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DIASTEREOSELECTIVITY, DIASTEREOFACIAL SELECTIVITY AND REGIOSELECTIVITY IN THE REACTIONS OF CINNAMYL CHLORIDE WITH ALDEHYDES MEDIATED BY TIN AND ALUMINIUM

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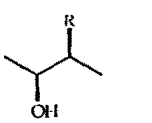
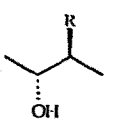
The reaction of cinnamyl chloride with a series of aryl and alkyl aldehydes mediated by tin and aluminium has been shown to be regioselective and threo *diastereoselective. For aldehydes with chirality adjacent to the carbonyl function some diastereofacial selectivity is observed. Conjugated aldehydes undergo regioselective 1,2-addition to the carbonyl.*

The commercial importance of macrolide and polyether antibiotics has stimulated efforts to develop synthetic methods which provide a high yield of products with relative and absolute asymmetric induction.[1] These methods include crossed aldol reactions,[2] reaction of organometallic compounds with carbonyl compounds,[3,4] ring opening reactions of cyclic compounds,[5] expoxidation of allylic alcohols,[6] hydroboration of olefinic compounds,[7] reduction of carbonyl derivatives,[8] sigmatropic rearrangements[9] and selected reactions of carbohydrates[10].

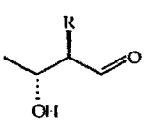
Erythro (1) and *threo* (2) β-methyl alkanol units occur in a number of macrolide and polyether antibiotics and the diastereoselective synthesis of α-alkyl-β-hydroxycarbonyls (3) and of homoallylic alcohols (4) provide an entry to the synthesis of these materials. The stereoselective formation of C-C bonds between prochiral centres is most generally accomplished by the addition of metal enolates[2] or 2-alkenylmetal derivatives[3] to aldehydes. Homoallylic alcohols have become one of the most useful intermediates in acyclic synthesis because of the facility the hydroxyl group and the double bond offer for chemical modification. This dual functionality allows easy entry to a variety of bifunctionalized molecules. Furthermore they can undergo a facile one-carbon homologation to δ-lactones via hydroformylation[11] or can be epoxidised thereby introducing a third chiral centre.[12]



erythro
1



threo
2



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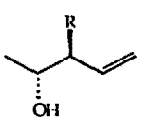

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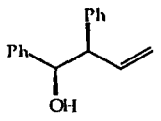
Allylations of aldehydes or ketones to give homoallylic alcohols can be achieved using conventional organometallic reactions (eg Grignard or Barbier reactions) or by the reaction of allylic organometallics with aldehydes in the presence of catalysts.[13] Mild conditions employing Sn-Al have recently been developed by Nokami et al.,[4] for the preparation of homoallylic alcohols from reaction of 1-bromobut-2-ene and aldehydes and ketones.

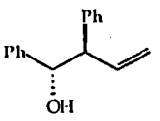
We now report an investigation of the diastereoselectivity, diastereofacialselectivity and regioselectivity of the reaction of cinnamyl chloride with aldehydes under these conditions.

Results and Discussion

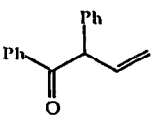
The reaction of (E)-cinnamyl magnesium chloride with benzaldehyde under Barbier conditions[14] has been reported to give a 7:3 mixture of the homoallylic 1,2-diphenyl-3-buten-1-ols **5a** and **5b**.[15] When we repeated this reaction the *erythro* product was fractionally crystallized[16] from a 1:1 mixture of diastereoisomers. All attempts to purify the *threo* diastereoisomer (**5b**) were unsuccessful and we now report our investigations directed towards a stereospecific synthesis of this diastereoisomer.



erythro-5a

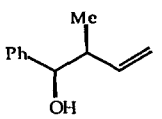


threo-5b

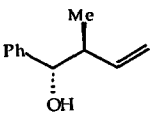


6

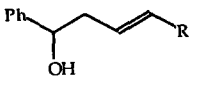
Reduction[17] of 1,2-diphenyl-3-buten-1-one (**6**) with lithium aluminium hydride gave a 9:2 mixture, and with sodium borohydride in the presence of cerium (III) chloride hexahydrate[18] a 2:1 mixture of **5a** and **5b** respectively. Chromium (II), generated *in situ* by reaction of chromium (III) chloride and lithium aluminium hydride, has been used to effect allylic addition to carbonyls and on reaction with cinnamyl chloride and benzaldehyde gave alcohols **5a** and **5b** in a ratio 17:83. The reaction was somewhat less *threo* selective than that reported by Hiyama[19] for reaction of crotyl bromide with benzaldehyde. In our hands this latter reaction gave the *threo* product (**7b**) and the linear regioisomer (**8a**) (30%).



erythro-7a



threo-7b



8a R=Me
8b R=Ph

Table 1

Metal mediated reactions of cinnamyl and crotyl halides with benzaldehyde

Metal	Allylic halide	Ratio *Erythro*	*Threo*	Linear
Mg	cinnamyl chloride	50	50	
Cr(II)	cinnamyl chloride	17	83	
Sn-Al	cinnamyl chloride	0	100	
Zn	cinnamyl chloride	25	75	
Mg	crotyl bromide	50	50	
Cr(II)	crotyl bromide	0	70	30
Sn-Al	crotyl bromide	58	42	
Zn	crotyl bromide	43	57	

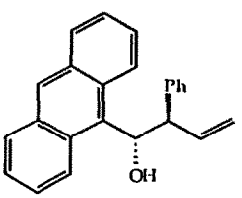
Reduction of ketone (**6**)

Reducing Agent	Allylic halide	Ratio *Erythro*	*Threo*
LAH	cinnamyl chloride	82	18
$NaBH_4/Ce(III)Cl_3$	cinnamyl chloride	67	33

The diastereoselectivity of zinc mediated addition of allylic halides to carbonyls[20] has not, to our knowledge, been reported. We have examined the diastereoselectivity of the reaction for both crotyl and cinnamyl halides with benzaldehyde. A mixture (57:43) of the *threo* alcohol (**7b**) and the *erythro* alcohol (**7a**) were obtained from the reaction of crotyl bromide with benzaldehyde while a 3:1 mixture of *threo* diastereoisomer (**5b**) and *erythro* diastereoisomer (**5a**) were produced from the reaction of cinnamyl chloride with benzaldehyde under the same conditions. The reaction is regiospecific with no linear products (**8a, 8b**) being formed in either reaction.

Nokami et al.[4] has described a procedure for the reaction of crotyl bromide with aldehydes using tin and aluminium powders in the presence of a trace of hydrobromic acid which exhibited some *erythro* selectivity. No definitive proof was reported for the structure of the products with benzaldehyde and the reaction was repeated to give alcohols **7a** and **7b** in the ratio 58:42 as previously reported and the identity of each isomer was unambiguously established by comparison with authentic samples.[21] There was reason to believe that the reaction of cinnamyl chloride with benzaldehyde mediated by tin and aluminium might be *threo* selective because *trans*-crotyl tri-n-butyltin has been shown to react with benzaldehyde with opposite stereoselectivity (*erythro*) to that of *trans*-cinnamyl tri-n-butyltin.[22] Indeed the reaction of cinnamyl chloride with benzaldehyde in the presence of tin and aluminium powders successfully gave the *threo* alcohol (**5b**) as the only detectable product.[23] In the absence of tin no reaction could be detected, and the same reactants in the presence of tin but not aluminium gave the homoallylic alcohol but in poor yield (< 10%).

In view of the remarkably high diastereoselectivity in the tin and aluminium promoted formation of **5b** the method was investigated with a variety of selected aldehydes. A series of aryl and alkyl aldehydes (*RCHO; R = Ph, 4-MeOPh, 4-NCPh, 9-anthracenyl, Me, Et, iPr, $CH_3(CH_2)_5$, $PhCH_2$*) were reacted with cinnamyl chloride in the presence of tin and aluminium and each aldehyde gave only one diastereoisomer.[24,25] The homoallylic alcohol, or a derivative, from each of the reactions of $PhCH_2CHO$, Me_2CHCHO, and 9-anthraldehyde were selected for X-ray analysis as representative of the homoallylic alcohols. X-Ray crystal structures confirmed the stereochemistry of these compounds as (1RS, 2SR)-1-(9-anthracenyl)-2-phenyl-3-buten-1-ol (**9**), (2RS, 3RS, 4SR)-4,5-epoxy-1,3-diphenyl-4-penten-2-ol (**10a**) and (3RS, 4RS)-2-methyl-4-phenyl-5-hexen-3-yl 3,5-dinitrobenzoate (**11**). These results establish the *threo* selectivity for each of these reactions and it is therefore reasonable to conclude that each of the above reactions is *threo* selective.



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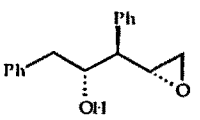
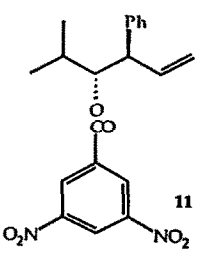
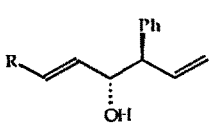


10a

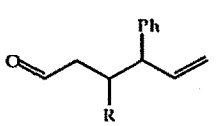


11

Reaction of the conjugated aldehydes crotonaldehyde and cinnamaldehyde with cinnamyl chloride mediated by tin and aluminium gave only the 1,2-addition, *threo* diastereoisomers **12b** and **13b** respectively. Thus under these conditions reaction with these conjugated aldehydes occurs with both high regioselectivity and diastereoselectivity. In contrast reaction of these conjugated aldehydes with cinnamyl chloride under Barbier conditions gave a mixture of several products including the *threo* and *erythro* products and 1,4-addition products (**14a, 14b**).



