β-Halogeno-ether Synthesis of Olefinic Alcohols: Stereochemistry of the Ring-scission of 2-Substituted 3-Halogenotetrahydro-pyrans and -furans

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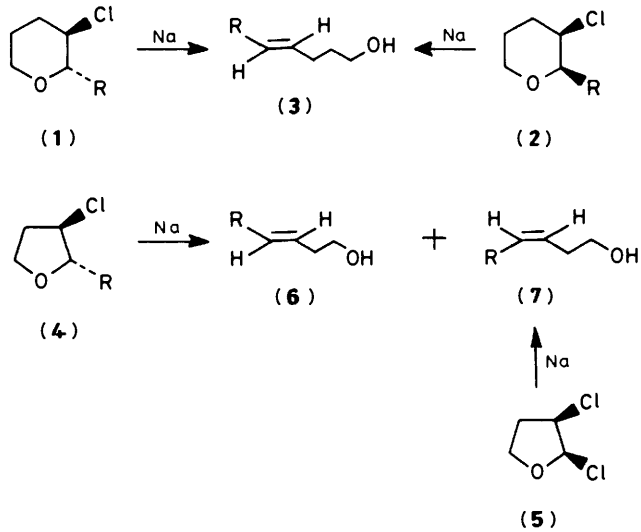
The stereochemical outcome of the sodium ring-scission of 2-substituted 3-halogenotetrahydro-pyrans and -furans, with 2-substitution represented by alkyl, alkenyl or aryl, is presented. Although the *cis*- and the *trans*-tetrahydropyran scissions are highly stereoselective for (*E*)-5-substituted pent-4-enols, this stereoselectivity breaks down when the 2-substituent is conformationally undiscriminating (deuterium) or has substantial anomeric effects (methoxy). Consideration of this, along with conformational data from the preceding paper, provides an explanation of the stereoselectivity of the tetrahydropyran scission. Evidence against a radical, and for a carbanion intermediate is presented and a common, very rapidly inverting, 3-carbanion is considered to be formed from either *cis*- or *trans*-stereoisomers. Ring scission is also rapid (the carbanion cannot be trapped), but less rapid than carbanion inversion, and takes place before the slower conformational inversion can occur so that the (*E*)/(*Z*)-nature of the unsaturated alcohol produced is controlled by the initial tetrahydropyran conformation. The unstereospecific nature of the ring scission of both *cis*- and *trans*-2-alkyl-3-chlorotetrahydrofurans is explained as a consequence of their existence in conformational equilibria.

The high stereoselectivity of the ring scission of *cis*- and *trans*-3-chloro-2,3-dimethyltetrahydropyrans, and the poor stereoselectivity of the scission of 2-alkyl-2-3-chloro-2-methyltetrahydropyrans, is explained; the reaction of sodium with 2-butyl-3,3-dichlorotetrahydropyran is considered. Using the ring-scission of 3-chloro-2-ethyltetrahydropyran, short syntheses of (±)-*exo*-and (±)-*endo*-brevicomin are described to illustrate the utility of β-halogen ether synthesis.

It has been shown that on treatment with powdered sodium both the *cis*- and the *trans*-stereoisomers of 3-chloro-2-methyltetrahydropyran (**2**; R = Me) and (**1**; R = Me) give (*E*)-hex-4-enol (**3**; R = Me), regiospecifically and in high yield, and with high *trans*-stereoselectivity.[1] Since that time many similar ring scissions with R = primary or secondary alkyl, or aryl, have been carried out, all with high *trans*-stereoselectivity.[2] By contrast ring scission of *cis*- or *trans*-2-alkyl-3-chlorotetrahydrofurans (**5**) and (**4**) does not lead to alk-3-enols having a single geometry.[1] The reaction proceeds regiospecifically in excellent yield but the *trans*-isomer (**4**) gives an (*E*)-(**6**)/(*Z*)-(**7**) mixture containing 80—87% (*E*) whilst the *cis*-isomer (**5**) gives a mixture containing 56—57% (*E*), as determined by i.r. analysis.[3] The present investigation was undertaken to gain an understanding of the reason for differences in stereoselectivity in these and a number of cognate ring-scission reactions.

Results for the sodium ring-scission of three pairs of 2-alkyl-3-chlorotetrahydropyrans are given in Table 1. Within usual scrutiny by ^{1}H n.m.r. and i.r. spectroscopy the products appear to be purely (*E*)-isomers and they have been used preparatively as such with success on many occasions. However, close scrutiny by ^{13}C n.m.r. spectroscopy indicates that a few percent of the (*Z*)-isomer are formed, *e.g.* for the case R = Pr^i, integration shows 3.8—4.3% (*Z*)-configuration. Consequently, a limit of (*E*)-purity of >95% is set on the examples. Other more complicated cases were also looked at. Thus 3-chloro-2-vinyltetrahydropyran, as a *cis*/*trans*-mixture (**8**) and employing a 0.5 molar excess of sodium gave four product alcohols which eluted on g.l.c. (PEGA) in the order (**9**) (16%), (**10**) (37%), (**11**) (22%), and (**12**) (12%). Using an excess of the halide gave the dienol (**12**) in much higher yield (80% of the mixture) though the remaining 20% was still made up of over-reduction products. A sample of pure hepta-4,6-dien-1-ol was isolated by preparative g.l.c. and showed the 4-H resonance as a doublet of triplets, *J* 7 and 17 Hz signifying the expected (4*E*) geometry.

The related case of the 2-propenyl derivative, examined as the mixture of (*E*)-*cis*/*trans* and (*Z*)-*cis*/*trans* compounds (**13**) and

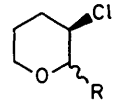


Scheme 1.

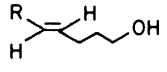
(**14**) formed by treating 2,3-dichlorotetrahydropyran with prop-1-enylmagnesium bromide, proceeded, on sodium ring scission, without any appreciable accompanying over-reduction. G.l.c. and n.m.r. [Pr(fod)$_3$] analysis showed the product to be a mixture of 4(*E*), 6(*Z*)- and 4(*E*), 6(*E*)-stereoisomers (**15**) and (**16**) (ratio 58:42). No product with (4*Z*)-configuration was detected and the praseodymium shifted spectrum ($CDCl_3$) showed only two methyl doublets with the lanthanide shift for (**15**) > than that for (**16**). The 4-H resonances shifted as two symmetrically overlapping doublets of triplets (*J* 7 and 17 Hz). The ring scission situation is thus stereochemically similar to the first three entries in Table 1. The aryl entries also fall into line.

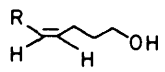
On the other hand the entries for 3-chloro-2-deuteriotetrahy-

Table 1. (*E*)- and (*Z*)-Alk-4-en-1-ols by ring scission of 2-substituted-3-chlorotetrahydropyrans with sodium in ether



Ring scission alcohols[a]

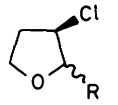




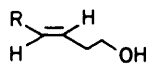
	(*E*) %	(*Z*) %
cis- R = Me	>95	<5
trans- R = Me		
cis- R = Et	>95	<5
trans- R = Et		
cis- R = Pr^i	>95	<5
trans- R = Pr^i		
trans- R = Ph[b]	>95	<5
trans- R = *p*-MeC$_6$H$_4$[c]	>95	<5
cis- R = D (28—35%)[d] [e]	64	36
trans- R = D (65—72%)[d] [e]		
cis- R = OMe (78%)[f] [g]	60	40
trans- R = OMe (22%)[f] [g]		

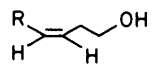
[a] Analysis by ^{1}H n.m.r. and [Eu(fod)$_3$] shift reagent and/or g.l.c. (±4%). [b] 30% 5-Phenylpentan-1-ol was also formed. [c] 20% 5-*p*-Tolylpentan-1-ol was also formed; this was reduced to 2% by using sodium in toluene. [d] Analysis by ^{1}H n.m.r. using i, direct integration; ii, the same, after addition of [Eu(fod)$_3$]. [e] The corresponding 3-bromo compound (65—70% *trans*) also gave 64% (*E*)- and 36% (*Z*)-alcohol. [f] Analysis by ^{1}H n.m.r. using direct integration. [g] The corresponding 3-bromo compound (73% *trans*) gave 74% (*E*)- and 26% (*Z*)-alcohol.

Table 2. (*E*)- and (*Z*)-Alk-3-en-1-ols by ring scission of 2-substituted-3-chlorotetrahydrofurans with sodium in ether



Ring scission alcohols[a]





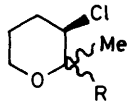
	(*E*) %	(*Z*) %
cis- R = Me[g]	53	47
trans- R = Me[b,g]	82	18
cis- R = Pr	53	47
trans- R = Pr[c]	83	17
cis- R = Pr^i	53	47
trans- R = Pr^i	82	18
cis- R = CH_2=$CHCH_2$	53	47
trans- R = CH_2=$CHCH_2$	82	18
trans- R = Ph[d]	90	10
trans- R = *p*-MeC$_6$H$_4$[e]	90	10
cis- R = D [f]	58	42
trans- R = D [f]		

[a] Analysis by ^{1}H n.m.r. + [Eu(fod)$_3$] shift reagent and/or g.l.c. (±4%). [b] The corresponding *trans*-bromo compound gave 71% (*E*)- and 29% (*Z*)-alcohols. [c] The corresponding *trans*-bromo compound gave 74% (*E*)- and 26% (*Z*)-alcohols. [d] Product was 70% 4-phenylbut-3-en-1-ols plus 30% 4-phenylbutan-1-ol. Using sodium in toluene only 6% of saturated material was found. [e] Product was 80% *p*-tolylbut-3-en-1-ols plus 20% 4-*p*-tolylbutanol. [f] The relative *cis*-/*trans*-proportions for the tetrahydrofuran were not available. [g] Literature determination by i.r. methods:[3] the *cis*-furan gave 57(*E*):43(*Z*) and *trans*-furan gave 87(*E*):13(*Z*).

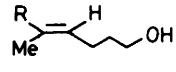
dropyran and 3-chloro-2-methoxytetrahydropyran are clearly out of line, giving (*E*)/(*Z*) mixtures. These are important cases, providing some insight into the control of a stereoselective ring-scission, and will be discussed later.

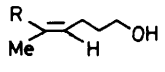
Data for 2-alkyl-3-chlorotetrahydrofurans (Table 2), obtained by n.m.r. and/or g.l.c. methods agreed with our early i.r. estimates,[3] none of the scissions showing high stereoselectivity. Ring scission of *trans*-3-chloro-2-phenyltetrahydrofuran gave 4-phenylbut-3-en-1-ol but the reaction was accompanied by some reduction of the styryl group when sodium in ether was used. The 2-*p*-tolyl compound behaved similarly but it was found that the use of sodium in toluene reduced the amount of over-reduction to only a few percent. The ring-scission alcohol was a 9:1 (*E*)/(*Z*) mixture in each case and pure (*E*) (**17**) was particularly easy to obtain, (m.p. 53 °C), by crystallisation.

Table 3. (*E*)- and (*Z*)-5-Methylalk-4-en-1-ols by ring scission of 2-substituted-3-chloro-2-methyltetrahydropyrans with sodium in ether



Ring scission alcohols[a]





	(*E*) %	(*Z*) %
cis-/*trans*- R = Et (*ca.* 3:2)[b]	44	54
cis-/*trans*- R = Bu (10:90)[b]	50	50
cis-/*trans*- R = Bu (39:61)[b]	54	46
cis-/*trans*- R = Bu (60:40)[b]	58	42
cis[c]- R = Pr^i	62	38
trans-[d] R = Pr^i	74	26
R = Ph[b,e]	65	35

[a] Analysis by ^{1}H n.m.r. using [Eu(fod)$_3$] where necessary, or by g.l.c. [b] The actual *cis* and *trans* assignments are uncertain. [c] *cis*- Here means the halogen with reference to the 2-Me. [d] *trans*- Here means the halogen with reference to the 2-Me. [e] In toluene, 71% (*E*), 29% (*Z*).

