3 ml of THF was added. After 30 min a THF (3 ml) solution of benzaldehyde (2.33 mmole) and BF_3 ET_2O (2.33 mmole) was added. The reaction mixture was stirred at -78°C for 30 min and then allowed to warm to RT. Quenching with sat. aqueous NH_4Cl and worked up as usual gave the α-regioisomers 3c and 4c. The same results were obtained for a longer reaction time.
Reaction of allyltriethyllithium borate 2f and 2n with benzaldehyde. - The reaction of 2f is described. To a stirred solution of 2c (2.85 mmole) in 3 ml of THF triethylborane (THF 1M solution, 3.41 ml, 3.41 mmole) was added dropwise at -78°C under nitrogen. After 20 min benzaldehyde (3.41 mmole) in 3 ml of THF was added and the reaction mixture was stirred at -78°C for 30 min, then allowed to warm to RT and quenched with sat aqueous NH_4Cl after 2 h. Usual workup gave the γ-regioisomer 5c. In contrast only α-regioisomers 3c and 4c were obtained on quenching the reaction mixture at -78°C 5 min after mixing the reactants.
Reaction of allylcopper 2i and 2r with benzaldehyde. - The reaction of 2i is described. To a stirred solution of 2c (3.23 mmole) in 5 ml of THF at -78°C under nitrogen CuI (3.88 mmole) was added portionwise. After 30 min at -78°C a solution of benzaldehyde (3.88 mmole) in 3 ml of THF was added dropwise. Stirring at -78°C was continued for 1 h; then the reaction mixture was allowed to warm to RT and quenched with NH_4Cl. Usual workup furnished the γ-regioisomer 5c.
Reaction of allyltriethyltin 2h and 2p with benzaldehyde. - The reaction of 2h is described. The allyllithium 2c was prepared in n-hexane. To a stirred solution of 2c (2.23 mmole) in 5 ml of n-hexane at -78°C under nitrogen, a solution of Et_3SnBr (3.88 mmole) in 5 ml of n-hexane was added dropwise. After 30 min at -78°C, a solution of benzaldehyde (3.88 mmole) in 3 ml of n-hexane was added and stirring was continued for 30 min. Then the reaction mixture was allowed to warm to RT, kept there overnight and quenched with NH_4Cl. Usual workup provided the γ-regioisomer 5c.
Reaction of allylbenzothiazole 1a with aldehydes in the presence of $TiCl_4$ and Et_3N. - To a stirred solution of $TiCl_4$ (3.14 mmole) in 10 ml of CH_2Cl_2 at 0°C under nitrogen a solution of 1a (2.85 mmole) and benzaldehyde (3.14 mmole) in 3 ml of CH_2Cl_2 was added. After 5 min at 0°C, triethylamine (3.28 mmole) was added via a syringe. The reaction mixture was kept for 1 h at 0°C. TLC showed the presence of regioisomers 3a and 4a (3a predominant). Then mixture was warmed to RT and kept there for 48 h. Quenching with NH_4Cl and usual workup gave the α-regioisomer 4a togheter with γ-regioisomer 5a. Similarly the reaction of 1a with p-chlorobenzaldehyde afforded the α-regioisomer 4f and the γ-regioisomer 5f.
Reaction of allyllithium 2s with CH_3I. - To a stirred THF (20 ml) solution of 1d (1.73 mmole) at -78°C and under nitrogen BuLi (1.45 M, 2.07 mmole, 1.42

ml) was added dropwise. After 30 min a solution of methyl iodide (2.24 mmole) in 5 ml of THF was added. Stirring at -78°C was maintained for 2 h. Then the reaction mixture was allowed to warm to RT, quenched with sat aqueous NH_4Cl and worked up as usual to give 3-(2-benzoxazolyl)-1-butene, 7a further purified by flash chromatography. Oil; δ_H ($CDCl_3$) 1.6-1.83 (s, 6H), 5.03-5.43 (m, 2H), 6.06-6.66 (m,1H), 7.23- 8.0 (m, 4H).