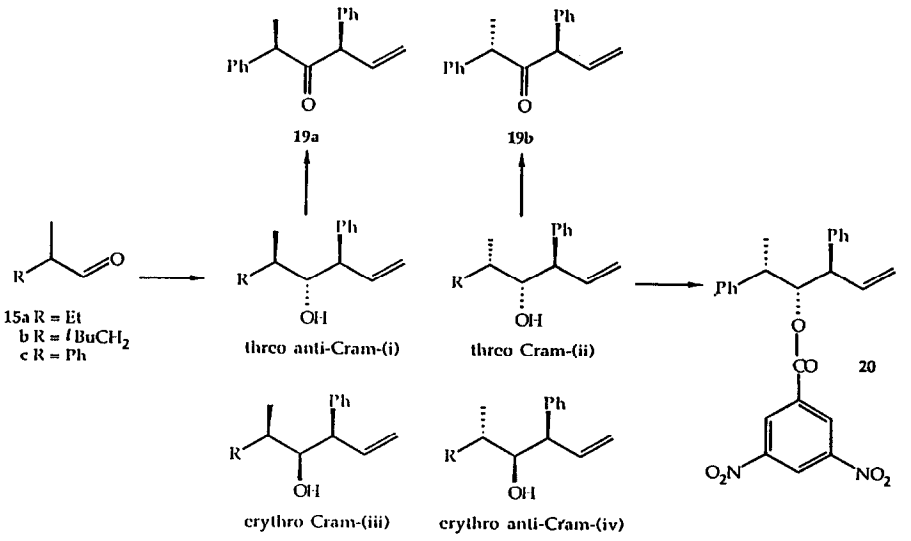
(3RS, 4RS)-**12b** R=Me
(3RS, 4RS)-**13b** R=Ph



14a R=Me
14b R=Ph

In view of the high selectivities found for the above aldehydes when the reaction is mediated with tin and aluminium it was of interest to examine the possibility of using this procedure for the synthesis of molecules containing more than two chiral centres. For the aldehydes 2-methylbutanal (**15a**), 2,4,4-trimethylpentanal (**15b**) and 2-phenylpropanal (**15c**) which contain a chiral centre adjacent to the carbonyl group the products of 1,2-addition will contain three contiguous chiral centres, i.e. four possible diastereomers (Scheme 1).

Scheme 1



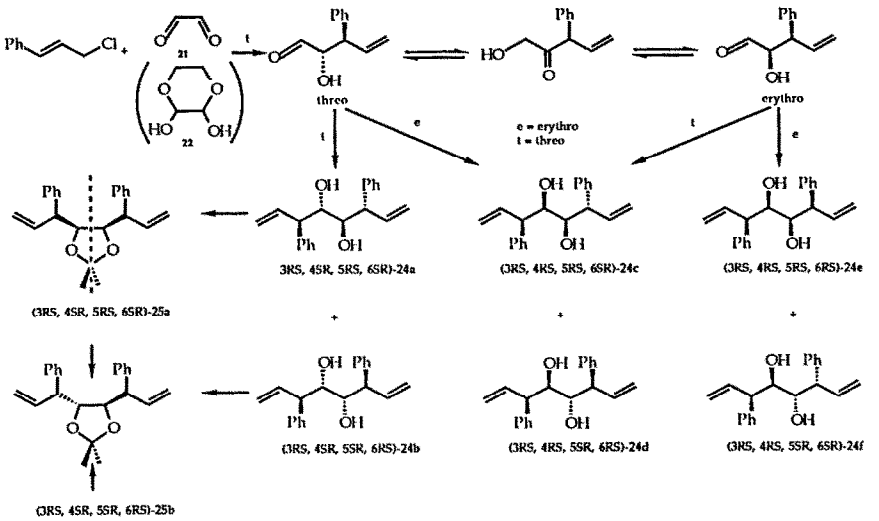
Reaction of 2-phenylpropanal (**15c**) with cinnamyl chloride in the presence of tin and aluminium gave two diastereoisomers in a 3:1 ratio in the isolated product mixture. The major diastereoisomer was determined to be the *threo*-Cram diastereoisomer (2RS, 3SR, 4SR)-2,4-diphenyl-5-hexen-3-ol (**18ii**) by X-ray crystal structure analysis of the 3,5-dinitrobenzoate derivative (**20**). Oxidation of the reaction product mixture with pyridinium chlorochromate gave a ca. 3:1 mixture of ketones **19b** and **19a** thereby establishing the relative configurations of C2 and C4 in the minor alcohol product. This product is therefore assumed to be *threo-anti*-Cram (**18i**) since the tin-aluminium reaction in all the above cases has been established as *threo* selective. The reaction occurs not only with diastereoselective carbon-carbon bond formation (*threo* selectivity), but also with marked selectivity between the enantiomeric faces of the carbonyl group (Cram selectivity). 2-Methylbutanal (**15a**) and 2,4,4-trimethylpentanal (**15b**) also showed a diastereofacial preference giving respectively a 5:2 and a >9:1 mixture of two of the four possible diastereoisomers. In each case the major diastereoisomer is assumed by analogy with the above reaction to be *threo* Cram (**16ii, 17ii**) and the minor diastereoisomer *threo* anti-Cram (**16i, 17i**). The carbonyl face selectivity is known to be dependent on the steric bulk and polarity effects[26] at the chiral centre adjacent to the aldehyde. The facial selectivity at the carbonyl for this reaction with cinnamyl chloride is less than the induced *threo* diastereoselectivity.

By comparison with the reaction catalysed by tin and aluminium reaction of 2-phenylpropanal with cinnamyl chloride under Barbier conditions gave a mixture of the four possible branched homoallylic alcohols (**18i-iv**) which on oxidation with pyridinium chlorochromate gave a ca. 1:1 mixture of the isomeric ketones (**19a**) and (**19b**).

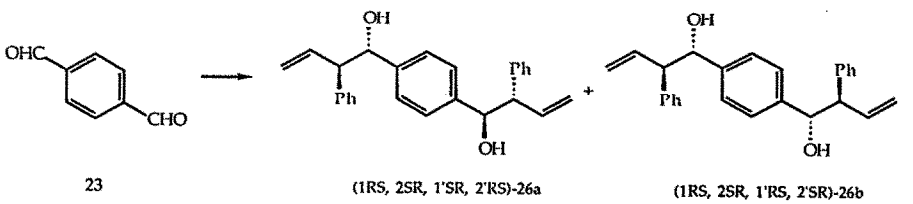
An attempt to extend the use of this tin-aluminium procedure to the synthesis of molecules containing more than two chiral centres was made by studying the reaction of glyoxal (**21**), 2,4-dihydroxy-1,4-dioxane (**22**) and terephthaldicarboxaldehyde (**23**) with cinnamyl chloride. The ^{13}C n.m.r. and ^{1}H n.m.r. spectra of the product mixture from the reaction with glyoxal, and 3,4-dihydroxy-1,4-dioxane, which could give six isomers (**24a-f**), showed the presence of three diastereoisomers and a trace of possibly a fourth diastereoisomer. Even if the addition of the first cinnamyl is *threo* selective tautomeric eqilibrium will generate both the *erythro* and *threo* intermediate (Scheme 2). Each of these two intermediates can further

react with a second cinnamyl group in a reaction presumed to occur *threo* selectively thereby resulting in the formation of **24a-d**. One diastereoisomer was separated by radial chromatography and shown to be symmetrical by n.m.r. spectroscopy, thereby identifying it as either **24a** or **24b**. Conversion of the diol to the acetonide derivative (**25**) and the non-identity of the acetonide methyl groups in the ^{1}H n.m.r. spectrum established the acetonide as **25a** (cf **25b**) and hence the alcohol as **24a**.

Scheme 2



Reaction of terephthaldicarboxaldehyde with cinnamyl chloride mediated by tin and aluminium gave only two (**26a, 26b**) of the six possible diastereomers consistent with each addition of a cinnamyl group being *threo* selective.



We have found that this wide range of aldehydes react with cinnamyl chloride in this complex multiphase system to produce exclusively the *threo* homoallylic alcohols, and neither electronic nor steric effects of the aldehyde affect the diastereoselectivity of the reaction. For other metal mediated allylation reactions *threo* selectivity is considered to be the result of a cyclic mechanism (Scheme 3) involving preferential equatorial substitution in the six membered ring.[7]

Scheme 3

In the Sn-Al mediated reaction hydrobromic acid is added in catalytic quantities and is probably involved in generating an active metal site and does not appear to effect the diastereoselectivity of the reaction.[28] The aluminium is thought to promote the formation of an allylic tin compound, probably diallylic tin dihalide,[29] by activating tin insertion and reducing any tin salts formed. Following addition to the carbonyl hydrolysis forces the equilibrium to the product homoallylic alcohol.