Attention was then turned to the stereochemistry of the ring scission of 2-substituted-3-chloro-2-methyltetrahydropyrans (Table 3). The two separated 2-isopropyl stereoisomers show that mixtures of (*E*)- and (*Z*)-alcohols are formed by either the *cis*- or *trans*-isomer and the results with the *cis*-/*trans*-mixtures of the 2-n-butyl compound are in agreement, even though the precursor mixture could not be completely separated. Isomer ratios for these trisubstituted olefinic alchols were obtained by integration using [Eu(fod)$_3$]-shifted spectra. Apart from the quantitative aspect such data permit identification of the (*E*) or (*Z*) geometry. The shift reagent complexes with the alcohol as shown in (**26**) and (**27**) and values of θ were obtained either from a plot of induced shift *versus* molar ratio of shift reagent to substrate, or where the shift was substantial, a single measurement.[4] Mixtures of (*Z*)- and (*E*)-alcohols can thus be investigated quantitatively without isolation. All our values do not fall within Van Rein's limits[4] but they are readily interpreted and (**28**)—(**31**) illustrate some examples. In the case of the 5-phenylhex-4-en-1-ols (Table 3) configurations were assigned through chemical shifts of the 4-protons. For the (*Z*)-alcohol this was a triplet of quartets (*J* 7.5, 1.5 Hz) at δ5.42 (calculated δ5.33 by Pascual's formula*).[5] For the (*E*)-alcohol it was also a triplet of quartets (*J* 7.5, 1.5 Hz) but at δ5.75 (calculated 5.77).

Not unexpectedly, the 2-substituted-3-chloro-2-methyltetrahydrofurans also show little stereoselectivity as reflected by

* δC=C–H = 5.25 + $\Sigma_i Z_i$ (Used with a table of shielding coefficients) (*Z* values).

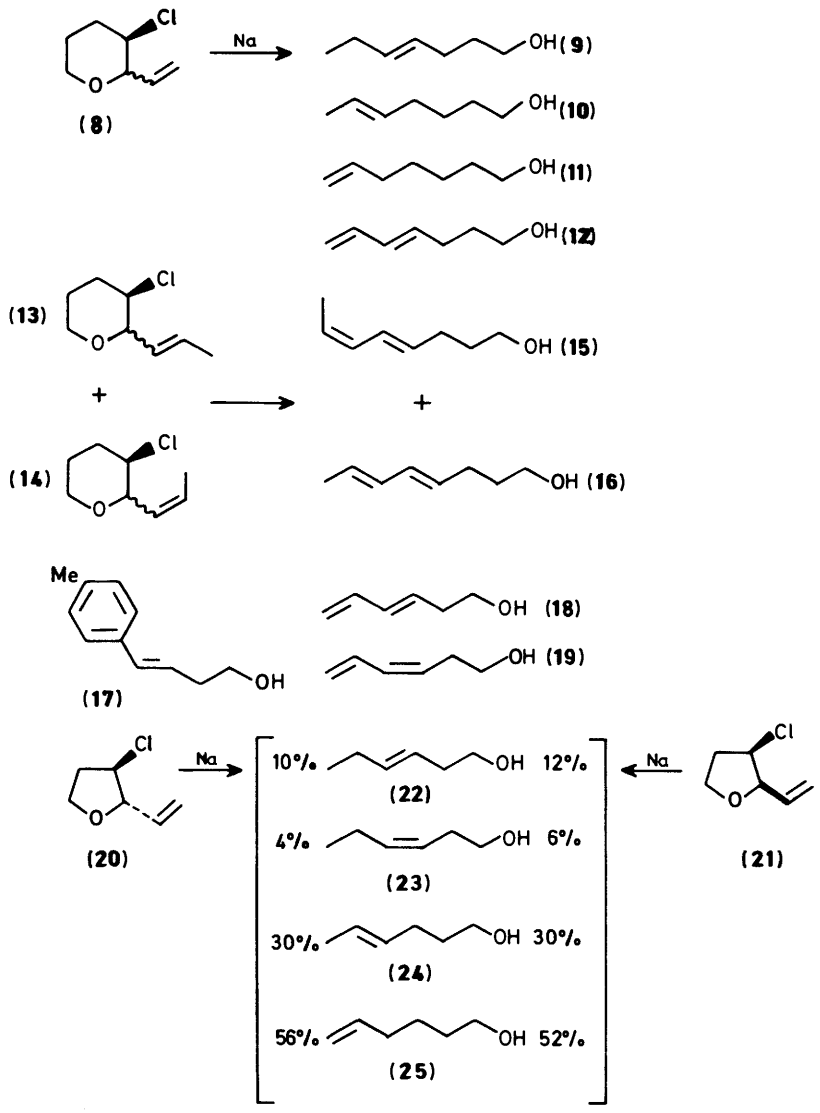
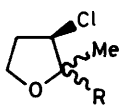
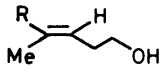
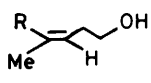


Table 4. (*E*)- and (*Z*)-4-Methylalk-3-en-1-ols by ring scission of 2-substituted-3-chloro-2-methyl-3-chlorotetrahydrofurans with sodium in ether

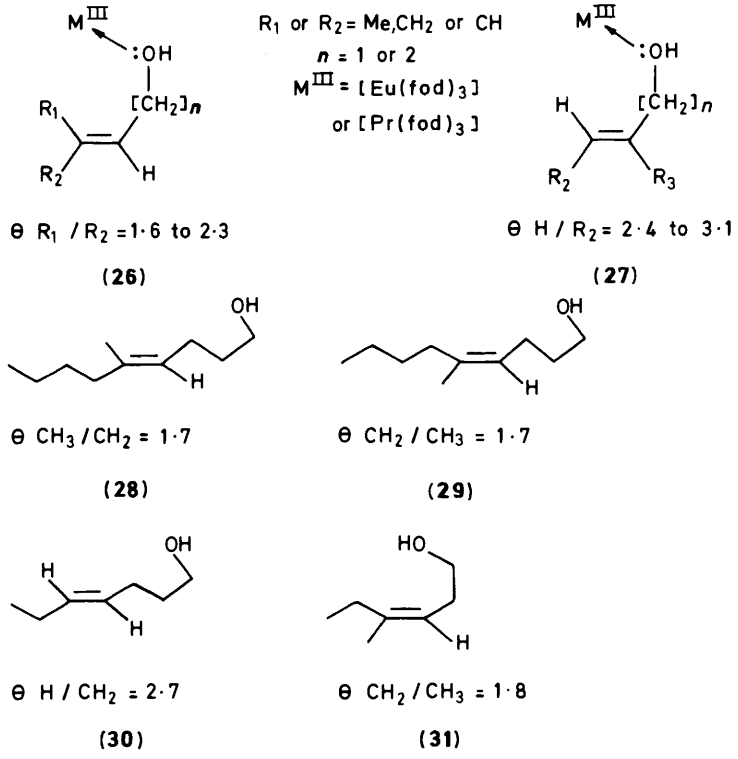
	Ring scission alcohols[a]	
	 (*E*) %	 (*Z*) %
cis- (36%)/*trans*- (64%)[b]- R = Et	47	53
cis- (70%)/*trans*- (30%)[b]- R = (*E*)-MeCH=CH[CH_2]$_3$	66	34
cis-[f] R = Pr^i	66	34
trans- R = Pr^i	35	65
R = Ph[c–e]	84	16

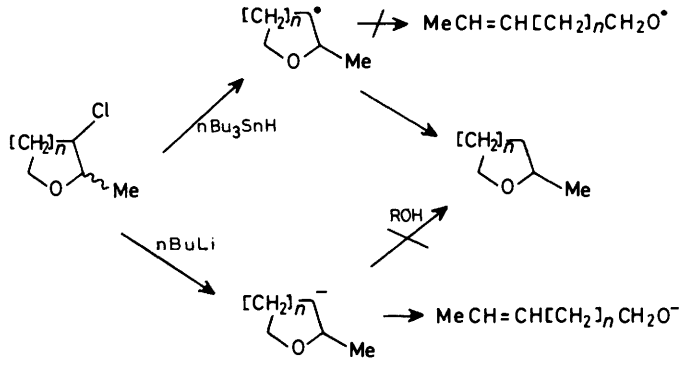
[a] Analysis by ^{1}H n.m.r. using [Eu(fod)$_3$]. [b] Estimates by g.l.c. (PEGA) or ^{1}H n.m.r. Assignments by employing deshielding effect of chlorine on reference *cis*-methyl. [c] Stereochemistry uncertain. [d] 21% 4-Phenylpentanol was also formed. [e] In toluene 81% (*E*), 19% (*Z*) with formation of virtually no saturated material. [f] *cis*- Here means the halogen with reference to the 2-methyl. The same system is used in the other examples in the Tables.

the mixture of (*E*)- and (*Z*)-alcohols produced (Table 4). This is clearly shown for the separated *cis*- and *trans*-*r*-methyl tetrahydrofuran isomers, but is implicit in the other examples.

β-Halogeno Ether Ring Scission: Discussion.—The ring scission of both *cis*- and *trans*-2-alkyl- or aryl-3-halogenotetrahydropyrans yields (*E*)-alk-4-enols with high stereoselectivity making it a valuable synthetic reaction. Early proposals attempted to account for this by assigning a concerted mechanism to the *trans*-pyran ring scission and a stepwise mechanism to the *cis*; alternatively an E_2-*trans*-elimination for the *trans*-pyran and an E_2-*cis*-elimination for the *cis*-pyran was considered.[1,7] It seems more likely that the ring opening of a common intermediate is involved and this might be a radical or a carbanion. These possibilities were first considered.

A mixture of *cis*- and *trans*-3-chloro-2-methyltetrahydrofurans was treated with tri-n-butyltin hydride initiated with benzoyl peroxide and the product was 2-methyltetrahydrofuran only, with no pent-3-enol being detected by g.l.c. (Scheme 2). Similarly a mixture of *cis*- and *trans*-3-chloro-2-methyltetrahydropyrans gave 2-methyltetrahydropyran and no hex-4-enol. In view of the radical nature of tin hydride reductions,[8] these results do not support a view that secondary β-radicals undergo ring scission and this is in accord with the work of Garst.[9]





Scheme 2. Radical and anion pathways

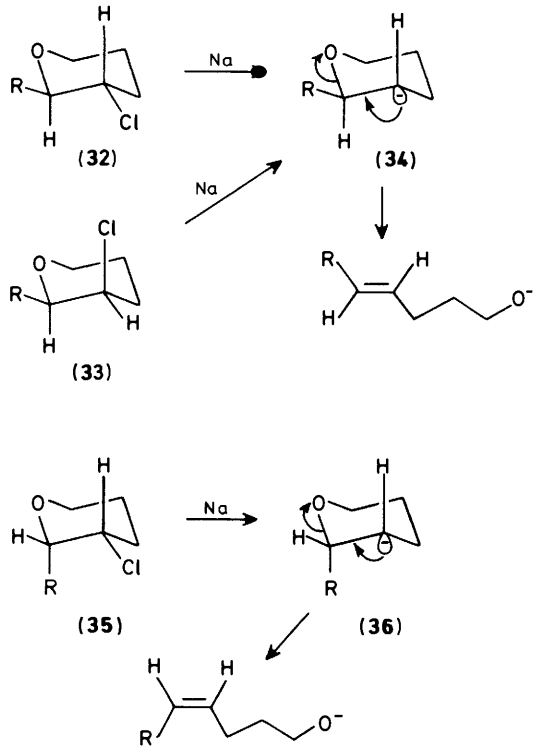
On the other hand, treatment of the β-halogeno ethers with n-butyl-lithium resulted in ring opening (Scheme 2). Reaction with *cis*- or *trans*-3-chloro-2-methyltetrahydrofuran gave in each case mixtures of (*Z*)- and (*E*)-pent-3-enols identical with those produced from the sodium ring-scission. Since g.l.c. showed that butyl chloride was produced, it is reasonable to conclude that carbanions were being formed and that the sodium ring scission involved the same species. However, all attempts to trap the carbanion by quenching, *e.g.* with methanol, were unsuccessful. Protonation of the carbanion intermediate in the ring scission of tetrahydrofurfuryl bromide, has similarly been reported not to compete with ring opening.[9,10] It may therefore be concluded that the β-carbanion life-times are short and ring opening is very rapid.