Reaction of allyllithium 2s with allyl bromide. - Reaction carried out as described for the reaction with CH_3I. 3-(2-benzoxazolyl)-4-phenyl-1-butene, 7b: oil; δ_H ($CDCl_3$) 1.56-1.66 (s, 3H), 3.2 (d, 1H, J=13 Hz), 3.5 (d, 1H, J=13Hz), 5.0-5.5 (m, 2H), 6.13-6.66 (m, 1H), 7.0-8.0 (m, 9H).

Reaction of allyllithium 2s with benzyl chloride. - Reaction carried out as described for the reaction with CH_3I. 3-(2-benzoxazolyl)-1,5-hexadiene, 7c: oil; δ_H ($CDCl_3$ D_2O) 1.53-1.66 (s, 3H), 2.53-2.86 (m, 2H), 4.93-5.06 (m, 4H), 5.46-6.6 (m, 2H), 7.23-8.0 (m, 4H).

Isomerisation of allylbenzothiazole 1a to vinylbenzothiazole 1e. - The isomerisation of 1a to 1e was complete after 25 day at RT. 1e: oil; δ_H ($CDCl_3$) 2.56-2.7 (m, 3H), 7.4-7.6 (m, 2H), 8.0-9.0 (m, 4H).

Isomerisation of allylpyrimidine 1c to vinylpyrimidine 1f. - The isomerisation of 1c to 1f was complete after 25 day at RT. 1f: oil; δ_H ($CDCl_3$) 1.87-2.14 (m, 3H), 6.25-6.7 (m, 1H), 6.85-7.6 (m, 2H), 8.62 (d, 1H, J=5Hz).

For the new compounds not described in Ref. 7 data are given here:

syn-2-(2-benzoxazolyl)-1-phenyl-but-3-en-1-ol, 3b: m.p. 78-80°C (ether-petroleum ether); ν_{max} (nujol) 3257 cm^{-1} (OH); δ_H ($CDCl_3$-D_2O) 4.3 (dd, 1H, J=4.4Hz, J=8.2Hz), 5.25-5.82 (m, 3H), 6.2-6.82 (m, 1H), 7.5-8.14 (m, 9H).

anti-2-(2-benzoxazolyl)-1-phenyl-but-3-en-1-ol, 4b: m.p. 112-113°(ether-petroleum ether); ν_{max} (nujol) 3230 cm^{-1} (OH); δ_H ($CDCl_3$-D_2O) 3.9-4.3 (m, 1H), 4.82-5.45 (m, 3H), 5.6-6.23 (m, 1H), 7.11-7.74 (m, 9H).

trans-4-(2-benzoxazolyl)-1-phenyl-but-3-en-1-ol, 5b: oil; ν_{max} (film) 3311 cm^{-1} (OH); δ_H ($CDCl_3$-D_2O) 2.6-2.9 (m, 2H), 4.85-5.15 (m, 1H), 6.49 (d, 1H, J=16.4Hz), 6.71-7.83 (m, 10H).

syn-3-(2-chloropyrimidin-4-yl)-1-phenyl-pent-4-en-2-ol, 3h: oil; ν_{max} (film) 3410 cm^{-1} (OH); δ_H ($CDCl_3$-D_2O) 2.8 (d, 2H, J=7Hz), 3.5 (dd, 1H, J= 3.2Hz, J=9.2Hz), 4.3-4.6 (m, 1H), 5.1-5.6 (m, 2H), 6.0-6.6 (m, 1H), 7.2-7.5 (m, 6H), 8.5 (d, 1H, J=5Hz).

anti-3-(2-chloropyrimidin-4-yl)-1-phenyl-pent-4-en-2-ol, 4h: oil; ν_{max} (film) 3410 cm^{-1} (OH); δ_H ($CDCl_3$-D_2O) 2.4-3.28 (m, 2H), 3.54 (dd, 1H, J=8Hz), 4.13-4.59 (m, 1H), 5.1-5.5 (m, 2H), 5.88-6.57 (m, 1H), 7.2-7.6 (m, 6H), 8.5 (d, 1H, J=5Hz).