It is notable that cinnamyl chloride reacts with aldehydes in the presence of tin and aluminium and *trans*-cinnamyl trialkyltin reacts with aldehydes with *threo* selectivity while crotyl bromide in the presence of tin and aluminium and crotyl trialkyltin afford an *erythro* rich mixture of products. A linear transition state (Scheme 4) can result in the formation of *erythro*-products from both *trans*- and *cis*-crotyl trialkyltins.[30]

Scheme 4

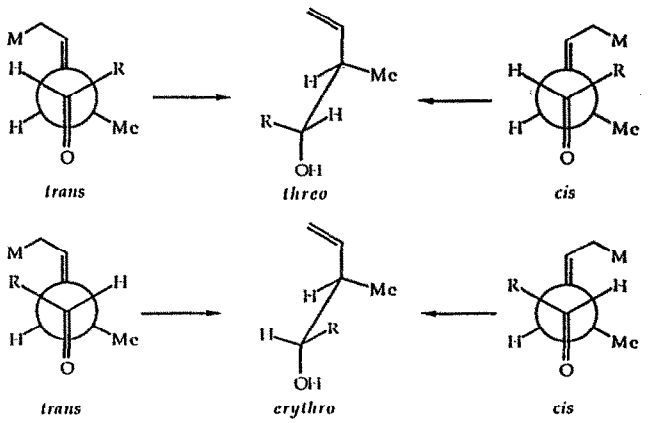


Table 2

Reaction of benzaldehyde with allylic species.

Allylic species	Reaction	Yield	*Erythro*	*Threo*	Reference
67% *trans*-crotyl dibutyltin chloride[31]	thermal	75%	44	56	32
55% *cis*-crotyl dibutyltin chloride[33]	thermal	75%	54	46	32
trans-crotyl tributyltin	BF_3	90%	98	2	34
40%*cis*-crotyl tributyltin[35]	BF_3	90%	98	2	34
trans-crotyl triphenyltin	BF_3	92%	83	17	22
trans-cinnamyl triphenyltin	BF_3	65%	1	99	22
trans-cinnamyl tributyltin	BF_3	81%	10	90	22
crotyl bromide	Sn-Al	87%	60	40	4
cinnamyl chloride	Sn-Al	72%	-	100	25

Yamamoto[36] found *trans*-crotyl tributyltin reacted with benzaldehyde in the presence of BF_3 to give a 98:2 preference for the *erythro* product.[37] Koreeda and Tanaka[22] with the same conditions reported that *trans*-crotyl triphenyltin reacted with benzaldehyde with somewhat reduced selectivity to give a 83:17 preference for the *erythro* product. In contrast *trans*-cinnamyl triphenyltin reacted with benzaldehyde[22] to give 99:1 mixture of *threo* and *erythro* alcohols while cinnamyl tributyltin under the same conditions is slightly less selective, resulting in a 90:10 preference for the *threo* alcohol. These experiments show that the ligands on tin (phenyl or n-butyl) have an influence on the stereospecificity of the reaction. The inductive effect of the phenyl ligands relative to n-butyl ligands is considered to increase the relative positive charge on the tin centre[38] thereby increasing coordination to carbonyl and biasing the reaction towards a cyclic mechanism and *threo* formation.

The tin will be more electropositive for cinnamyl trialkyltin than for crotyl trialkyltin and favour coordination with carbonyl resulting in a preference for a cyclic transition state and *threo* selectivity. The

electron density at tin of the organometallic species formed in the tin-aluminium reaction of crotyl and cinnamyl halides will also be influenced by the methyl and phenyl groups. The cyclic transition state should therefore become more competitive with consequent formation of *threo*-homoallylic alcohols for reaction of cinnamyl chloride with aldehyde compared with crotyl bromide where the *erythro* isomer is formed in diastereomeric excess.

The selectivity observed for reaction of cinnamyl chloride in the reaction with aldehydes mediated by tin and aluminium should find increasing importance in stereoselective synthesis because of the regioselectivity and diastereoselectivity and diastereofacial selectivity.

Experimental

General. Infrared spectra were recorded on a Shimadzu IR27G or Pye Unicam SP3-300 spectrophotometer. Mass spectra were recorded on an A.E.I. MS902 or Kratos MS80RFA spectrometer. Radial chromatography was performed on a Chromatotron (Harrison and Harrison) using Merck type 60 P.F. 254 silica gel. ^{1}H n.m.r. spectra were recorded on a Varian T60 or XL-300 spectrometer and ^{13}C n.m.r. were recorded on a Varian CFT20 or XL-300 spectrometer, for $CDCl_3$ solutions with $(CH_3)_4Si$ as an internal standard. Melting points were determined using an Electrothermal melting point apparatus and are uncorrected.

Preparation of 1,2-Diphenyl-3-buten-1-ols by Reduction of 1,2-Diphenyl-3-buten-1-one.
(i) *With lithium aluminium hydride.* 1,2-Diphenyl-3-buten-1-one (**6**) (111 mg, 0.5 mmol) was dissolved in dry ether (5 ml) and added dropwise to a stirred suspension of lithium aluminium hydride (111 mg) in dry ether (2 ml) and the resulting mixture heated under reflux for 5 hours in a nitrogen atmosphere. Excess lithium aluminium hydride was destroyed by the addition of sodium sulphate decahydrate and the mixture diluted with 1% sulphuric acid and the product extracted into ether, washed with water, and dried with sodium sulphate. The solvent was removed by distillation to give a 9:2 mixture of (1RS, 2RS)- and (1RS, 2SR)-1,2-diphenyl-3-buten-1-ol[15] (**5a, 5b**). ^{1}H n.m.r. (CCl_4) δ_H 7.10, 5b ArH; 7.16, 5a ArH.
(ii) *With cerium (III) chloride hexahydrate-sodium borohydride.*[18] To a solution of 1,2-diphenyl-3-buten-1-one (**6**) (1 mmol, 221 mg) and cerium (III) chloride hexahydrate (1 mmol, 355 mg) in methanol (2.5 ml) was added sodium borohydride (1 mmol, 38 mg) in one portion with stirring. Vigorous gas evolution occurred and the temperature rose. Stirring was continued for a few minutes and the pH adjusted to neutrality by controlled addition of dilute aqueous hydrochloric acid. The product was extracted with ether, dried with sodium sulphate and after removal of solvent gave a 2:1 mixture of (1RS, 2RS)- and (1RS, 2SR)-2-methyl-1-phenyl-3-buten-1-ol[15] (**5a, 5b**) (0.21 g). ^{1}H n.m.r. (CCl_4) δ_H 7.10, 5b ArH; 7.17, 5a ArH.

Barbier Preparations of Homoallylic Alcohols.
The procedure used for the preparation of the 1,2-diphenyl-3-buten-1-ols is representative of that used for the preparation of a number of homoallylic alcohols.[15]
1,2-Diphenyl-3-buten-1-ols. (E)-3-Chloro-1-phenylpropene (0.1 ml) and a crystal of iodine were added to magnesium turnings (1.8 g) and dry ether (10 ml) and the mixture vigorously stirred and heated to initiate reaction. A solution of (E)-3-chloro-1-phenylpropene (2 g, 13 mmol) and benzaldehyde (1.2 g, 11 mmol) in dry ether (10 ml) was added at such a rate as to maintain a gentle reflux (30 min). The mixture was stirred and kept under reflux for a further 3 hours, cooled and poured into ice-cold saturated aqueous ammonium chloride solution (20 ml). The ether layer was separated and the aqueous layer extracted several times with ether. The combined ether extracts were washed with water, dried over magnesium sulphate and after removal of solvent gave a yellow oil (3 g) shown by g.l.c. to be a 1:1 mixture of (1RS, 2SR)- and (1RS,2RS)-1,2-diphenyl-3-buten-1-ol[15] (**5b, 5a**). υ_{max} 3450, 920, 760, 700 cm^{-1}. ^{1}H n.m.r. (CCl_4) δ_H 1.87, $W_{h/2}$ 9 Hz, OH; 2.18, $W_{h/2}$ 7 Hz, OH; 3.3 - 3.65, H2; 4.6 - 5.3, H1, (H4)$_2$; 5.6 - 6.5, H3; 7.10, 7.17, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 58.4, 59.0, C2; 77.2, 77.4, C1; 117.1, 118.2, C4; 137.7, 137.8, C3; 126.5, 126.6, 127.0, 127.3, 127.7, 127.9, 128.1,128.3, 128.6, 128.7, 128.8, 140.3, 140.7, 141.9, phenyl carbons. The oil crystallized to give (1RS, 2RS)-1,2-diphenyl-3-buten-1-ol (**5a**) which was recrystallized from dichloromethane : pentane; m.p. 76°C. ^{1}H n.m.r. (CCl_4) δ_H 1.62 $W_{h/2}$ 8 Hz, OH; 3.47 $J_{1,2}$ 7 Hz, H2; 4.6 - 5.1, H1, (H4)$_2$; 5.87 $J_{3,4\ cis}$ 10 Hz, $J_{3,4\ trans}$ 16 Hz, $J_{2,3}$ 7 Hz, H3; 7.17, $W_{h/2}$ 2 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 58.4, C2; 77.4, C1; 117.1, C4; 137.7, C3; 127.0, 127.7, 127.9, 128.1, 128.6, 128.8, 140.3, 141.9 phenyl carbons.
3-Phenylhept-1,5-dien-4-ol. (E)-3-Chloro-1-phenylpropene (0.55 g, 3.7 mmol) was reacted with (E)-2-butenal (0.26 g, 3.7 mmol) to give an oil (0.65 g) shown by ^{13}C n.m.r. to be a mixture of at least three compounds. ^{1}H n.m.r. ($CDCl_3$) δ_H 1.5 - 1.9, 2.5 - 2.8, 3.3 - 3.6, 4.2 - 5.3, 6.0 - 6.8, 7.0 - 7.6, 9.5 - 10. ^{13}C n.m.r. ($CDCl_3$) δ_C (**12a**) 57.0, C3; 117.1, C1; (**12b**) 17.7, C7; 57.3, C3; 75.5, C4; 117.7, C1; 131.4, C5; 138.2, C2.
1,4-Diphenylhexa-1,5-dien-3-ol. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with (E)-1-phenylpropenal (2.64 g, 20 mmol) to give an oil (2.37 g) shown by ^{13}C n.m.r. to be a mixture of several compounds. υ_{max} 3425, 1680 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$) δ_H 1.85 - 1.88, 2.60 - 2.67, 3.37 - 3.54, 4.27 - 4.30, 4.47 - 4.56, 5.04 - 5.28, 6.03 - 6.75, 7.03 - 7.48, 9.66, 10.0 from which **13b** could be identified ^{13}C n.m.r. ($CDCl_3$) δ_C (**13b**) 57.5, C4; 75.0, C3; 118.0, C6; 129.7, 131.0, C1, C2; 137.7, C5; 126.4, 126.7, 127.4, 128.5, 128.6, 140.4, phenyl carbons.