With evidence for the carbanion nature of the sodium ring scission reaction available, a more satisfactory rationalisation of the product stereochemistry can be given. Carbanions adopt a rapidly inverting sp^3 pyramidal structure analogous to isoelectronic amine systems; indeed preconceptions relating to carbanionic structure have depended on such analogies and in this respect the work of Lemieux and Booth is of interest.[11] In a study of tetrahydro-1,3-oxazines using variable temperature n.m.r. they have demonstrated that nitrogen inversion is a very rapid process; the energy barriers associated with chair–chair or chair–boat interconversions are undoubtedly much larger than those for nitrogen inversions. Nitrogen inversion can occur without conformational changes in the ring and, by analogy, properties of carbanions are likely to be similar.

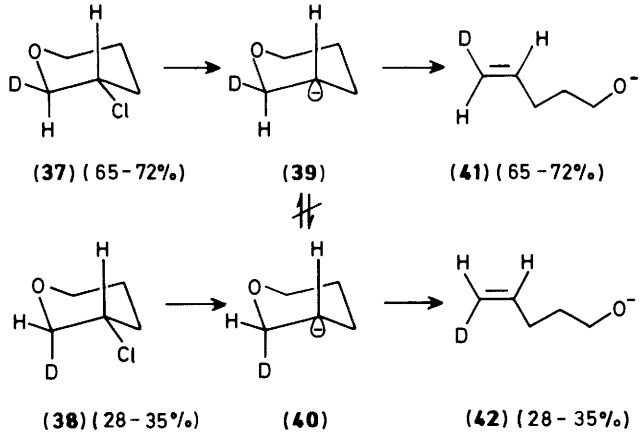
Electron transfer reactions are also recognised as extremely fast processes.[12,13] Thus the steps leading to the olefinic alcohols involve three very fast processes—electron transfer, carbanion inversion, and ring cleavage and it is postulated that the sum of these is faster than ring inversion, *i.e.* that the Curtin-Hammett principle[14] is not operative and that ground state conformation is reflected in the product stereochemistry.

The preferred conformations of *cis*- and *trans*-2-alkyl-3-chlorotetrahydropyrans (**33**) and (**32**) were discussed in the previous paper and ring scission is considered to involve the common carbanion intermediate (**34**) in which the 2-alkyl (or aryl) group is equatorial and the 3-proton is axial (Scheme 3). This conformation for the carbanion is appropriate for a *trans*-coplanar elimination of alkoxide ion leading to an (*E*)-alk-4-enol and in this way ring scission of both the *cis*- and *trans*-tetrahydropyrans would be highly stereospecific. A few percent of (*Z*) material may accompany the main (*E*) product and this probably originates from the alternative *cis*-conformation (**35**), in equilibrium to a small extent with (**33**), the ring scission proceeding *via* (**36**).

Further support for this interpretation comes from study of the 2-deuterio-3-halogenotetrahydropyrans and the 3-halogeno-2-methoxytetrahydropyrans where ring scission shows no substantial stereoselectivity. Ring scission of 2-(H/D)-3-chlorotetrahydropyran is expected to involve a carbanion intermediate which does not adopt one substantially preferred conformation (Scheme 4). If a situation is envisaged in which the carbanion underwent ring inversion whilst the 3-proton effectively remained axial through carbanion inversion, the deuterium, being a small substituent, would scramble approximately equally

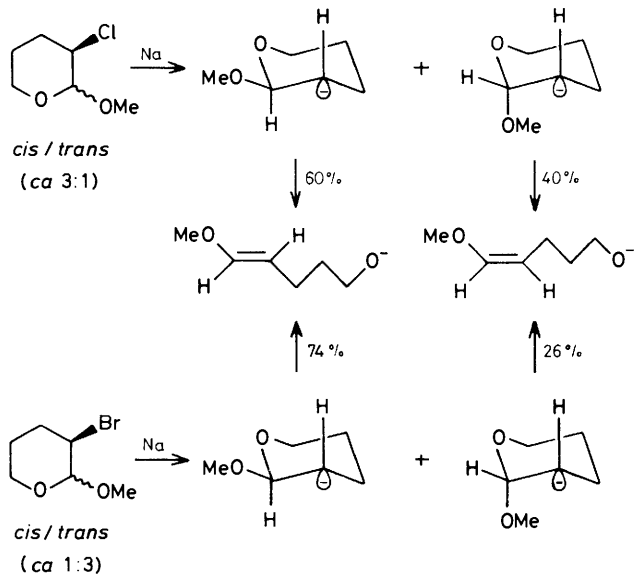


Scheme 3. Ring scission mechanism for 2-alkyl and aryl-3-chloro-tetrahydropyrans

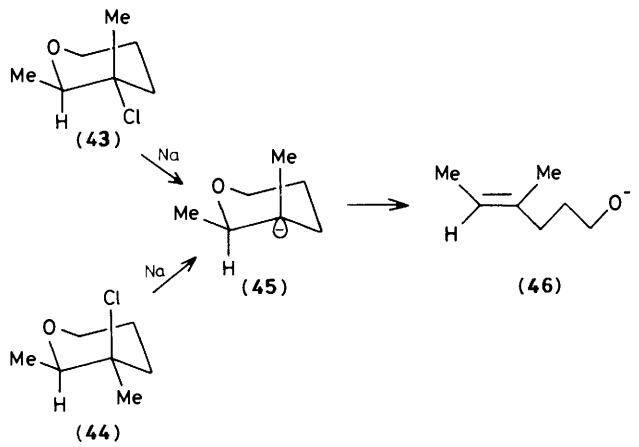


Scheme 4. Ring scission of 3-chloro-2-deuteriotetrahydropyrans

between the 2_e- and 2_a-positions. Ring scission of the *cis*/*trans* mixture of 3-chloro-2-deuteriotetrahydropyran (65—72% *trans*-2-D_e see preceding paper) would therefore be expected to produce *via* the anion, a *ca.* 50:50 mixture of (*Z*)- and (*E*)-deuteriopent-4-enols. This is not the case; the product (Table 1) is richer (64%) in the (*E*)-isomer. However, if the carbanion is short-lived, *i.e.* ring opening is rapid, yet carbanion inversion is still faster, the electron pair will be put *trans*-coplanar with the ring oxygen, and ring opening occur, before ring inversion has time to take place. Thus the carbanion will be non-equilibrated in terms of ring inversion and the deuterium distribution, *i.e.* the (*Z*)- and (*E*)-proportions, should correlate with that of the originating pyrans. Thus the initial pyran mixture, 65—72% *trans*-2-D_e should produce 65—72% of the (*E*)-alcohol. This is so within experimental error [64% (*E*)], and in confirmation



Scheme 5. Ring scission of 2-alkoxy-3-halogenotetrahydropyrans

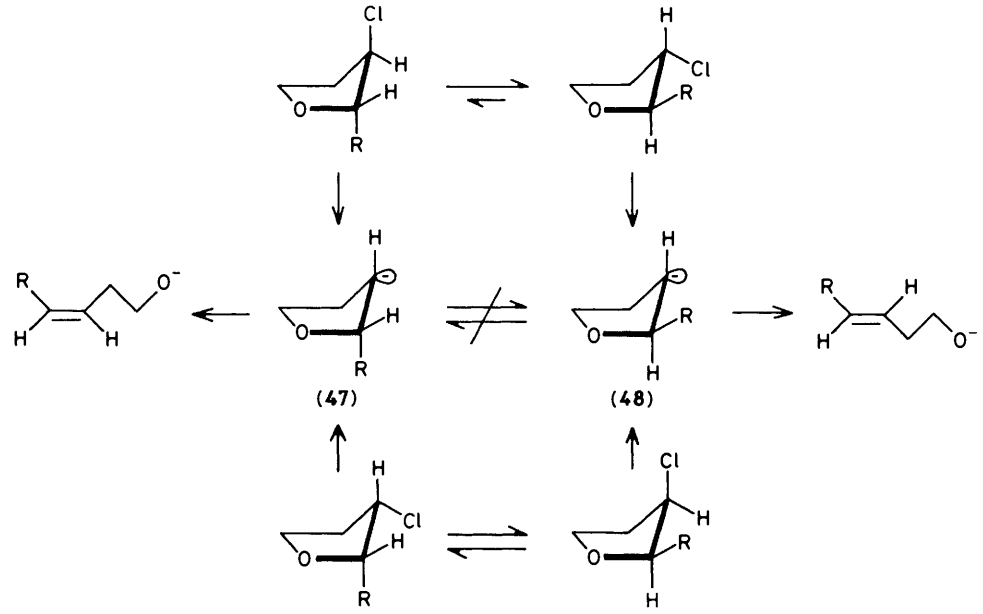


Scheme 6. Ring scission of *cis*- and *trans*-3-chloro-2,3-dimethyltetrahydropyrans

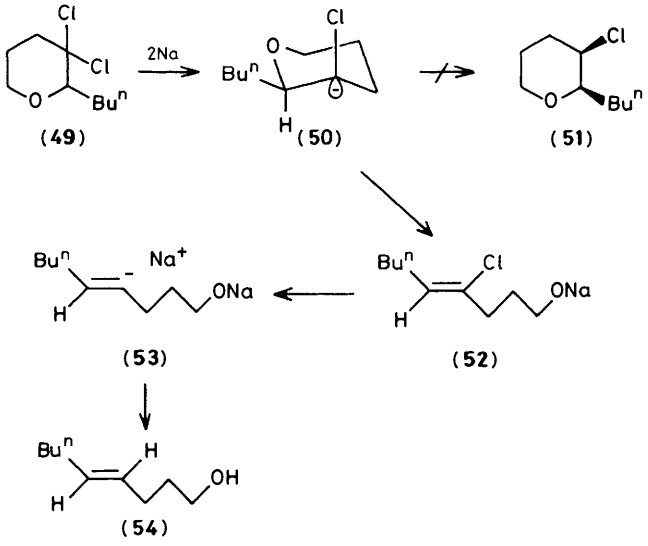
the corresponding 3-bromo-2-deuteriotetrahydropyran mixture (65—70% *trans*-2-D_e) gave 64% (*E*)-alcohol (Table 1). This substantiates our view that the highly stereoselective nature of the ring scission of *cis*- and *trans*-2-alkyl (or aryl)-3-chloro-tetrahydropyrans is to be attributed to the ground-state conformation being reflected in the short-lived, rapidly inverting, carbanion which has not the life-time necessary to undergo ring-inversion.

Further evidence that the carbanion produced in the ring scission process does not conformationally equilibrate before cleavage is indicated in Scheme 5. The chloro- and bromo-methoxypyrans produce mixtures of (*Z*)- and (*E*)-alcohols because of the operation of the anomeric effect. However, the (*Z*)/(*E*) ratios of the products are not identical in the two examples, showing that an equilibrated ring-inverted carbanion of the type (**34**) $\rightleftharpoons$ (**36**) is not involved as a common intermediate. The example is however complicated by extensive exocyclic cleavage accompanying the endocyclic cleavage.

Ansell and Gadsby [7] have reported that mixed *cis*- and *trans*-3-chloro-2,3-dimethyltetrahydropyrans give only (*E*)-4-methyl-hex-4-en-1-ol on ring scission by sodium and this can be rationalised on the same lines as the examples above. The



Scheme 7. Conformation and ring-scission products in the 2-alkyl- (or aryl-)-3-chlorotetrahydrofuran series



Scheme 8. Reactions of 2-butyl-3,3-dichlorotetrahydropyran

preferred *cis*-(**43**) and *trans*-(**44**) conformations have the 2-methyl equatorial and lead to anion (**45**) which on ring opening gives the (*E*)-olefin [*cf.* (**46**)].