syn-2-(2-benzothiazolyl)-1-(4-chlorophenyl)-but-3-en-1-ol, 3i: oil; ν_{max} (film) 3330 cm^{-1} (OH); δ_H ($CDCl_3$-D_2O) 4.1 (dd, 1H, J=3.6Hz, J=8.4Hz), 4.9-5.45 (m, 2H), 5.5 (d, 1H, J=3.6Hz), 5.9-6.55 (m, 1H), 7.25-8.25 (m, 8H).

anti-2-(2-benzothiazolyl)-1-(4-chlorophenyl)-but-3-en-1-ol, 4i: oil; ν_{max} (film) 3300 cm^{-1} (OH); δ_H ($CDCl_3$-D_2O) 3.9-4.25 (m, 1H), 5.1-5.4 (m, 3H), 5.8-6.5 (m, 1H), 7.3-8.3 (m, 8H).

syn-2-(2-chloropyrimidin-4-yl)-1-(4-chlorophenyl)-but-3-en-1-ol, 3f: oil; ν_{max} (film) 3390 cm^{-1} (OH); δ_H (acetone-d_6-D_2O) 3.83 (dd, 1H, J=5.6Hz, J=9.6Hz), 4.95-5.4 (m, 2H), 6.0-6.75 (m, 1H), 7.35-7.5 (m, 3H), 8.65 (d, 1H, J=5Hz).

anti-2-(2-chloropyrimidin-4-yl)-1-(4-chlorophenyl)-but-3-en-1-ol, 4f: oil; ν_{max} (film) 3390 cm^{-1} (OH); δ_H (acetone-d_6-D_2O) 3.7-4.1 (m, 1H), 4.8-5.35 (m, 2H), 5.7-6.4 (m, 1H), 7.5 (s, 4H), 8.62 (d, 1H, J=5Hz), 8.75 (d, 1H, J=5HZ).

trans-4-(2-benzothiazolyl)-1-(4-chlorophenyl)-but-3-en-1-ol, 5f: oil; δ_H ($CDCl_3$-D_2O) 2.6-2.9 (m, 2H), 4.8-5.1 (m, 1H), 6.75-7.05 (m, 1H), 7.25-8.15 (m, 5H).

syn-3-(2-benzothiazolyl)-pent-4-en-2ol, 3g: oil; δ_H ($CDCl_3$-D_2O) 1.25 (dd, 3H, J=6Hz), 3.85 (dd, 1H, J=3.8Hz, J=8.8Hz), 4.1-4.75 (m, 1H), 5.55-5.7 (m, 2H), 5.85-6.75 (m, 1H), 7.35-8.25 (m, 1H).

syn-3-(2-chloropyrimidin-4-yl)-pent-4-en-2-ol, 3l: oil; ν_{max} (film) 3420 cm^{-1} (OH); δ_H ($CDCl_3$-D_2O) 1.23 (d, 3H, J=4.48Hz, J=9.2Hz), 4.12-4.65 (m, 1H), 5.2-5.6 (m, 2H), 5.95-6.15 (m, 1H), 7.35 (d, 1H, J=5Hz), 8.61 (d, 1H, J=5Hz).

anti-3-(2-chloropyrimidin-4-yl)-pent-4-en-2-ol, 4l: oil; ν_{max} (film) 3420 cm^{-1} (OH); δ_H ($CDCl_3$-D_2O) 1.23 (d, 3H, J=6Hz), 3.3-3.65 (m, 1H), 4.12-4.65 (m, 1H), 5.12-5.5 (m, 2H), 5.8-6.5 (m, 1H), 7.4 (d, 1H, J=5Hz), 8.7 (d, 1H, J=5Hz).

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