2,4-Diphenyl-5-hexen-3-ol. (E)-3-Chloro-1-phenylpropene (0.55 g, 3.6 mmol) was reacted with 2-phenylpropanal (0.5 g, 3.7 mmol) to give an oil (0.8 g), a mixture, (ca. 4:3:1:3) of four isomers of 2,4-diphenyl-5-hexen-3-ol (**18i, 18ii, 18iii, 18iv**). υ_{max} 3475, 1500, 1460 cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ_H 1.29 - 1.60, (H1)$_3$; 2.38 - 2.40, 2.56 - 2.95, 3.26 - 3.41, 3.59 - 3.70, 3.93 - 4.05, C3, C4; 4.90 - 5.23, C6; 6.03 - 6.47, C5; 7.19 - 7.33, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 14.5, 15.1, 17.6, 19.2, C1; 40.2, 41.9, 42.1, 42.6, C2; 53.7, 54.0, 54.1, C4; 78.1, 78.6, C3; 116.3, 117.5, 117.9, C6; 137.4, 137.7, 138.0, 139.2, C5. Radial chromatography and elution with 10% - 30% ether - petroleum ether mixtures gave (2RS, 3RS, 4RS)-2,4-diphenyl-5-hexen-3-ol (**18i**). ^1H n.m.r. ($CDCl_3$) δ_H 1.36, $J_{1,2}$ 7 Hz, (H1)$_3$; 2.85, $J_{1,2}$ 7 Hz, $J_{2,3}$ 6.4 Hz, H2; 3.31, $J_{3,4}$ 7.4 Hz, $J_{4,5}$ 8 Hz, H4; 4.01, $J_{2,3}$ 6.4 Hz, $J_{3,4}$ 7.4 Hz, H3; 5.04, $J_{5,6a}$ 17 Hz, $J_{6a,6b}$ 2.5 Hz, $J_{4,6a}$ 1.5 Hz, H6a; 5.13, $J_{5,6b}$ 10 Hz, $J_{6a,6b}$ 2.5 Hz, H6b; 6.12, $J_{4,5}$ 8 Hz, $J_{5,6a}$ 17 Hz, $J_{5,6b}$ 10 Hz, H5; 7.23 - 7.32, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 19.4, C1; 42.6, C2; 54.1, C4; 78.3, C3; 116.4, C6; 139.6, C5; 126.5, 126.7, 128.2, 128.43, 128.46, 128.53, 128.7, 128.9, phenyl carbons.

(2RS, 4SR)- and (2RS, 4RS)-2,4-diphenyl-5-hexen-3-one. The above mixture of diastereoisomers (**18i-iv**) (150 mg) in dichloromethane (4 ml) was added to a vigorously stirred mixture of pyridinium chlorochromate (1 g), anhydrous sodium acetate (0.11 g) and dichloromethane (50 ml). After six hours ether (50 ml) was added with stirring and the mixture was decanted from the tarry residue and washed with ether (3 * 50 ml). The combined organic solutions were filtered through Florosil, dried with sodium sulphate and after removal of solvent gave a mixture (ca. 1:1) of (2RS, 4SR)- and (2RS, 4RS)-2,4-diphenyl-5-hexen-3-one (**19a, 19b**) as an oil (0.17 g). (Found CIMS (NH_3): $M+H^+$ = 251.1417; $C_{18}H_{19}O$ requires 251.1437). υ_{max} 1700 cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ_H 1.17 - 1.53, (H1)$_3$; 3.96, $J_{1,2}$ 7 Hz, H2; 4.53, $J_{4,5}$ 8 Hz, H4; 4.93 - 5.37, (H6)$_2$; 5.76 - 6.67, H5; 6.83 - 8.17, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C (**19b**) 18.0, C1; 52.1, C2; 61.3, C4; 117.8, C6; 129.0, C5; 183.7, C3; and (**19a**) 26.5, C1; 51.4, C2; 60.6, C4; 116.7, C6; 136.6, C5; and phenyl carbons (**19a, 19b**) 126.9, 127.2, 128.1, 128.3, 128.5, 128.7, 129.0.

Chromous chloride Mediated Addition of Allylic halides to Aldehydes.

2-Methyl-1-phenyl-3-buten-1-ols. Lithium aluminium hydride (418 mg, 11 mmol) was added portionwise to anhydrous chromic chloride[39] (3.49 g, 22 mmol) and the mixture stirred in anhydrous tetrahydrofuran (30 ml) at 0°C in a nitrogen atmosphere for 5 minutes. After 20 minutes at room temperature a tan suspension was obtained which was cooled to 0°C and benzaldehyde (834 mg, 7.9 mmol) in anhydrous tetrahydrofuran (5 ml) added. (E)-1-Bromo-2-butene (1.49 g, 11 mmol) in anhydrous tetrahydrofuran (30 ml) was added dropwise over 15 minutes. Aliquots of the reaction mixture were taken at intervals and the course of the reaction monitored by ^1H n.m.r. After 3 hours the reaction was poured into water and ether and the organic layer washed with water, dried with sodium sulphate and after removal of solvent gave (1RS, 2RS)-2-methyl-1-phenyl-3-buten-1-ol[21,32,40] (**7b**) and 1-phenyl-3-penten-1-ol[41] (**8a**) as an oil (0.84 g). ^1H n.m.r. (CCl_4) δ_H (**7b**) 0.86, $J_{2,5}$ 7 Hz, Me; 2.47, $J_{2,5}$ 7 Hz, $J_{2,3}$ 7 Hz, H2; 4.34, $J_{1,2}$ 7.8 Hz, H1; 5.14 - 5.21, (H4)$_2$; 5.8, $J_{2,3}$ 8.1 Hz, $J_{3,4a}$ 10.3 Hz, $J_{3,4b}$ 17.1 Hz, H3; 7.2 - 7.4, ArH; ^{13}C n.m.r. ($CDCl_3$) δ_C (**7b**) 16.5, C2-Me; 46.1, C2; 77.8, C1; 116.5, C4; 140.4, C3. ^1H n.m.r. (CCl_4) δ_H (**8a**) 1.67, $J_{3,5}$ 1.2 Hz, $J_{4,5}$ 5 Hz, (H5)$_3$; 2.41, (H2)$_2$; 4.63 - 4.67, H1; 5.35 - 5.47, 5.52 - 5.65, H3, H4; 7.2 - 7.4, ArH; ^{13}C n.m.r. ($CDCl_3$) δ_C (**8a**) 18.0, C5; 42.7, C2; 73.4, C1; 142.6, 144.2, C3, C4. ^{13}C n.m.r. ($CDCl_3$) δ_C (**7b, 8a**) 125.8, 126.8, 127.3, 127.5, 128.1, 128.3, 129.1 phenyl carbons.

1,2-Diphenyl-3-buten-1-ols. (E)-3-Chloro-1-phenylpropene (1.61 g, 11 mmol) was reacted as above with benzaldehyde (863 mg, 8.1 mmol) to give an oil (0.72 g); shown by g.l.c. to be a mixture (83:17) of (1RS, 2SR)- and (1RS, 2RS)-1,2-diphenyl-3-buten-1-ols[15] (**5b, 5a**). ^1H n.m.r. (CCl_4) δ_H 7.10, **5b** ArH; 7.17, **5a** ArH.

Zinc Mediated Addition of Allylic halides to Aldehydes.