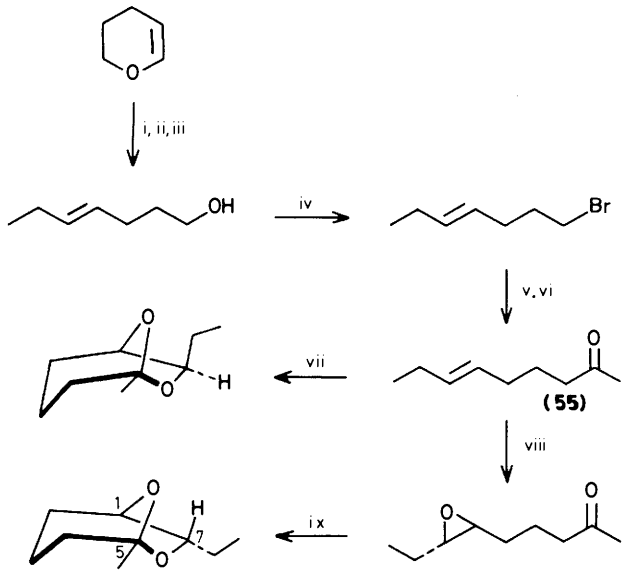
However, a similar mechanistic approach within the tetrahydrofuran series must recognise the uncertainties concerning their conformational properties. 2-Alkyl-3-chlorotetrahydrofurans are not expected to adopt preferred conformations but to take part in conformational equilibria. The 2-substituent must consequently occupy, in part, an axial orientation and ring scissions are expected to give some (*Z*)-alk-3-en-1-ol, as observed. Ring inversion of the carbanion intermediate (**47**) $\rightleftharpoons$ (**48**), although expected to be rapid,* does not appear to be fast enough to determine the outcome of the reaction. It is found (Table 2), that *cis*- and *trans*-tetrahydrofurans give different mixtures of (*Z*)- and (*E*)-alk-3-enols and this indicates that the anion is not equilibrated by ring inversion (Scheme 7). Consequently, the *trans*-tetrahydrofurans probably gave *ca.* 82% of the (*E*)-alcohol because their conformational equilibria favour R being predominantly equatorial, whereas the *cis*-tetrahydrofurans which possibly only slightly favour R as an equatorial substituent, gave 53% of the (*E*)-alcohol. Applying considerations similar to those used for the tetrahydropyrans, a reasonable explanation for the scission product distribution can thus be arrived at; pseudorotation (ring inversion) of the carbanion is not fast enough to compete with anion inversion and ring opening.

The non-stereospecific ring-scissions of 2-alkyl-3-chloro-2-methyltetrahydropyrans (Table 3) may similarly be ascribed to the nature of their conformational equilibria. Thus the conformations of the *cis*- and *trans*-2-isopropyl-*r*-2-methyl-3-chlorotetrahydropyrans both appear to have the 2-isopropyl substituent mainly equatorial.[2] On this basis both isomers should yield mixtures of (*E*) and (*Z*)-alcohols with the former predominating.

It will be apparent that the broad results of Table 4 for 2-alkyl-3-chloro-2-methyltetrahydrofurans are not unexpected but little can be said in detail about these ring scissions because of the greater uncertainties relating to their stereochemical assignments and conformational properties.

Riobé[15] has reported an interesting experiment in which ring-scission of 2-butyl-3,3-dichlorotetrahydropyran (**49**), when treated with sodium (4 mol) in tetrahydrofuran gave (*E*)- non-4-en-1-ol (**54**), whilst the same reaction with sodium (2 mol) gave the latter alcohol along with *cis*-2-butyl-3-chlorotetrahydropyran (**51**). It was proposed that the latter was an intermediate in the reaction. These findings can also be interpreted in terms of Scheme 8. In this, the carbanion (**50**) is stabilised by a chlorine and might have a longer lifetime; ring scission would give the (*Z*)-chloro olefin (**52**). Further reaction of the chloro olefin with sodium could produce (**53**), to give the observed (*E*)-alcohol (**54**). In our experiments however we were unable to isolate any *cis*-2-butyl-3-chlorotetrahydropyran (**51**) (g.l.c., solvents THF or benzene) by using 2 mol sodium, although both this and the 4 mol experiment gave the reported alcohol (**54**) on work-up. When our reaction (using 4 mol sodium) was worked up with

* Low temperature n.m.r. studies do not show slowing of the psuedorotation of the initial tetrahydrofurans; psuedorotation (*i.e.* ring inversion) of the carbanion is similarly expected to be a fast process.



Scheme 9. Synthesis of *exo*- and *endo*-brevicomin. *Reagents:* i, Cl_2, Et_2O; ii, EtMgBr; iii, Na, Et_2O; iv, PBr_3, pyridine; v, Mg, Et_2O; vi, dimethylacetamide, −10 °C; vii, OsO_4, H_2S; viii, *m*-chloroperbenzoic acid; ix, H^+

D_2O we were surprised to find that no deuterium was incorporated into the 4-position of (**54**). However, use of deuteriobenzene as a solvent in the reaction caused deuteriation in the 4-position to the extent of 35—40%. Our results thus show that the carbanion (**50**) has a short life-time and that protonation does not compete effectively with ring opening: also the vinyl carbanion (**53**) is scavenged before D_2O work-up. This scavenging may be partly by the solvent, but side-reactions may also provide proton sources (yields of the alcohol were < 50%). It is possible that the reaction follows in part a radical pathway which would more readily account for scavenging by benzene; however, no biphenyl could be detected as a reaction product by g.l.c.

Synthesis of exo- *and* endo-*Brevicomin.*—In conclusion, the utility of β-halogeno ether synthesis is briefly illustrated by simple highly stereoselective syntheses of *exo*- and *endo*-brevicomin (Scheme 9). The former is the principle component of the sex-attractant of the female western pine-beetle *Dendroctonus brevicomis* (Coleoptera: Scolytidae)[16] and has been the subject of much synthetic interest.[17] It is present along with myrcene and frontalin in the frass produced by the female boring in ponderosa pine. Although the *endo*-epimer also occurs in frass, it appears to be inactive.

β-Halogeno ether synthesis was used to produce (*E*)-hept-4-enol which was converted into the bromide by phosphorus tribromide and pyridine. Grignard formation followed by reaction with dimethylacetamide at −10 °C gave (*E*)-non-6-en-2-one (**55**) in 27% yield from dihydropyran. The ketone was treated with osmium tetraoxide in dioxane to give the osmate ester which, when treated with hydrogen sulphide, yielded *exo*-brevicomin in 50% yield (13% from dihydropyran). N.m.r. and i.r. spectra were virtually identical with those of the natural product and the n.m.r. spectrum characterises the product as the *exo*- isomer since the 7-proton triplet (*J* 6.2 Hz) at δ3.80 (CCl_4) showed no coupling with the 1-proton (models show them to be at right angles).[18] Careful g.l.c. analysis on Carbowax 20M showed that the *exo*-isomer contained *ca.* 4% of the *endo*-isomer and some or all of this probably arises from a contaminant in the ring-scission alcohol.

The inactive *endo*-epimer was synthesised by epoxidation of (*E*)-non-6-en-2-one with *m*-chloroperbenzoic acid followed by acid hydrolysis of the *trans*-epoxide to give *endo*-brevicomin in 22% overall yield based on dihydropyran. G.l.c. (Carbowax 20M) showed the presence of *ca.* 5% *exo*-isomer. N.m.r. and i.r. data were virtually identical with the natural inactive material and the 7-proton appeared as a multiplet at δ4.02 due to additional coupling with the 1-proton.[18]

Experimental

Alk-3- and -4-en-1-ols. General Procedure.—Sodium (2.5 mol) was powdered under xylene, thoroughly rinsed with dry ether, and covered with ether (400 cm^3). A little of the β-halogeno ether was added and the suspension stirred until reaction commenced, as shown by the surface of the sodium becoming indigo-blue and by the refluxing of the ether. The remaining β-halogeno ether (1 mol) was added dropwise, so that steady refluxing was maintained. The thick blue suspension was stirred for a further 2 h and kept at room temperature overnight. Ice and water were cautiously added (N_2 atmosphere) and the ethereal layer was separated. The aqueous layer was further extracted with ether and the combined ethereal extracts were washed with aqueous acid and water, dried and evaporated. Distillation of the residue afforded the alcohol.

Unless otherwise stated, a 0.5 mol excess of sodium was used.

Alk-4-en-1-ols from 2-Substituted 3-Chlorotetrahydropyrans. Hept-4-en-1-ol.—Ring scission of mixed *cis*- and *trans*-3-chloro-2-ethyltetrahydropyrans (55% *trans*) (2 mol) gave (*E*)-hept-4-en-1-ol (190 g, 88%), b.p. 84—85 °C/19 mmHg, n_D^{21} 1.4441 (lit.,[1] b.p. 74—76 °C/11 mmHg, n_D^{20} 1.4439); $\nu_{max.}$ 3 370, 1 055, and 970 cm^{-1}; δ(CCl_4) 5.40 (2 H, m, olefinic), 3.80 (1 H, s, OH), 3.50 (2 H, t, *J* 6.3 Hz, CH_2OH), 2.00 (4 H, m), 1.60 (2 H, pent, *J* 7 Hz, CH_2CH_2OH), and 0.97 (3 H, t, *J* 7 Hz, CH_3CH_2H); δ{$CDCl_3$ + [Eu(fod)$_3$]} θ H/CH_2 = 2.7. Ring scission of the *cis*-pyran similarly gave the (*E*)-alcohol [(88%) b.p. 78—82 °C/17 mmHg, n_D^{20} 1.4438, θ H/CH_2 = 2.7], as did the *trans*-pyran, [(89%), b.p. 80—82 °C/14 mmHg, n_D 1.4425, θ H/CH_2 = 2.7].

Authentic (*E*)-hept-4-en-1-ol (5.3 g, 75%), b.p. 103 °C/50 mm Hg, n_D^{19} 1.4444, θ H/CH_2 = 2.7, was prepared from hept-4-yn-1-ol (7 g) by reduction with sodium in liquid ammonia (*cf.* Crombie and Harper[1]). Authentic (*Z*)-hept-4-en-1-ol, (2.5 g, 79%), b.p. 102—104 °C/43 mmHg, n_D^{20} 1.4440 (lit.,[19] b.p. 78—79 °C/15 mmHg, n_D^{20} 1.4467); δ {$CDCl_3$ + [Eu(fod)$_3$]} θ CH_2/H = 0.9), was prepared by semi-hydrogenation of hept-4-yn-1-ol (3.1 g, 0.028 mol), over Lindlar catalyst (*cf.* Crombie and Harper[1]).

Hex-4-en-1-ol.—Ring scission of mixed *cis*- and *trans*-3-chloro-2-methyltetrahydropyrans (68% *cis*) (80 g, 0.64 mol) gave (*E*)-hex-4-en-1-ol (53 g, 83%), b.p. 81—82 °C/32 mmHg, n_D^{20} 1.4403 (lit.,[1] b.p. 68.5 °C/15 mmHg, n_D^{20} 1.4403); $\nu_{max.}$ 3 360, 1 055, and 970 cm^{-1}; δ($CDCl_3$) 5.49 (2 H, m, olefinic) 3.62 (2 H, t, *J* 7 Hz, CH_2OH), 2.50 (1 H, s, OH), 2.02 (2 H, m) and 1.64 (5 H, including Me, d, *J* 5 Hz, at 1.64); δ {$CDCl_3$ + [Eu(fod)$_3$]} θ H/Me = 2.6. Ring scission of the independent *cis*- and *trans*-pyrans gave identical results. Authentic (*Z*)-hex-4-en-1-ol had θ Me/H = 1.0 and (*E*)-hex-4-en-1-ol, θ H/Me = 2.6.

6-Methylhept-4-en-1-ol.—Ring scission of mixed *cis*- and *trans*-3-chloro-2-isopropyltetrahydropyrans (55% *trans*) (53 g, 0.32 mol) gave (*E*)-6-methylhept-4-en-1-ol (36 g, 84%), b.p. 81—82 °C/14 mmHg, n_D^{22} 1.4440 (lit.,[20] b.p. 87 °C/14 mmHg, n_D^{21} 1.4430); $\nu_{max.}$ 3 380, 1 055, and 970 cm^{-1}; δ(CCl_4) 5.39 (2 H, m, olefinic), 4.00 (1 H, s, OH), 3.56 (2 H, t, *J* 6.2 Hz, CH_2OH), 2.05 (3 H, m), 1.62 (2 H, m), and 0.97 (6 H, d, *J* 7 Hz, CH-Me_2); δ {$CDCl_3$ + [Eu(fod)$_3$]} θ H/CH = 1.8.

5-*Phenylpent*-4-*en*-1-*ol*.—Ring scission of *trans*-3-chloro-2-phenyltetrahydropyran (23 g, 0.12 mol) gave a mixture (15.6 g) of (*E*)-5-phenylpent-4-en-1-ol [70% by g.l.c. (Apiezon)] and 5-phenylpentan-1-ol (30%), b.p. of the mixture 150—164 °C/17 mmHg; $\nu_{max.}$ 3 400, 1 601, and 970 cm^{-1}; $\delta(CDCl_3)$, 7.30 and 7.20 (m, 2 × Ph), 6.42 (1 H, olefinic, half of AB double doublet, *J trans* 16 Hz), 6.19 (1 H, olefinic, dt, ABX_2 with $J_{AX_2} = 0$, *J* 16, 7 Hz), 3.62 and 3.55 (2 × CH_2OH, t, *J* 6 Hz), 3.00 (OH, brs), 2.62 (benzylic 2 H, t, *J* 7 Hz), 2.28 ($PhCH{=}CHCH_2$, q, *J* 7 Hz), and 1.68 (m), (Riobé[21] reports b.p. 157 °C/16 mmHg but does not mention a reduction side product).

5-p-*Tolylpent*-4-*en*-1-*ol*.—Ring scission of *trans*-3-chloro-2-*p*-tolyltetrahydropyran (15 g, 0.075 mol) gave a mixture of (*E*)-5-*p*-tolylpent-4-en-1-ol [80% by g.l.c. (Apiezon)] and 5-*p*-tolylpentan-1-ol (20%). Recrystallisation from pentane yielded exclusively (*E*)-5-p-*tolylpent*-4-*en*-1-*ol* (4 g, 30%), as white plates, m.p. 43 °C (Found: C, 81.7; H, 8.9; *m/z* 176. $C_{12}H_{16}O$ requires C, 81.9; H, 9.1%; M, 176); $\nu_{max.}$ (Nujol) 3 310, 1 055, and 970 cm^{-1}; $\delta(CDCl_3)$. 7.20 (4 H, dd, ArH), 6.44 (1 H, olefinic, half of AB double doublet, J_{trans} 17.5 Hz), 6.18 (1 H, olefinic, dt, ABX_2 with $J_{AX_2} = 0$, *J* 17.5, 7 Hz), 3.70 (2 H, t, *J* 6 Hz, CH_2OH), 2.42 (3 H, s, Me), 2.33 (2 H, q, *J* 7 Hz), 1.76 (2 H, quintet, *J* 7 Hz), and 1.60 (1 H, s, OH). Irradiation of the δ2.33 quartet caused the olefinic 4-H resonance at 6.18 to be observed as a doublet (J_{trans} 17.5 Hz).

When the ring scission was repeated using toluene as the solvent the reduction product was minimised (2% of the mixture) and the isolated yield of the recrystallised *trans*-olefin was 69%.

Hepta-4,6-*dien*-1-*ol*.—Ring scission of mixed *cis*- and *trans*-3-chloro-2-vinyltetrahydropyran (**8**) (10 g) gave a mixture of alcohols (5 g), b.p. 80—83 °C/15 mmHg. Preparative g.l.c. (PEGA) afforded (*E*)-hept-4-en-1-ol (**9**) (see above), hept-5-en-1-ol (**10**), n_D^{20} 1.4438 (lit.,[22] n_D^{23} 1.4420) (Found: C, 73.5; H, 11.9. Calc. for $C_7H_{14}O$: C, 73.7; H, 12.2%); $\nu_{max.}$ 3 400, 1 050, and 970 cm^{-1} (the intensity at 970 cm^{-1} showed a *cis*/*trans* mixture); $\delta(CDCl_3)$, 5.42 (2 H, m, olefinics), 3.62 (2 H, t, *J* 6 Hz, CH_2OH), 2.40 (1 H, s, OH), 2.09 (2 H, q, *J* 7 Hz), and 1.80—1.35 (7 H, m) with 1.60 (Me, d, *J* 5 Hz); and hept-6-en-1-ol (**11**) (in admixture with hept-5-en-1-ol), $\delta(CDCl_3)$ *inter alia*, 5.88 (1 H, ddt, olefinic, *J* 17, 11, 7 Hz), 4.97 (1 H, d, olefinic, J_{cis} 11 Hz), and 4.93 (1 H, olefinic d, J_{trans} 17 Hz).

Ring scission of mixed *cis*- and *trans*-3-chloro-2-vinyltetrahydropyran (10 g, a 0.3 mol excess) gave a mixture of alcohols (3 g), b.p. 80—84 °C/15 mmHg. Preparative g.l.c. (PEGA) yielded (4E, 6E)-*hepta*-4,6-*dien*-1-*ol* (**12**) (80% of the mixture) (Found: C, 75.4; H, 10.5. $C_7H_{12}O$ requires C, 75.0; H, 10.7%); $\nu_{max.}$ 3 350, 1 645, 1 603, and 1 003 cm^{-1}; $\delta(CDCl_3)$ 6.75—5.30 (3 H, m), 5.08 (1 H, d, J_{trans} 17 Hz), 5.15 (1 H, d, J_{cis} 11 Hz), 3.62 (2 H, t, *J* 6 Hz, CH_2OH), 2.70 (1 H, s, OH), 2.20 (2 H, q, *J* 7 Hz), and 1.66 (2 H, p, *J* 7 Hz).

Octa-4,6-*dien*-1-*ol*.—2,3-Dichlorotetrahydropyran [prepared by chlorination of 2,3-dihydro-4*H*-pyran (0.3 mol) in ether (200 cm^3)] was added to prop-1-enylmagnesium bromide [prepared from (*Z*)/(*E*)-1-bromoprop-1-ene (50:50) (0.41 mol) and magnesium (0.41 mol) in THF (250 cm^3)], to give a mixture of *trans*-(*E*)-, *trans*-(*Z*)-, *cis*-(*E*)-, and *cis*-(*Z*)-3-chloro-2-prop-1-enyltetrahydropyrans (27 g, 56%), b.p. 68—71 °C/4 mmHg, n_D^{20} 1.4818 (lit.,[23] b.p. 83—84 °C/13 mmHg, n_D^{22} 1.4082); $\delta(CDCl_3)$ 6.10—4.98 (2 H, m, olefinics), 4.22—3.25 (4 H, m), and 2.69—1.40 [7 H, m, including 1.85, (3 H, d, *J* 6 Hz, Me)]. G.l.c. analysis (PEGA) showed four peaks, *trans*-pyrans (88%) (unassigned ratio 62:38) and *cis*-pyrans (12%) (unassigned ratio 73:27).

Ring scission of the tetrahydropyran mixture (12 g, 0.075 mol) gave (4*E*, 6*Z*)- [58% by g.l.c. (PEGA)] and (4*E*, 6*E*)-(42%) octa-4,6-dien-1-ols (**15**) and (**16**) (5.8 g, 62%), b.p. 74—75 °C/2 mmHg, n_D^{20} 1.4931 (lit.,[23] b.p. 100 °C/13 mmHg, n_D^{22} 1.4925); $\nu_{max.}$ 3 380, 1 651, and 992 cm^{-1}; $\delta(CDCl_3)$ 6.60—5.20 (4 H, m, olefinics), 3.60 (2 H, t, *J* 6 Hz, CH_2OH), 2.52 (1 H, s, OH), 2.12 (2 H, m), 1.72 (3 H, d, *J* 6 Hz, Me), and 1.9—1.35 (2 H, m).

5-*Methoxypent*-4-*en*-1-*ol*.—Ring scission of mixed *cis*- and *trans*-3-chloro-2-methoxytetrahydropyrans (78% *cis*-) (49 g) gave 2,3-dihydro-4*H*-pyran (major product, removed with ether) and (*Z*)- and (*E*)-5-methoxypent-4-en-1-ols (ratio 40:60) (5.2 g, 14%), b.p. 90—92 °C/18 mmHg, n_D^{17} 1.4510 (lit.,[24] 15%, b.p. 95.5 °C/16 mmHg, n_D^{11} 1.4521); $\nu_{max.}$ 3 395 and 1658s cm^{-1}; $\delta(CDCl_3)$, 6.29 (*trans*-5-H, dt, *J* 13, 1 Hz), 5.90 (*cis*-5-H, dt, *J* 6.4, 1.3 Hz), 4.72 (*trans*-4-H dt, *J* 13, 7.3 Hz), 4.35 (*cis*-4-H, td, *J* 7.9, 6.4 Hz), 3.80—3.30 [5 H, with MeO singlets at 3.56 (*cis*) and 3.48 (*trans*)], 2.60 (1 H, s, OH), 2.06 (2 H, quintet, *J* 7 Hz), and 1.57 (2 H, q, *J* 7 Hz). The isomer ratio, through relative integration of the 5-proton multiplets, was taken from the crude undistilled product since enrichments occurred during distillation. When the product was heated at the distillation temperature in a sealed n.m.r. tube, cyclisation gave 2-methoxytetrahydropyran (100%), b.p. 124—125 °C, n_D^{16} 1.4279, (lit.,[25] b.p. 125 °C, n_D^{25} 1.4227), identical with an authentic sample.

Ring scission of mixed *cis*- and *trans*-3-bromo-2-methoxytetrahydropyrans (73% *trans*) (40 g, 0.2 mol) similarly gave (*Z*)- and (*E*)- (ratio 26:74) 5-methoxypent-4-en-1-ols (5.7 g, 25%) b.p. 88—90 °C/13 mmHg, n_D^{17} 1.4521.

[5-^{1}H]- *and* [5-^{2}H]-*Pent*-4-*en*-1-*ols*.—Ring scission of 3-chlorotetrahydropyran (8 g) gave pent-4-en-1-ol (5.2 g, 90%), b.p. 135—136 °C, n_D^{20} 1.4304 (lit.,[3] b.p. 134—137 °C, n_D^{20} 1.4301); $\nu_{max.}$ 3 380, 1 640, and 1 060 cm^{-1}, *m/z* 68 and 67 (base peaks) (corresponding to $M^+ - H_2O$ and $M^+ - H_3O$); $\delta(CDCl_3)$, 5.90 (4-H, ddt, *J* 17.5, 10 and 6 Hz), 5.05 (5-H, dd, *J* 17.5, 1.5 and 3 Hz), 5.00 (5-H, ddt, *J* 10, 1.5 and 3 Hz), 3.65 (2 H, t, *J* 6 Hz, CH_2OH), 2.85 (1 H, s, OH), 2.16 (2 H, q, *J* 6 Hz), and 1.66 (2 H, quintet, *J* 6 Hz).

Ring scission of 3-chloro-2-deuteriotetrahydropyran (65—72% *trans*-2-D_e) (9 g) gave [5-^{2}H]pent-4-en-1-ol (3.8 g, 60%), b.p. 135—137 °C; $\nu_{max.}$ 3 380, 1 620, and 978 cm^{-1}; *m/z* 69 and 68 (base peaks); $\delta(CDCl_3)$ 5.04 (5-H, dt, *J* 17.5, 3 Hz) and 4.99 (5-H, dt, *J* 10, 3 Hz) (corresponding to a loss of the $J_{5,5}$ geminal coupling of 1.5 Hz; the 5-proton multiplets integrated as 1 H). Similar ring scission of 3-bromo-2-deuteriotetrahydropyrans (65—70% *trans* 2-D_e) gave [5-^{2}H]pent-4-en-1-ol (72%), b.p. 135—137 °C. The deuteriated alcohols [64% *trans*-(*E*)] were analysed *via* the [Eu(fod)$_3$]-shifted n.m.r. spectra.