2-Methyl-1-phenyl-3-buten-1-ols. A mixture of (E)-1-bromo-2-butene (2.6 g, 20 mmol) and benzaldehyde (2.2 g, 20 mmol) was dissolved in tetrahydrofuran (1 ml) and saturated aqueous ammonium chloride (5 ml). Zinc powder (1.3 g, 20 mmol) was added and the mixture stirred for 1 hour at room temperature, filtered and the solid washed with ether (2 x 100 ml). The filtrate was washed with water (50 ml), dried with sodium sulphate and after removal of solvent gave an oil (3.1 g), shown to be a mixture (57:43) of (1RS, 2RS)- and (1RS, 2SR)-2-methyl-1-phenyl-3-buten-1-ol[21,32,40] (**7a, 7b**). υ_{max} 3440, 1455, 1190, 700 cm^{-1}. ^{13}C n.m.r. ($CDCl_3$) δ_C 14.1, 16.5, Me; 44.6, 46.1, C2; 77.2, 77.7, C1; 115.3, 116.5, C4; 134.2, 140.1, C3.

1,2-Diphenyl-3-buten-1-ols. (E)-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with benzaldehyde (2.2 g, 20 mmol) to give an oil (3.9 g), a mixture, 3:1 (ratio determined by inspection of resonances at δ_C 58.4 and 58.9 of ^{13}C n.m.r. spectrum) of (1RS, 2SR)- and (1RS, 2RS)-1,2-diphenyl-3-buten-1-ol[15] (**5b, 5a**). ^1H n.m.r. ($CDCl_3$) δ_H 2.23, $W_{h/2}$ 8 Hz, OH; 3.2 - 3.67, H2; 4.7 - 5.3, H1, (H4)$_2$; 5.77 - 6.57, H3; 7.13, 7.17, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 58.4, 58.9, C2; 77.1, 77.3, C1; 116.9, 117.9, C4; 137.9, C3; 126.0, 126.4, 126.6, 127.2, 127.8, 128.2, 128.4, 128.9, 129.6, phenyl carbons.

Tin and aluminium mediated addition of allylic halides to aldehydes.

The general procedure used for the preparation of homoallylic alcohols mediated by tin and aluminium metal to direct carbon - carbon bond formation[4] is described for the preparation of the 2-methyl-1-phenyl-3-buten-1-ols. Where product homoallylic alcohols were unstable to g.l.c. analysis ^{13}C n.m.r. and ^1H n.m.r. spectroscopy was used to establish the absence or otherwise of erythro stereoisomers.

2-Methyl-1-phenyl-3-buten-1-ols. To a mixture of (E)-1-bromo-2-butene (2.82 g, 20 mmol) and benzaldehyde (2.32 g, 22 mmol) in ether (5 ml) and water (3 ml) was added tin powder (1 g, 8.4 mmol), aluminium

powder (0.5 g, 18.5 mmol) and 3 drops of hydrobromic acid. The mixture was stirred for 24 hrs at room temperature, filtered, the solid washed with ether (2 x 100 ml), and the filtrate washed with water (2 * 50 ml). The combined ether fractions were dried with sodium sulphate and after removal of solvent gave an oil (2.08 g) shown to be a mixture, (58:42, g.l.c., 2% carbowax 20M on chromosorb W, column temperature 90°C) of (1RS, 2SR)- and (1RS, 2RS)-2-methyl-1-phenyl-3-buten-1-ols[21,32] (**7a, 7b**). υ_{max} 3440, 1455, 1190, 700 cm^{-1}. ^1H n.m.r. (CCl_4) δ_H (**7a**) 1.0, $J_{2,5}$ 7 Hz, Me; 4.40, $J_{1,2}$ 6 Hz, H1; (**7b**) 0.87, $J_{2,5}$ 8 Hz, Me; 4.28, $J_{1,2}$ 8 Hz, H1; the following signals coincide 2.2 - 2.6, H2; 4.6 - 5.2, $(H4)_2$; 5.3 - 6.0, H3; 7.30, $W_{h/2}$ 4 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C (**7a**) 14.2, Me; 44.6, C2; 77.3, C1; 115.3, C4; 140.4, C3; (**7b**) 16.5, Me; 46.1, C2; 77.9, C1; 116.6, C4; 140.6, C3; (**7a, 7b**) 126.6, 126.8, 127.3, 127.6, 128.0, 128.2, 142.5, 142.7, phenyl carbons.

3-Phenyl-4-penten-2-ol. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with acetaldehyde (2 g, 50 mmol) in tetrahydrofuran (5 ml) and water (3 ml) to give an oil (3.2 g). Radial chromatography with 10% - 30% ether - petroleum ether mixtures gave (2RS, 3RS)-3-phenyl-4-penten-2-ol. (Found CIMS (C_4H_{10}): $M+H^+-H_2O$ = 145.1013; $C_{11}H_{13}$ requires 145.1017). υ_{max} 3425, 760, 705 cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ_H 1.16, $J_{1,2}$ 6 Hz, $(H1)_3$; 2.06, $W_{h/2}$ 6 Hz, OH; 3.23, $J_{2,3}$ 8 Hz, $J_{3,4}$ 8 Hz, H3; 4.03, $J_{1,2}$ 6 Hz, $J_{2,3}$ 8 Hz, H2; 5.03 - 5.43, $(H5)_2$; 5.9 - 6.66, H4; 7.33, $W_{h/2}$ 5 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 20.7, C1; 59.0, C3; 70.2, C2; 117.7, C5; 126.7, p; 128.0, 128.6, o, m; 138.5, C4; 141.6, i.

4-Phenyl-5-hexen-3-ol. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with propanal (1.16 g, 20 mmol) to give an oil (3.2 g). Radial chromatography gave (3RS, 4RS)-4-phenyl-5-hexen-3-ol. (Found CIMS (C_4H_{10}): $M+H^+-H_2O$ = 159.1165; $C_{12}H_{15}$ requires 159.1175). υ_{max} 3430, 1460, 710 cm^{-1} ^1H n.m.r. (CCl_4) δ_H 0.7 - 1.5, $(H1)_3$, $(H2)_2$; 1.8, $W_{h/2}$ 14 Hz, OH; 3.17, $J_{3,4}$ 8 Hz, $J_{4,5}$ 8 Hz, H4; 3.57, $J_{3,4}$ 8 Hz, $J_{2,3}$ 7 Hz, H3; 4.9 - 5.4, $(H6)_2$; 5.88 - 6.4, H5; 7.18, $W_{h/2}$ 3 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 10.0, C1; 27.3, C2; 56.9, C4; 75.4, C3; 117.6, C6; 126.6, p; 128.0, 128.7, o, m; 138.4, C5; 141.8, i.

2-Methyl-4-phenyl-5-hexen-3-ol. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with 2-methylpropanal (1.47 g, 20 mmol) to give an oil (3.6 g). Radial chromatography gave (3RS, 4RS)-2-methyl-4-phenyl-5-hexen-3-ol. (Found CIMS (C_4H_{10}): $M+H^+-H_2O$ = 173.1314; $C_{13}H_{17}$ requires 173.1331). υ_{max} 3450, 705 cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ_H 0.93, $W_{h/2}$ 12 Hz, $(H1)_3$, H2-Me; 1.33 - 1.83, H2; 1.76, $W_{h/2}$ 3 Hz, OH; 3.23 - 3.78, H3, H4; 5.0 - 5.4, $(H6)_2$; 5.9 - 6.6, H5; 7.3, $W_{h/2}$ 3 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 15.8, 20.1, C1, C2-Me; 29.8, C2; 54.6, C4; 78.5, C3; 117.4, C6; 126.5, p; 128.0, 128.7, o, m; 138.8, C5; 142.1, i. ArH. *(3RS, 4RS)-2-methyl-4-phenyl-5-hexen-3-yl-3,5-dinitrobenzoate* (**11**); m.p. 128 - 30°C. ^1H n.m.r. ($CDCl_3$) δ_H 0.95, $J_{1,2}$ 7 Hz, 1.1, $J_{1,2}$ 8 Hz, $(H1)_3$, C2-Me; 1.86, H2; 3.75, $J_{4,5}$ 9 Hz, $J_{3,4}$ 9 Hz, H4; 5.03, $J_{5,6a}$ 10 Hz, H6a; 5.04, $J_{5,6b}$ 17 Hz, H6b; 5.53, $J_{3,4}$ 9 Hz, $J_{2,3}$ 4 Hz, H3; 6.07, $J_{4,5}$ 9 Hz, $J_{5,6a}$ 10 Hz, $J_{5,6b}$ 17 Hz, H5; 7.18 - 7.35, 9.1 - 9.2, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 15.9, 20.0, C1, C2-Me; 29.1, C2; 53.3, C4; 82.8, C3; 117.4, C6; 138.0, C5; 162.3, C=O; 122.3, 127.2, 127.9, 129.0, 129.3, 140.3, phenyl carbons.

3-Phenyl-2-decen-4-ol. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with heptanal (2.28 g, 20 mmol) to give an oil (4.5 g). Radial chromatography gave (3RS, 4RS)-3-phenyl-2-decen-4-ol. (Found CIMS(C_4H_{10}): $M+H^+-H_2O$ = 215,1801; $C_{16}H_{23}$ requires 215.1801). υ_{max} 3450, 2950, 1070, 710 cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ_H 0.7 - 1.4, $(H5)_2$, $(H6)_2$, $(H7)_2$, $(H8)_2$, $(H9)_2$, $(H10)_3$; 1.75, $W_{h/2}$ 8 Hz, OH; 3.2, $J_{2,3}$ 8 Hz, $J_{3,4}$ 8 Hz, H3; 3.8, $W_{h/2}$ 14 Hz, H4; 5.0 - 5.4, H12; 5.8 - 6.6, H2; 7.3, $W_{h/2}$ 2 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 14.1, C10; 22.6, C9; 25.7, C6; 29.3, C7; 31.8, C8; 34.5, C5; 57.5, C3; 74.1, C4; 117.8, C1; 126.6, p; 128.7, o, m; 138.5, C2; 141.8, i.