5-*Methylalk*-4-*en*-1-*ols from* 3-*Chloro*-2-*alkyl*-(2-*methyl*)-*tetrahydropyrans*

3-*Chloro*-2-*alkyl*-(2-*methyl*)*tetrahydropyrans*. *General Procedure*.—2-Methyl-5,6-dihydro-4*H*-pyran[26] (1 mol) was chlorinated in ether at −40 °C and added to the Grignard reagent [from the alkyl bromide (1.5 mol) and magnesium (1.6 mol) in ether] whilst maintained at this temperature, the Grignard reagent was also cooled at −40 °C and the ethereal solution of the 2,3-dichloride was added through a solid CO_2—methanol jacketted dropping funnel. After addition the mixture was stirred at room temperature overnight and worked up in the usual manner.

Unless otherwise stated 2-alkyl-3-chloro-2-methyltetrahydropyrans were prepared on a 0.1 mol scale, and their ring scissions were performed on a 0.015 mol scale.

5-Methylhept-4-en-1-ol.—*cis-* and *trans*-3-Chloro-2-ethyl-2-methyltetrahydropyran (48%), b.p. 82—85 °C/20 mmHg, n_D^{20} 1.4656 (lit.,[26] b.p. 81 °C/18 mmHg, n_D^{19} 1.4662); δ($CDCl_3$) 4.22—3.40 (3 H, m), 2.55—1.37 (6 H, m), 1.23 (3 H, s, Me), and 0.88 (3 H, t, *J* 7 Hz, $-CH_2Me$), were prepared as above (low b.p. and high b.p. side-products were also produced). The product was estimated as a *ca.* 3:2 mixture of isomers (assignments uncertain) from the [Eu(fod)$_3$]-shifted n.m.r. spectrum which revealed two different methyl singlets. Ring scission of the pyran mixture yielded (*Z*)- and (*E*)-5-methylhept-4-en-1-ols (ratio 54:46 by n.m.r.) (85%), b.p. 85—87 °C/13 mmHg, n_D^{20} 1.4532 (lit.,[26] b.p. 87 °C/13 mmHg, n_D^{16} 1.4548); $\nu_{max.}$ 3 350 and 1 062 cm^{-1}; δ($CDCl_3$) 5.10 (1 H, t, *J* 7 Hz, olefinic), 3.60 (2 H, t, *J* 6 Hz, CH_2OH), 2.40 (1 H, s, OH), 2.07 (4 H, q, *J* 7 Hz), 1.9—1.4 (5 H, m, with 2 × Me, s, at 1.68 and 1.60), and 0.97 (3 H, t, *J* 7 Hz, $MeCH_2$).

5-Methylnon-4-en-1-ol.—*cis-* and *trans*-2-Butyl-3-chloro-2-methyltetrahydropyrans (41%), were prepared as a mixture, b.p. 84—86 °C/3 mmHg, n_D^{19} 1.4702 (lit.,[26] b.p. 102—105 °C/13 mmHg, n_D^{21} 1.4668); δ($CDCl_3$), 4.2—3.4 (3 H, m), 2.3—1.15 (13 H, m, with Me, s, at 1.27), and 0.95 (3 H, br t, *J* 7 Hz, $MeCH_2$). G.l.c. analysis (PEGA) showed two peaks (unassigned ratio 39:61). Low b.p. and high b.p. side products were also produced. The low b.p. product proved to be *2-butyl-2-methyltetrahydropyran*, b.p. 54—56 °C/3 mmHg (Found: C, 76.9; H, 13.0%; M^+ 156. $C_{10}H_{20}O$ requires C, 77.0; H, 12.8%; *M*, 156) *m/z* 141 (M^+ − Me) 99 (M^+ − Bu^n); δ($CDCl_3$) 3.62 (2 H, m, 6-H), 2.2—1.1 (15 H, m, with Me, s, at 1.15), and 0.91 (3 H, br t, $MeCH_2$). Ring scission of the β-halide mixture (*cis* + *trans*) yielded (*Z*)- and (*E*)-5-methylnon-4-en-1-ols (81%), b.p. 111—113 °C/14 mmHg, n_D^{20} 1.4565 (lit.,[26] b.p. 108 °C/11 mmHg, n_D^{18} 1.4575); $\nu_{max.}$ 3 390, 1 665, and 1 059 cm^{-1}, δ($CDCl_3$), 5.12 (1 H, t, *J* 7 Hz, olefinic), 3.60 (2 H, t, *J* 6 Hz, CH_2OH), 2.20 (1 H, s, OH), 2.02 (4 H, m), 1.8—1.1 (9 H, m, with 2 × Me, s, at 1.68 and 1.60), and 0.81 (3 H, br t, $MeCH_2$). Ring scission of two g.l.c. enriched β-halide mixtures gave similar results.

5,6-Dimethylhept-4-en-1-ol.—*cis-* and *trans*-3-Chloro-2-isopropyl-2-methyltetrahydropyrans [45:55 by g.l.c. (PEGA)] were prepared as a mixture, b.p. 76—82 °C/5 mmHg [Found: C, 61.3; H, 9.5%; M^+, 176, 178 (3:1). Calc. for $C_9H_{17}ClO$: C, 61.3; H, 9.6%; *M*, 176, 178 (3:1)]. Low b.p. and high b.p. side products were also produced. Preparative g.l.c. (PEGA) yielded the *cis*-3-chloro-*r*-2-methylpyran, *m/z* 176, 178 (M^+, 3:1), 161, 163 (M^+ − Me, 3:1), 133, 135, (M^+ − Pr^i, 3:1); δ($CDCl_3$) 4.05 (1 H, dd, *J* 9.2 and 5.5 Hz, 3-H), 3.58 (2 H, m, 6-H), 2.04 (3 H, m), 1.65 (2 H, m), 1.24 (3 H, s, Me), and 1.00 and 0.92 (6 H, Me_2CH, d, *J* 7 Hz) and the *trans*-3-chloro-*r*-2-methylpyran, *m/z* 176, 178 (M^+, 3:1), 161, 163 (M^+ − Me, 3:1), 133, 135 (M^+ − Pr^i, 3:1); δ($CDCl_3$) 4.00 (1 H, t, *J* 3 Hz, 3-H), 3.70 (2 H, m, 6-H), 2.13 (4 H, m), 1.37 (1 H, m), 1.14 (3 H, s, Me), and 0.90 and 0.86 (6 H, Me_2CH, d, *J* 7 Hz). Small scale ring scissions of these isomers gave (*Z*)- and (*E*)-5,6-dimethylhept-4-en-1-ol mixtures (88%). The mixtures were purified by preparative g.l.c. (PEGA) (Found: C, 76.3; H, 12.5. Calc. for $C_9H_{18}O$: C, 76.1; H, 12.7%); $\nu_{max.}$ 3 380, 1 660, and 1 060 cm^{-1}; δ($CDCl_3$) 5.13 and 5.05 (1 H, overlapping triplets, *J* 7 Hz, olefinic), 3.60 (2 H, t, *J* 6 Hz, CH_2OH), 3.0—1.9 [4 H, m, with 2.20, (s, OH); 2.08 (2H, q, *J* 7 Hz); and Me_2CH submerged], 1.85—1.45 [5 H, m, with 1.57, (3H, s, Me)], and 0.95 (6 H, d, *J* 7 Hz, Me_2CH).

5-Phenylhex-4-en-1-ol.—3-Chloro-2-methyl-2-phenyltetrahydropyran (35%), b.p. 110—114 °C/1.5 mmHg, n_D^{22} 1.5480 (lit.,[26] b.p. 100 °C/0.7 mmHg, n_D^{22} 1.5522), *m/z* 210, 212 (3:1) (M^+), 195, 197 (3:1) (M^+ − Me), 105 (base peak); δ($CDCl_3$) 7.32 (5 H, m, ArH), 4.38 (1 H, dd, *J* 7.3, 4.5 Hz, 3-H), 3.74 (2 H, m, 6-H), 2.00 (3 H, m), and 1.80—1.40 (4 H, with 3 H, s, Me at 1.59), prepared by the usual method, was of single configuration. Ring scission of this product yielded (*Z*)- and (*E*)-5-phenylhex-4-en-1-ols (75%) [ratio 71:29 using toluene; ratio 63:35 using ether, by g.l.c. (SE30)], b.p. 101—102 °C/0.6 mmHg, n_D^{20} 1.5406 (lit.,[21] b.p. 101—102 °C/0.6 mmHg, n_D^{21} 1.5412). Preparative g.l.c. (SE30, 150 °C) afforded the major (*Z*)-alcohol (low retention time), n_D^{22} 1.5631, *m/z* 176 (M^+) $\nu_{max.}$ 3 375, 1 600, and 1 058 cm^{-1}; δ($CDCl_3$), 7.20 (5 H, m, ArH), 5.42 (1 H, tq, *J* 7.5, 1.5 Hz, olefinic), 3.49 (2 H, t, *J* 6 Hz, CH_2OH), 2.30—1.85 (5 H, with Me, d, *J* 1.5 Hz, at 2.00), 1.58 (2 H, pent, *J* 7 Hz, CH_2CH_2OH), and 1.70 (1 H, s, OH), and the minor (*E*)-alcohol, n_D^{23} 1.5498, *m/z* 176 (M^+); $\nu_{max.}$ 3 375, 1 600, and 1 088 cm^{-1}; δ($CDCl_3$) 7.25 (5 H, m, ArH), 5.75 (1 H, tq, *J* 7.5, 1.3 Hz, olefinic), 3.67 (2 H, t, *J* 6 Hz, CH_2OH), 2.28 (2 H, q, *J* 7 Hz, C=CHCH_2), 2.03 (3 H, s, Me), 1.72 (2 H, quintet, *J* 7 Hz, $CH_2CH_2CH_2OH$), and 1.50 (1 H, s, OH).

Alk-3-en-1-ols from 2-Substituted 3-Chlorotetrahydrofurans

(E)-*Pent-3-en-1-ol.*—Pent-3-yn-1-ol (12 g) was reduced with sodium in liquid ammonia[27] to yield (*E*)-pent-3-en-1-ol (8 g, 66%), b.p. 45—46 °C/15 mmHg, n_D^{20} 1.4342 (lit.,[27] b.p. 136—137 °C, n_D^{20} 1.4340); $\nu_{max.}$ 3 360 and 970 cm^{-1}; δ($CDCl_3$) 5.42 (2 H, m, olefinic) 4.05 (1 H, s, OH), 3.51 (2 H, t, *J* 6 Hz, CH_2OH), 2.19 (2 H, m), and 1.67 (3 H, dd, *J* 4, 1 Hz, Me); δ{$CDCl_3$ + [Eu(fod)$_3$]} θ H/CH_3 = 3.1.

(Z)-*Pent-3-en-1-ol.*—Pent-3-yn-1-ol (5.9 g) in methanol (100 cm^3) was hydrogenated over Lindlar catalyst (500 mg) to yield (*Z*)-pent-3-en-1-ol (4.9 g, 80%), b.p. 47—48 °C/16 mmHg, n_D^{20} 1.4379 (lit.,[27] b.p. 139—142 °C, n_D^{20} 1.4387); $\nu_{max.}$ 3 360 and 1 655 cm^{-1} (no band at 970 cm^{-1} was observed); δ($CDCl_3$), 5.45 (2 H, m, olefinic), 4.02 (1 H, s, OH), 3.52 (2 H, t, *J* 6 Hz, CH_2OH), 2.27 (2 H, q, *J* 6 Hz), and 1.62 (3 H, d, *J* 5 Hz, Me); δ{$CDCl_3$ + [Eu(fod)$_3$]} θ CH_3/H = 0.8.

Pent-3-en-1-ol from Ring Scission.—Ring scission of separated *trans*-3-chloro-2-methyltetrahydrofuran (10 g) [stereochemically pure by g.l.c. (PEGA)] gave pent-3-en-1-ol (5.3 g, 75%), b.p. 48—50 °C/16 mmHg, n_D^{20} 1.4343 (lit.,[1] b.p. 136—137 °C, n_D^{20} 1.4343. Similar scission of *cis*-3-chloro-2-methyltetrahydrofuran (pure by g.l.c.) also gave pent-3-en-1-ol (85%), b.p. 48—50 °C/16 mmHg, n_D^{20} 1.4360 (lit.,[1] n_D^{20} 1.4355). G.l.c. analyses (PEGA, 80 °C, N_2 60 cm^3 min^{-1}) of the ring scission products [(*Z*)- + (*E*) mixtures] gave the isomer ratios (see text). The validity of the analytical method (peak area ratios) was confirmed for weighed mixtures of the stereoisomeric pent-3-en-1-ols.

Hept-3-en-1-ol.—*cis-* and *trans*-3-Chloro-2-propyltetrahydrofurans were obtained stereochemically pure by preparative g.l.c. (PEGA). Small scale ring scissions of each isomer followed by g.l.c. analysis (PEGA, 90 °C) gave the (*E*)-/(*Z*)-hept-3-en-1-ol product ratios. The (*E*)-alcohol was assigned as the major low retention time alcohol from the i.r. spectra of the mixtures (970 cm^{-1} band intensity).

Hepta-3,6-dien-1-ol.—Ring scission of mixed *cis-* and *trans*-2-allyl-3-chlorotetrahydrofurans (11.5 g) gave a mixture of (*Z*)- and (*E*)-*hepta-3,6-dien-1-ols* (7.4 g, 86%), b.p. 79—82 °C/17 mmHg (Found: C, 75.2; H, 10.6. $C_7H_{12}O$ requires C, 75.0; H, 10.7%); $\nu_{max.}$ 3 410, 1 638, and 970 cm^{-1}; δ($CDCl_3$) 5.86 (1 H, ddt, *J* 17,10, 6 Hz, 6-H), 5.52 (2 H, m, 3-H and 4-H), 5.03 (1 H, d, J_{trans} 17 Hz, 7-H), 5.00 (1 H, d, J_{cis} 10 Hz, 7-H), 3.62 (2 H, t, *J* 6 Hz, CH_2OH), 2.92 (1 H, s, OH), 2.86 (2 H, m, 5-H_2), and 2.31 (2 H, m, CH_2CH_2OH). Small scale ring scissions of the individual

stereochemically pure *cis*- and *trans*- halides, followed by g.l.c. analysis (PEGA, 90 °C, N_2 80 cm^3 min^{-1}) gave the isomer product ratios from each scission (the *trans*-isomer was shown to be the major low retention time component from the 970 cm^{-1} i.r. band intensity).

5-*Methylhex*-3-*en*-1-*ol*.—Ring scission of mixed *cis*- and *trans*-3-chloro-2-isopropyltetrahydrofurans (15 g) gave a mixture of (*Z*)- and (*E*)-5-methylhex-3-en-1-ols (9.9 g, 86%), b.p. 161—164 °C, n_D^{20} 1.4350 (lit.,[3] n_D^{20} 1.4335—1.4372); $\nu_{max.}$ 3 380 and 970 cm^{-1}; δ($CDCl_3$) 5.42 (2 H, m, olefinic), 3.62 (2 H, t, *J* 6 Hz, CH_2OH), 2.28 (3 H, m), 2.20 (1 H, s, OH), and 0.97 (6 H, d, *J* 6 Hz, Me_2CH); δ{$CDCl_3$ + [Eu(fod)$_3$]} θ CH/H = 2.4 (*Z*), θ H/CH = 1.0 (*E*). Small scale individual *cis*- and *trans*-β-halide scissions, followed by g.l.c. analysis (PEGA) gave the isomer ratio from each scission.

4-*Phenylbut*-3-*en*-1-*ol*.—Ring scission of *trans*-3-chloro-2-phenyltetrahydrofuran (10 g) gave a mixture (6.8 g) of 4-phenylbut-3-en-1-ol [70% by g.l.c. (Apiezon)] and 4-phenylbutan-1-ol (30%), b.p. 148—150 °C/17 mmHg, n_D^{23} 1.5525 (lit.,[28] b.p. 134—140 °C/12 mmHg). Preparative g.l.c. (Apiezon) afforded pure 4-phenylbut-3-en-1-ol [90%-(*E*)], *m*/*z* 148 (M^+); $\nu_{max.}$ 3 370, 1 600, and 970 cm^{-1}; δ($CDCl_3$) 7.22 (5 H, m, ArH), 6.47 (1 H, half of AB dd, *J* 17 Hz, 4-H), 6.08 (1 H, dt, ABX_2 with J_{AX_2} = 0, *J* 17 Hz, 6 Hz, 3-H), 3.67 (2 H, t, *J* 6 Hz, CH_2OH), 2.41 (2 H, q, *J* 6 Hz, CH_2CH_2OH), and 2.12 (1 H, s, OH). [Irradiation of the 2.41 quartet caused the 3-H signal to collapse to a doublet (J_{trans} 17 Hz); irradiation of the *cis*-4-H doublet (J_{cis} 11 Hz) in the shifted [Pr(fod)$_3$] spectrum caused the *cis*-3-H doublet of triplets (J_{cis} 11, J_H, CH_2 6 Hz) to collapse to a triplet (*J* 6 Hz)].

Hydrogenation of the ring scission mixture (1 g) over 10% palladium on charcoal (100 mg) in methanol (50 cm^3) afforded solely 4-phenylbutan-1-ol (800 mg). This product co-chromatographed (Apiezon) with the minor ring scission component. (Normant[28] reports 4-phenylbutan-1-ol to be formed as 15% of the ring scission mixture using ether as the solvent).

When the ring scission was repeated with toluene as the solvent, 4-phenylbut-3-en-1-ol [90% (*E*)] was obtained in 81% yield and the reduction product constituted only 6% of the mixture.

4-p-*Tolylbut*-3-*en*-1-*ol*.—Ring scission of *trans*-3-chloro-2-*p*-tolyltetrahydrofuran (13.5 g) yielded 4-*p*-tolylbutan-1-ol [20% by g.l.c. (Apiezon)] and 4-*p*-tolylbut-3-en-1-ol (80% by g.l.c.). Recrystallisation afforded pure (*E*)-4-p-*tolylbut*-3-*en*-1-*ol* (4.6 g, 43%) as white plates, m.p. 52 °C (pentane) (Found: C, 81.2; H, 8.4; *m*/*z* 162. $C_{11}H_{14}O$ requires C, 81.5; H, 8.6%; *M*, 162), $\nu_{max.}$ 3 320 and 970 cm^{-1}; δ($CDCl_3$) 7.17 (4 H, dd, AA′BB′, ArH), 6.46 (1 H, half of ABdd, *J* 17.5 Hz, 4-H), 6.10 (1 H, dt, ABX_2 with J_{AX_2} = 0, *J* 17.5, 6 Hz, 3-H), 3.72 (2 H, t, *J* 6 Hz, CH_2OH), 2.44 (2 H, q, *J* 6 Hz, CH_2CH_2OH), 2.30 (3 H, s, Me), and 1.69 (1 H, s, OH). Irradiation of the δ 2.44 quartet caused the olefinic region to be observed as a half of an ABdd with J_{trans} 17.5 Hz. The n.m.r. spectrum of the crude product showed the presence of a benzylic triplet at δ2.57 (4-*p*-tolylbutan-1-ol). Addition of [Pr(fod)$_3$] resolved the olefinic region [shift magnitude 3-H (*Z*) > 3-H (*E*) > 4-H (*E*) > 4-H (*Z*)] and revealed the presence of (*Z*)-4-*p*-tolylbut-3-en-1-ol; the (*Z*) 4-H signal appeared as a doublet (J_{cis} 12 Hz) and the 3-H signal as a doublet of triplets (*J* 12, 6 Hz). Double resonance confirmed that these signals were coupled to each other and integration of the two different 4-proton doublets showed a (*Z*)/(*E*) ratio of 10:90.

Hexa-3,5-*dien*-1-*ol*.—Ring scission of mixed *cis*- and *trans*-3-chloro-2-vinyltetrahydrofurans (14 g) gave a mixture of alcohols (7.8 g), b.p. 63—63.5 °C/15 mmHg. Preparative g.l.c. (PEGA) afforded (*Z*)- and (*E*)-hex-3-en-1-ols (confirmed by comparison with authentic samples[37]), hex-4-en-1-ol (**24**) [$\nu_{max.}$ 970 cm^{-1}, mainly (*E*), confirmed by comparison with an authentic sample[37]], and hex-5-en-1-ol (**25**) (in admixture with some hex-4-en-1-ol).

Ring scission using a 0.3 mol excess of the β-halide followed by preparative g.l.c. (PEGA) gave the hexa-3,5-dien-1-ol (formed as 48% of the mixture), n_D^{20} 1.4699 [lit.,[29] (*Z*) n_D^{23} 1.4714]; $\nu_{max.}$ 3 350, 1 645, 1 601, and 1 000 cm^{-1}; δ($CDCl_3$) 6.80—4.80 (5 H, m, olefinics), 3.63 (2 H, t, *J* 6 Hz, CH_2OH), 2.32 (2 H, q, *J* 6 Hz, CH_2CH_2OH), and 2.44 (1 H, s, OH). The product was expected to be a (*Z*)/(*E*) mixture.

[4-^{1}H]- *and* [4-^{2}H]-*But*-3-*en*-1-*ols*.—Ring scission of 3-chlorotetrahydrofuran (7 g) gave but-3-en-1-ol (4 g, 84%), b.p. 112—114 °C, n_D^{20} 1.4220 (lit.,[3] b.p. 111—114 °C, n_D^{20} 1.4218); $\nu_{max.}$ 3 400 and 1 642 cm^{-1}; *m*/*z* 72 (M^+), 41 (base peak); δ($CDCl_3$) 5.92 (1 H, ddt, *J* 17.5, 10.5, 6 Hz, 3-H), 5.17 (1 H, d, *J* 17.5 Hz, 4-H), 5.13 (1 H, d, *J* 10.5 Hz, 4-H), 3.78 (2 H, t, *J* 6 Hz, CH_2OH), 3.22 (1 H, s, OH), and 2.38 (2 H, q, *J* 6 Hz, CH_2CH_2OH); δ{$CDCl_3$ + [Eu(fod)$_3$]} θ H/H = 1.5.

Ring scission of 3-chloro-2-deuteriotetrahydrofuran gave (*Z*)- and (*E*)-[4-^{2}H]but-3-en-1-ols (ratio 42:58 by n.m.r.) (85%), b.p. 112—114 °C; $\nu_{max.}$ 3 400, 1 620, and 975 cm^{-1}; *m*/*z* 73 (M^+), and 42 (base peak); δ($CDCl_3$) as above but the 4-protons integrated as 1 H.

Alk-3-*en*-1-*ols from* 2-*Alkyl*-3-*bromotetrahydrofurans*

cis- and *trans*-3-Bromo-2-methyltetrahydrofurans [27:73 by g.l.c. (PEGA)] (54%), b.p. 42—51 °C/14 mmHg, were prepared as described above. Distillation afforded the low b.p. *trans* isomer (90% stereochemical purity) [Found: C, 36.5; H, 5.3; M^+, 164, 166 (1:1). C_5H_9BrO requires C, 36.4; H, 5.45%; *M*, 164, 166 (1:1)] *m*/*z*, 149, 151 (1:1) (base peaks) (corresponding to M^+ − Me); δ($CDCl_3$) 4.18—3.68 (4 H, m), 2.74—2.02 (2 H, m, 11 lines), and 1.26 (3 H, d, *J* 6 Hz, Me). Ring scission of this sample gave (*Z*)- and (*E*)-pent-3-en-1-ols [ratio 29:71 by g.l.c. (PEGA)].

cis- and *trans*-3-Bromo-2-propyltetrahydrofurans [27:73 by g.l.c. (PEGA)] (51%) b.p. 69—81 °C/15 mmHg, were prepared. Distillation afforded the low b.p. *trans*-isomer (92% stereochemical purity) [Found: C, 43.6; H, 6.4; M^+, 192, 194 (1:1). $C_7H_{13}BrO$ requires C, 43.5; H, 6.75%; *M*, 192, 194 (1:1)]; *m*/*z* 149, 151 (1:1) (base peaks) (corresponding to *M* − Pr); δ($CDCl_3$) 5.10—3.80 (4 H, m), 2.68—2.11 (2 H, m, 11 lines), 1.51 (4 H, m), and 0.96 (3 H, br t, $MeCH_2$). Ring scission of this sample gave (*Z*)- and (*E*)-hept-3-en-1-ol [ratio 26:74 by g.l.c. (PEGA)].