1,3-Diphenyl-4-penten-2-ol. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with 1-phenylethanal (2.4 g, 20 mmol) to give (2RS, 3RS)-1,3-diphenyl-4-penten-2-ol as an oil (4.5 g). (Found CIMS (C_4H_{10}): $M+H^+-H_2O$ = 221.1314; $C_{17}H_{17}$ requires 221.1331). υ_{max} 3440, 750, 700 cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ_H 2.6, $J_{1,2}$ 6 Hz, $(H1)_2$; 3.3, $J_{2,3}$ 7 Hz, $J_{3,4}$ 7 Hz, H3; 3.83 - 4.16, H2; 4.96 - 5.36, $(H5)_2$; 5.83 - 6.63, H4; 7.23, $W_{h/2}$ 2 Hz, 7.33, $W_{h/2}$ 2 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 41.2, C1; 56.4, C3; 75.1, C2; 117.8, C5; 138.1, C4; 126.3, 126.7, 128.1, 128.4, 128.7, 129.4, 138.8, 141.7, phenyl carbons.

Epoxidation of (2RS, 3RS)-1,3-Diphenyl-4-penten-2-ol. To (2RS, 3RS)-1,3-diphenyl-4-penten-2-ol (**6b**) (200 mg) in dry ether (10 ml) was added metachloroperbenzoic acid (400 mg) and the solution kept at room temperature 72 hours. The solution was washed with saturated aqueous sodium bisulphite (10 ml), saturated aqueous sodium bicarbonate (10 ml) and water (10 ml) and dried with sodium sulphate. Removal of solvent gave an oil. υ_{max} 3425 cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ_H 2.33 - 2.93, $(H1)_2$, H3, $(H5)_2$; 3.27 - 3.6, H4; 3.93 - 4.37, H2; 7.0 - 7.57, ArH. Radial chromatography gave pure fractions of (2RS, 3RS, 4RS)-4,5-epoxy-1,3-diphenyl-4-penten-2-ol (**10b**); (Found CIMS(C_4H_{10}): $M+H^+-H_2O$ = 237.1309; $C_{17}H_{17}O$ requires 237.1280). ^{13}C n.m.r. ($CDCl_3$) δ_C 41.6, C1; 45.6, C5; 53.7, C4; 54.5, C3; 75.8, C2; 126.4, 127.3, 128.4, 128.8, 129.5, 138.4, 139.3, phenyl carbons and (2RS, 3RS, 4SR)4,5-epoxy-1,3-diphenyl-4-penten-2-ol (**10a**); (Found CIMS(C_4H_{10}): $M+H^+-H_2O$ = 237.1248; $C_{17}H_{18}O_2$ requires 254.1308). ^{13}C n.m.r. ($CDCl_3$) δ_C 41.9, C1; 46.8, C5; 53.0, C4; 53.5, C3; 74.2, C2; 126.5, 127.3, 128.5, 128.7, 128.8, 129.4, 129.5, 138.3, phenyl carbons.

1,2-Diphenyl-3-buten-1-ol. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with benzaldehyde (2.12 g, 20 mmol) to give (1RS, 2SR)-1,2-diphenyl-3-buten-1-ol[15] (**5b**) as an oil (3.2 g). ^1H n.m.r. (CCl_4) δ_H 7.1, $W_{h/2}$ 3 Hz, ArH.

1-(4-Cyanophenyl)-2-phenyl-3-buten-1-ol. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with 4-cyanobenzaldehyde (2.62 g, 20 mmol) to give a solid which was recrystallised from carbon tetrachloride to give (1RS, 2SR)-1-(4-cyanophenyl)-2-phenyl-3-buten-1-ol (3.6 g). M.p. 93 - 94°C. (Found: C, 81.4; H, 6.0; N,

5.3%; $C_{17}H_{15}NO$ requires C, 81.9; H, 6.1; N, 5.6%). (Found CIMS(C_4H_{10}): M+H$^+$ = 250.1222; $C_{17}H_{16}NO$ requires 250.1233). υ_{max} 3425, 2250, 1055, 760, 710 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$) δ_H 2.63, $W_{h/2}$ 7 Hz, OH; 3.41, $J_{1,2}$ 8 Hz, $J_{2,3}$ 8 Hz, H2; 4.85, $J_{1,2}$ 8 Hz, H1; 4.96 - 5.35, (H4)$_2$; 6.18, $J_{2,3}$ 8 Hz, $J_{3,4\ trans}$ 16 Hz, $J_{3,4\ cis}$ 10 Hz, H3; 7.23, $W_{h/2}$ 20 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 59.2, C2; 76.5, C1; 110.9, p'; 119.0, C4; 127.0, p, 127.3, 128.2, 128.6, m, o', o; 131.6, m'; 136.9, C3; 139.8, i; 147.4, i'; CN not observed.

1-(4-Methoxyphenyl)-2-phenyl-3-buten-1-ol. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with 4-methoxybenzaldehyde (2.72 g, 20 mmol) to give an oil (3.87 g). Radial chromatography gave (1RS, 2SR)-1-(4-methoxyphenyl)-2-phenyl-3-buten-1-ol. (Found CIMS(C_4H_{10}): M+H$^+$ = 255.1394; $C_{17}H_{19}O_2$ requires 255.1386). υ_{max} 3450, 1520, 1240, 1035, 765, 710 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$) δ_H 2.25, $W_{h/2}$ 8 Hz, OH; 3.5, $J_{1,2}$ 8 Hz, $J_{2,3}$ 8 Hz, H2; 3.83, $W_{h/2}$ 2 Hz, OCH_3; 4.9, $J_{1,2}$ 8 Hz, H1; 5.06 - 5.46, (H4)$_2$; 6.06 - 6.66, H3; 6.73 - 7.5, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 55.1, OMe; 59.2, C2; 76.8, C1; 113.3, m'; 118.1, C4; 126.5, p; 127.8, 18.3, 128.4, o, m, o'; 134.1, i'; 138.2, C3; 140.8, i; 158.8, p'.

1-(9-Anthracenyl)-2-phenyl-3-buten-1-ol. (E)-3-Chloro-1-phenylpropene (1.6 g, 10 mmol) was reacted with 9-anthraldehyde (93%, 2.25 g, 6.6 mmol)to give a solid (3.52 g) which was recrystallised from benzene to give (1RS, 2RS)-1-(9-anthracenyl)-2-phenyl-3-buten-1-ol. **(9)** M.p. 153 - 4°C. (Found: C, 89.1; H, 6.4%. $C_{24}H_{20}O$ requires C, 88.9; H, 6.2%). (Found: M$^+$-OH = 307.1488; $C_{24}H_{19}$ requires 307.1488). ^{1}H n.m.r. ($CDCl_3$) δ_H 2.73, $W_{h/2}$ 12 Hz, OH; 4.46, $J_{1,2}$ 9 Hz, $J_{2,3}$ 9 Hz, H2; 5.25 - 5.52, (H4)$_2$; 6.25, $J_{1,2}$ 9 Hz, H1, H3; 6.77, $W_{h/2}$ 4 Hz, ArH; 7.17 - 7.5, 7.73 - 8.0, 8.2 - 8.67, Anthracenyl H. ^{13}C n.m.r. ($CDCl_3$) δ_C 57.0, C2; 73.3, C1; 118.3, C4; 138.5, C3; 124.4, 125.1, 126.2, 127.7, 128.3, 129.0, 129.9, 131.3, 132.1, phenyl and anthracenyl carbons.

3-Phenylhept-1,5-dien-4-ol. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with (E)-2-butenal (1.4 g, 20 mmol) to give (3RS, 4RS)-(E)-3-phenylhept-1,5-dien-4-ol **(12b)** as an oil (4.8 g). (Found CIMS (C_4H_{10}): M+H$^+$ = 189.1283; $C_{13}H_{17}O$ requires 189.1280). υ_{max} 3425 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$) δ_H 1.56, $J_{6,7}$ 5 Hz, (H7)$_3$; 3.3, $J_{2,3}$ 8 Hz, $J_{3,4}$ 8 Hz, H3; 4.26, $J_{3,4}$ 6 Hz, $J_{4,5}$ 6 Hz, H4; 5.0 - 5.4, H2; 5.1 - 5.7, H5, H6; 5.8 - 6.6, (H1)$_2$; 7.26, $W_{h/2}$ 4 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 17.7, C7; 57.3, C3; 75.2, C4; 117.7, C1; 126.6, p; 127.9, C6; 128.4, o, m; 131.4, C5, 138.2, C2; 141.0, i.

1,4-Diphenylhexa-1,5-dien-3-ol. (E)-3-chloro-1-phenylpropene (3 g, 20 mmol) was reacted with (E)-1-phenylpropenal (2.64 g, 20 mmol) to give an oil (4.38 g). Radial chromatography gave (3RS, 4RS)-(E)-1,4-diphenylhexa-1,5-dien-3-ol **(13b)**. (Found CIMS (C_4H_{10}): M+H$^+$-H_2O = 233.1349; $C_{18}H_{17}$ requires 233.1331). υ_{max} 3450, 1500, 1455, 755, 705 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$) δ_H 2.08, $W_{h/2}$ 12 Hz, OH; 3.53, $J_{4,5}$ 7 Hz, $J_{3,4}$ 7 Hz, H4; 4.6, $J_{2,3}$ 7 Hz, $J_{3,4}$ 7 Hz, H3; 5.1 - 5.46, H5, H1, H2; 7.36, $W_{h/2}$ 4 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 57.4, C4; 75.0, C3; 118.0, C6; 129.8, 131.0, C1, C2; 137.8, C5; 126.5, 126.8, 127.5, 128.5, 128.6, 140.6, phenyl carbons.

5-Methyl-3-phenyl-1-hepten-4-ols. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with 2-methylbutanal (1.7 g, 20 mmol) to give an oil (1.27 g) a mixture (2:5) of (3RS, 4RS, 5RS)-3-phenyl-5-methyl-1-hepten-4-ol and (3RS, 4RS, 5SR)-3-phenyl-5-methyl-1-hepten-4-ol **(16i, 16ii)**. (Found CIMS (C_4H_{10}): M+H$^+$-H_2O = 187.1494; $C_{14}H_{19}$ requires 187.1488). υ_{max} 3425, 1710, 700 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$) δ_H 0.79 - 0.94, (H7)$_3$, C5-Me; 1.0 - 1.7, (H6)$_2$, H5; 3.36, $J_{3,4}$ 7 Hz, $J_{4,5}$ 7 Hz, **(16ii)**-H4; 3,47, $J_{3,4}$ 6.5 Hz, $J_{4,5}$ 9 Hz, **(16i)**-H4; 3.61, $J_{3,4}$ 6.5 Hz, $J_{2,3}$ 5.3 Hz, **(16i)**-H3; 3.78, $J_{3,4}$ 7 Hz, $J_{2,3}$ 2.8 Hz, **(16ii)**-H3; 5.16 - 5.23, (H1)$_2$; 6.09, J=9.5 Hz, J=9.5 Hz, J=17.5 Hz, **(16ii)**-H2; 6.16, J=9 Hz, J=10.2 Hz, J=17 Hz, **(16i)**-H2; 7.15 - 7.35, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C **(16i)** 11.5, 16.1, C7, C5-Me; 23.2, C6; 36.7, C5; 53.9, C3; 78.5, C4; 117.6, C1; 138.1, C2. **(16ii)** 11.7, 12.3, C7, C5-Me; 27.0, C6; 35.8, C5; 55.0, C3; 75.8, C4; 117.3, C1; 139.7, C2. **(16i, 16ii)** 126.5, 127.9, 128.0, 128.1, 128.7, 141.7, phenyl carbons.

5,7,7-Trimethyl-3-phenyl-1-octen-4-ols. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with 2,4,4-trimethylpentanal (2.56 g, 20 mmol) to give an oil (5.13 g). Radial chromatography gave a mixture (>90:10) of (3RS, 4RS, 5SR)- and (3RS, 4RS, 5RS)-5,7,7-trimethyl-3-phenyl-1-octen-4-ol **(17ii, 17i)**. (Found CIMS (C_4H_{10}): M+H$^+$-H_2O = 229.1933; $C_{17}H_{25}$ requires 229.1958). υ_{max} 3450, 3000, 1710, 705 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$) δ_H 0.7, $W_{h/2}$ 2 Hz, C7-Me$_2$, (H8)$_3$; 0.7 - 1.66, H5, C5-Me, (H6)$_2$; 3.16, $J_{2,3}$ 8 Hz, $J_{3,4}$ 8 Hz, H3; 3.56, $J_{3,4}$ 8 Hz, $J_{4,5}$ 2 Hz, H4; 4.9 - 5.26, (H1)$_2$; 5.7 - 6.46, H2; 7.1, $W_{h/2}$ 3 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) **(17ii)** δ_C 14.6, C5-Me; 29.6, C7-Me$_2$, C8; 30.2, C6; 31.1, C7; 49.2, C5; 55.4, C3; 78.5, C4; 117.3, C1; 140.0, C2; 126.6, 127.9, 128.7, 141.5, phenyl carbons. Partial assignment only was possible for **(17i)** 20.3, C5-Me; 44.7, C5; 53.9, C3; 79.5, C4; 117.5, C1.

2,4-Diphenyl-5-hexen-3-ols. (E)-3-Chloro-1-phenylpropene (1.5 g, 10 mmol) was reacted with 2-phenylpropanal (1.34 g, 10 mmol) to give an oil (1.93 g). Radial chromatography gave a mixture (3:1) of (2RS, 3SR, 4SR)- and (2RS, 3RS, 4RS)-2,4-diphenyl-5-hexen-3-ol **(18ii, 18i)**. (Found CIMS(C_4H_{10}): M+H$^+$-H_2O = 235.1471; $C_{18}H_{19}$ requires 235.1488). υ_{max} 3475, 1495, 1455, 705 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$) δ_H 1.07 - 1.43, (H1)$_3$; 1.82, $W_{h/2}$ 6 Hz, OH; 2.75, $J_{3,4}$ 6 Hz, H4; 3.42, $J_{1,2}$ 7 Hz, $J_{2,3}$ 7 Hz, H2; 3.93, $J_{2,3}$ 7 Hz, $J_{3,4}$ 6 Hz, H3; 5.03 - 5.37, H6; 5.83 - 6.63, (H5)$_2$; 7.27, $W_{h/2}$ 4 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C **(18ii)** 15.2, C1; 42.0, C2; 53.6, C4; 78.6, C3; 117.8, C6; 137.7, C5; and **(18i)** 19.2, C1; 42.5, C2; 54.0, C4; 78.1, C3; 117.5, C6; 138.0, C5; **(18ii, 18i)** 126.3, 126.6, 127.8, 127.9, 128.3, 128.4, 128.5, 128.7, 142.3, 145.1, phenyl carbons. *2,4-Diphenyl-5-hexen-3-yl 3,5-dinitrobenzoates.* A solid mixture (ca. 4:1) of (2RS, 3SR, 4SR)- and (2RS, 3RS, 4RS)-2,4-diphenyl-5-hexen-3-yl 3,5-dinitrobenzoate was obtained. υ_{max} 1730 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$) δ_H 1.37, $J_{1,2}$ 7 Hz, (H1)$_3$; 3.1, $J_{3,4}$ 7 Hz, H2; 3.43 - 3.8, H4; 4.87 - 5.27, H6; 5.8, $J_{2,3}$ 6 Hz, $J_{3,4}$ 6 Hz, H3; 7.27, $W_{h/2}$ 4 Hz, 8.9 - 9.2, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C **(20a)** 15.6, C1; 40.9, C2; 53.3, C4; 82.7, C3; 118.5, C6; 132.5, C5; 161.8, C=O. **(20b)** 19.0, C1; 41.2, C2; 52.5, C4; 81.9, C3; 117.7, C6; 137.2, C5; **(20a,20b)** 122.3, 127.0, 127.1, 127.6, 127.7, 128.2, 128.4, 128.7, 129.0, 129.2, 140.5, 142.8, 148.7, phenyl

carbons. This mixture was recrystallised from ethanol to give crystals of (2RS, 3SR, 4SR)-2,4-diphenyl-5-hexen-3-yl 3,5-dinitrobenzoate (20a) m.p. 126 - 7°C. ^{13}C n.m.r. δ_C 15.6, 40.9, 52.5, 82.8.

(2RS, 4SR)- and (2RS, 4RS)-2,4-diphenyl-5-hexen-3-one. A mixture (ca. 3:1) of (2RS, 3SR, 4SR)- and (2RS, 3RS, 4RS)-2,4-diphenyl-5-hexen-3-ols (18ii, 18i) (500 mg), prepared from reaction of (E)-3-chloro-1-phenylpropene and 2-phenylpropanal in the presence of tin and aluminium, in dichloromethane (4 ml) was added to a vigorously stirred mixture of pyridinium chlorochromate (1.96 g), anhydrous sodium acetate (0.11 g) and dichloromethane (50 ml) to give a mixture (ca. 3:1) of (2RS, 4SR)- and (2RS, 4RS)-2,4-diphenyl-5-hexen-3-one (19b, 19a) as an oil (450 mg). υ_{max} 1700 cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ_H 1.17 - 1.53, $(H1)_3$; 3.96, $J_{1,2}$ 7 Hz, H2; 4.53, $J_{4,5}$ 8 Hz, H4; 4.93 - 5.37, $(H6)_2$; 5.76 - 6.67, H5; 6.83 - 8.17, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C (19b) 18.0, C1; 52.1, C2; 61.3, C4; 117.8, C6; 129.0, C5; 183.7, C3; and (19a) 26.5, C1; 51.4, C2; 60.6, C4; 116.7, C6; 136.6, C5; (19a, 19b) 126.9, 127.2, 128.1, 128.3, 128.5, 128.7, 129.0, 137.8, 139.8, phenyl carbons.

1,4-Di-(2-phenyl-3-buten-1-ol)-benzenes. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with terephthaldicarboxaldehyde (1.34 g, 10 mmol) to give 1,4-di-(2-phenyl-3-buten-1-ol)-benzene (26) as an oil (3 g). (Found CIMS(C_4H_{10}): M+H$^+$-H_2O = 353.1860, M-PhCHCH=CH_2 = 253.1232, M-PhCHCH=CH_2-H_2O = 235.1133; $C_{26}H_{25}O$ requires 353.1907). υ_{max} 3425, 1060, 915, 740, 705 cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ_H 2.36, $W_{h/2}$ 10 Hz, OH; 3.4 - 3.51, H2, H2'; 4.73 - 4.84, H1, H1'; 5.13 - 5.25, $(H4)_2$; 6.12 - 6.26, H3, H3'; 6.92 - 7.38, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 59.0, 59.3, C2, C2'; 76.9, C1, C1'; 118.1, 118.2, C4, C4'; 137.5, 137.6, C3, C3'; 125.97, 126.02, 126.3, 128.1, 128.3, 128.4, 140.2, 140.7, phenyl carbons.

3,6-Diphenylocta-1,7-dien-4,5-diols

(i) From glyoxal. (E)-3-chloro-1-phenylpropene (6 g, 40 mmol) was reacted with a 40% w/w solution of glyoxal (21) in water (2.9 g, 20 mmol) to give an oil (2.2 g) shown to be a mixture of four stereoisomers, (3RS, 4SR, 5RS, 6SR)-, (3RS, 4SR, 5SR, 6RS)-, (3RS, 4RS, 5RS, 6SR)- and (3RS, 4RS, 5SR, 6RS)-3,6-diphenylocta-1,7-dien-4,5-diol (24a-d). υ_{max} 3450, 705 cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ_H crude 3.4 - 3.7, 3.9 - 4.1, H3, H4, H5, H6; 5.0 - 5.3, H1, H8; 5.80, J=17.1 Hz, J=10.2 Hz, J=8.8 Hz, 5.95, J=17.7 Hz, J=9.6 Hz, J=8.6 Hz, 5.99, J=17 Hz, J=10.1 Hz, J=9 Hz, 6.14, J=16.5 Hz, J=10.6 Hz, J=8.8 Hz, 6.25, J=17 Hz, J=10 Hz, J=9 Hz, H2, H7; 6.9 - 7.5 ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C crude 53.8, 54.0, C3, C6; 72.0, 72.1, 72.5, 72.7, C4, C5; 117.1, 117.3, 117.4, 117.5, C1, C8; 138.0, 138.2, 139.3, C2, C7; 126.4, 126.7, 126.8, 128.1, 128.2; 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 140.7, 140.9, 141.1, phenyl carbons. Radial chromatography gave a mixture of 3,6-diphenylocta-1,7-dien-4,5-diols (Found CIMS (NH_3): M+NH_4^+ = 312.2006; $C_{20}H_{26}O_2N$ requires 312.1965). ^1H n.m.r. ($CDCl_3$) δ_H 2.27, $W_{h/2}$ 18 Hz, OH; 3.41 - 3.66, 3.94 - 4.06, H3, H4, H5, H6; 5.08 - 5.22, H1, H8; 5.74 - 6.61, H2, H7; 6.95 - 7.37, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 53.9, 54.2, C3, C6; 72.0, 72.1, 72.6, C4, C5; 117.1, 117.2, 117.3, 117.5, C1, C8; 138.0, 139.3, C2, C7; 126.8, 128.2, 128.3, 128.7, 128.8, 140.7, 140.9, phenyl carbons; and a second fraction gave the pure diastereomer (24b). ^1H n.m.r. ($CDCl_3$) δ_H 2.17, $W_{h/2}$ 10 Hz, OH; 3.33 - 3.83, H3, H4, H5, H6; 4.92 - 5.33, H1, H8; 5.5 - 6.75, H2, H7; 7.33, $W_{h/2}$ 10 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 54.2, C3, C6; 72.0, C4, C5; 117.4, C1, C8; 139.3, C2, C7; 126.7, 128.1, 128.4, 128.5, 128.7, 128.9, 140.6, phenyl carbons. *3,6-Diphenylocta-1,7-dien-4,5-diol acetonides*[42]. A solution of a (3RS, 4SR, 5RS, 6SR)-3,6-diphenylocta-1,7-dien-4,-diol (24b) (24 mg) and anhydrous ferric chloride (20 mg) in anhydrous acetone (5 ml) was heated under reflux for 30 minutes. The mixture was cooled and aqueous potassium carbonate (1 ml, 10%) and water (5 ml) was added. The mixture was extracted with dichloromethane (3 x 10 ml) and the combined organic extracts washed with water (10 ml), dried with sodium sulphate and the solvent evaporated to give 3,6-diphenylocta-1,7-dien-4,5-diol acetonide (25b) as an oil (27 mg). (Found: M$^+$ = 334.192170; $C_{23}H_{26}O_2$ requires 334.1934). ^1H n.m.r. ($CDCl_3$) δ_H 1.23, $W_{h/2}$ 2 Hz, 1.43, $W_{h/2}$ 2 Hz, $(H9)_3$, $(H10)_3$; 2.75 - 2.85, H3, H6; 4.0 - 4.2, H4, H5; 4.73 - 5.3, $(H1)_2$, $(H8)_2$; 6.15, $J_{7,8a}$ 16.8 Hz, $J_{7,8b}$ 9.8 Hz, $J_{6,7}$ 7.8 Hz, H2, H7; 7.23, $W_{h/2}$ 12 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 27.4, C9, C10; 53.0, C3, C6; 81.9, C4, C5; 108.7, C11; 116.9, C8, C1; 126.8, p; 128.4, 128.6, o, m; 137.6, C2, C7; 141.0, i.

(ii) From 2,3-dihydroxy-1,4-dioxane. (E)-3-Chloro-1-phenylpropene (3 g, 20 mmol) was reacted with 2,3-dihydroxy-1,4-dioxane (22) (1.2 g, 10 mmol) to give an oil (2.59 g) shown by ^{13}C n.m.r. to be a mixture of four stereoisomers, (3RS, 4SR, 5RS, 6SR)-, (3RS, 4SR, 5SR, 6RS)-, (3RS, 4RS, 5RS, 6SR)- and (3RS, 4RS, 5SR, 6RS)-3,6-diphenylocta-1,7-dien-4,5-diol (24a-d). υ_{max} 3450, 705 cm^{-1}. ^1H n.m.r. (CCl_4) δ_H 3.17 - 3.83, H3, H4, H5, H6; 4.67 - 5.17, H1, H8; 5.33 - 6.5, H2, H7; 7.17, $W_{h/2}$ 10 Hz, ArH. ^{13}C n.m.r. ($CDCl_3$) δ_C 53.8, 54.0, 54.1, C3, C6; 72.0, 72.1, 72.5, 72.7, C4; C5; 117.1, 117.3, 117.4, C1, C8; 138.0, 138.1, 139.3, C2, C7; 126.3, 126.4, 126.7, 126.8, 127.5, 127.6, 127.8, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 140.6, 140.9, 141.1, phenyl carbons.

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28 The addition of large quantities of hydrobromic acid did not effect the course of the reaction.

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30 If *trans* crotyltin undergoes isomerization to the *cis* isomer, involving a 1,3-tin migration, *erythro* selectivity could occur through a cyclic transition state. This has been excluded[34] by the following experiments: reaction of *trans* crotyl tributyltin with benzaldehyde in the presence of $BF_3.OEt_2$ was quenched immediately at -78°C with MeOH-H_2O and no isomerization of the recovered crotyltin could be detected. The reaction of isomeric 1-methylallyltin with benzaldehyde under the same conditions produced 1-phenyl-3-penten-1-ol in high yield.

31 66.6% *trans* crotyl dibutyltin chloride; 33.4% *cis* crotyl dibutyltin choride.

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35 60% *trans* crotyl tributyltin; 40% *cis* crotyl tributyltin.

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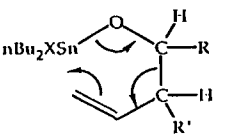
37 The presence of Lewis acid coordinated to aldehyde will reduce *threo* selectivity and favour of *erythro* formation by reducing the importance of a cyclic mechanism. The *erythro*-selectivity of the reactions of both *cis* and *trans* crotyl organotins reacting with aldehydes in the presence of boron trifluoride etherate has been suggested to result from the removal of the availability of the carbonyl oxygen as a ligand to the tin metal centre hence forcing a linear transition state with resultant *erythro* selectivity.[34,36] An X-ray crystallographic study has shown BF_3 to be complexed *anti* to the benzaldehyde phenyl group and this is supported in solution by heteronuclear Overhauser experiments. M T Reetz, M Hüllmann, W Massa, S Berger, P Rademacher, P Heymanns; *J. Am. Chem. Soc.* 108 (1986) 2405-2408.

38 Tagliavini et. al. showed that the ability of $RCH{=}CHCH_2)SnBu_{3-n}Cl_n$ (R = H, CH_3; n = 0,1,2,3) to bring about allylstannylation of ketones and aldehydes increases with the value of n; that is with increasing acceptor ability of the tin centre. The pericyclic reaction which occurs on reaction of a *threo* and *erythro* homoallylic alcohols with $(Bu_3Sn)_2O$ and $(Bu_2SnCl)_2O$ produces *trans*-allyltins and *cis*-allyltins respectively providing evidence for a cyclic transition state. This supports the contention[22] that the cyclic mechanism becomes more important the more polarised the carbon tin bond.



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