4-*Methylalk*-3-*en*-1-*ols from* 2-*Alkyl*-3-*chloro*-2-*methyltetrahydrofurans*

2-*Alkyl*-3-*chloro*-2-*methyltetrahydrofurans*.—The tetrahydrofurans were prepared from 2-methyl-4,5-dihydrofuran on a 0.15 mol scale *via* the procedure described for 2-alkyl-3-chloro-2-methyltetrahydropyrans. Ring scissions were performed on a 0.02 mol scale.

4-*Methylhex*-3-*en*-1-*ol*.—*trans*- and *cis*-3-Chloro-2-ethyl-2-methyltetrahydrofurans [ratio 64:36 by g.l.c. (PEGA)] (64%) were prepared as a mixture, b.p. 55—60 °C/14 mmHg, n_D^{20} 1.4530 (lit.,[30] b.p. 64—65 °C/20 mmHg, $n_D^{22.5}$ 1.4546). Ring scission afforded (*Z*)- and (*E*)-4-methylhex-3-en-1-ols (53:47 by n.m.r.) (84%), b.p. 80—82 °C/20 mmHg, n_D^{20} 1.4499 (lit.,[3] b.p.

80—81 °C/20 mmHg. n_D^{25} 1.4484); $\nu_{max.}$ 3 420 cm^{-1}; δ($CDCl_3$) 5.10 (1 H, t, *J* 6 Hz, olefinic), 3.59 (2 H, t, *J* 6 Hz, CH_2OH), 2.40 (1 H, s, OH), 2.50—1.80 (4 H, 6 lines, *J* 6 Hz), 1.70 (*Z*)- and 1.65 (*E*) (3 H, Me), and 0.99 (3 H, t, *J* 7 Hz, $MeCH_2$); δ{$CDCl_3$ + [Eu(fod)$_3$]} θ CH_2/Me [(*Z*)] = 1.8, θ CH_3/CH_2 [(*E*)] = 1.5.

4-*Methylundeca*-3,8-*dien*-1-*ol*.—(*E*)-Hept-4-en-1-ol was converted into (*E*)-1-bromo-hept-4-ene. Reaction of the Grignard reagent with 2,3-dichloro-2-methyltetrahydrofuran afforded trans- and cis-(*E*)-3-*chloro*-2-*hept*-4-*enyl*-2-*methyltetrahydrofuran* (50%) b.p. 89—93 °C/0.4 mmHg [Found: C, 66.4; H, 9.6; M^+, 216, 218 (3:1). $C_{12}H_{21}ClO$ requires C, 66.5; H, 9.7%; *M*, 216, 218 (3:1)]. Ring scission of this mixture gave (*Z*)- and (*E*)-4-*methylundeca*-3,8-*dien*-1-*ols* (34:66 by n.m.r.) (76%) (Found: C, 79.3; H, 12.0. $C_{12}H_{22}O$ requires C, 79.2; H, 12.1%); $\nu_{max.}$ 3 350, 1 660, and 1 620 cm^{-1}; δ($CDCl_3$) 5.36 (2 H, m, olefinic), 5.10 (1 H, t, *J* 6 Hz, olefinic, 3-H), 3.47 (2 H, t, *J* 6 Hz, CH_2OH), 2.45—1.20 [13 H, with 2 × Me, s, at 1.65 (*Z*) and 1.60 (*E*)], and 0.94 (3 H, t, *J* 7 Hz, $MeCH_2$). The product was purified by column chromatography [SiO_2, benzene–ethyl acetate (5:1)] followed by short path distillation (air bath temp. 80 °C/14 mmHg).

4,5-*Dimethylhex*-3-*en*-1-*ol*.—*trans*- and *cis*-3-Chloro-2-isopropyl-2-methyltetrahydrofuran [60:40 by g.l.c. (PEGA)] (35%), b.p. 70—80 °C/16 mmHg were prepared as a mixture. Preparative g.l.c. (PEGA) afforded the low b.p. *cis*-3-chloro-*r*-2-methyl-*isomer* [Found: C, 58.8; H, 9.30; M^+, 162, 164 (3:1). $C_8H_{15}ClO$ requires C, 59.1; H, 9.25%; *M*, 162, 164 (3:1)]; *m/z*, 147, 149 (3:1) (M^+ − Me), 119, 121 (3:1) (M^+ − Pr^i); δ($CDCl_3$) 4.14 (1 H, t, *J* 7 Hz, 3-H), 4.02—3.60 (2 H, m, 5-H_2), 2.64—2.06 (2 H, m, 4-H_2), 1.74 (1 H, septet, *J* 7 Hz, Me_2CH), 1.19 (3 H, s, Me), and 0.96 (6 H, Me_2CH, d, *J* 7 Hz), and the high b.p. *trans*-3-chloro-*r*-2-methyl-isomer [Found: C, 58.9; H, 9.3; M^+, 162, 164 (3:1); δ($CDCl_3$), 4.20 (1 H, *ca.* doublet, *J* 6 Hz, 3-H), 4.14—3.82 (2 H, m, 5-H_2), 2.66 (1 H, 10 lines, 4-H or 4′-H), 2.26 (2 H, m), 1.04 (3 H, s, Me), and 0.96 (6 H, Me_2CH, d, *J* 7 Hz). Ring scission of these isomers each afforded (*Z*)- and (*E*)-4,5-dimethylhex-3-en-1-ol mixtures (81%) (Found: C, 75.1; H, 12.4. Calc. for $C_8H_{16}O$: C, 75.0; H, 12.5%); $\nu_{max.}$ 3 387 cm^{-1}; δ($CDCl_3$) 5.13 and 5.02 (1 H, t, *J* 7 Hz, 2 × 3-H), 3.60 (2 H, t, *J* 6 Hz, CH_2OH), 2.78 (1 H, septet, *J* 7 Hz, Me_2CH), 2.28 (2 H, q, *J* 7 Hz, CH_2CH_2OH), 1.90 (1 H, s, OH), 1.60 (3 H, s, Me), and 0.97 and 0.95 (6 H, Me_2CH, d, *J* 7 Hz). The mixtures were purified by preparative g.l.c. (PEGA) prior to analysis.

4-*Phenylpent*-3-*en*-1-*ol*.—3-Chloro-2-methyl-2-phenyltetrahydrofuran (64%), b.p. 79 °C/0.6 mmHg, n_D^{19} 1.5420 (lit.,[31] b.p. 86 °C/1 mmHg, n_D^{25} 1.5396); δ(CCl_4) 7.19 (5 H, m, ArH), 4.40 (1 H, dd, *J* 5.2, 3.6 Hz, 3-H), 4.12 (1 H, q, second order, *J* 7.0 Hz, 5-H), 3.92 (1 H, td, second order *J* 7 and 5 Hz, 5′-H), 2.12 (2 H, m), and 1.52 (3 H, s, Me), prepared by the usual method, was of single configuration. Ring scission in ether yielded a mixture (45%) of (*Z*)-4-phenylpent-3-en-1-ol [13% by g.l.c. (SE30)], 4-phenylpentan-1-ol (21%), and (*E*)-4-phenylpent-3-en-1-ol (66%). Ring scission in toluene eliminated the reduction product and afforded a mixture (63%) of (*Z*)-4-phenylpent-3-en-1-ol [19% by g.l.c. (SE30)] and (*E*)-4-phenylpent-3-en-1-ol (81%), b.p. 104 °C/0.7 mmHg, n_D^{19} 1.5570 (lit.,[31] n_D^{25} 1.5695); $\nu_{max.}$ 3 375 and 1 050 cm^{-1}; δ($CDCl_3$) 5.72 (*E*)- and 5.41 (*Z*)-(1 H, tm, *J* 7 Hz, 1.5 Hz, olefinic, ratio *ca.* 77:23), 3.57 (*E*) and 3.44 (*Z*) (2 H, t, *J* 6 Hz, CH_2OH), 2.95 (1 H, s, OH), 2.40 (2 H, q, *J* 7 Hz, CH_2CH_2OH), and 2.01 (3 H, d, *J* 1.5 Hz, Me).

2-*Alkyl*-3,3-*dichlorotetrahydropyrans*.—Alkylmagnesium bromide (0.5 ml) in dry ether (250 cm^3) [from the alkyl bromide (R = Et, Bu; 0.5 mol) and magnesium (0.5 mol)][15] was cooled (ice-water) and stirred whilst finely divided anhydrous cadmium chloride (0.25 mol) was added. After refluxing for 3 h a negative Gilman test was observed, and the ether was distilled off and replaced with dry benzene (250 cm^3). Meanwhile, 3-chloro-5,6-dihydro-4*H*-pyran[32] (36 g, 0.3 mol) in dry ether (50 cm^3) was chlorinated at 0 °C and the solvent evaporated to yield 2,3,3-trichlorotetrahydropyran (100%); δ($CDCl_3$) 6.01 (1 H, s, 2-H), 4.40—3.60 (2 H, m, 6-H_a, 6-H_e), and 2.95—1.46 (4 H, m). A small purified sample had b.p. 98 °C/13 mmHg, m.p. 30 °C (lit.,[33] b.p. 88 °C/13 mmHg, m.p. 32 °C). The 2,3,3-trichloride in benzene (50 cm^3) was then added to the organometallic reagent (R = Et) to yield 3,3-dichloro-2-ethyltetrahydropyran (53%), b.p. 90—93 °C/17 mmHg, n_D^{20} 1.4771 (lit.,[15] b.p. 91—94 °C/20 mmHg, n_D^{22} 1.4762); δ($CDCl_3$) 4.04 (1 H, ddd, *J* 11.5, 4.5, 1.8 Hz, 6-H_e), 3.45 (1 H, td, *J* 11.5, 2.6 Hz, 6-H_a), 3.29 (1 H, dd, *J* 9.4, 2.3 Hz, 2-H), 2.69 (1 H, dm), 2.40—1.35 (5 H, m), and 1.00 (3 H, t, *J* 7 Hz, $MeCH_2$), and (R = Bu) 2-butyl-3,3-dichlorotetrahydropyran (49 g, 52%), b.p. 76—80 °C/2 mmHg, n_D^{20} 1.4761 (lit.,[15] b.p. 121—123 °C/18 mmHg, $n_D^{21.3}$ 1.4752); δ($CDCl_3$) 4.03 (1 H, dt, *J* 12, 2.6 Hz, 6-H_e), 3.70—3.20 (2 H, m, 6-H_a and 2-H), 2.95—1.10 (10 H, m), and 0.90 (3 H, br t, $MeCH_2$).

Ring Scission.—Ring scission of the β-dihalides (1 mol) with sodium (4 mol) in THF yielded (*E*)-hept-4-en-1-ol (R = Et) (43%) (identical with an authentic sample), and *trans*-(*E*)-non-4-en-1-ol (R = Bu) (45%), respectively. The latter had b.p. 101—102 °C/13 mmHg, n_D^{20} 1.4478 (lit.,[1] n_D^{20} 1.4476); $\nu_{max.}$ 3 330, 1 060, and 970 cm^{-1}; δ($CDCl_3$) 5.40 (2 H, m, olefinic), 3.60 (2 H, t, *J* 6 Hz, CH_2OH), 2.15 (1 H, s, OH), 1.97 (2 H, m), 1.85—0.97 (6 H, m), and 0.88 (3 H, br t, $MeCH_2$); δ{$CDCl_3$ + [Eu(fod)$_3$]} H/CH_2 = 2.6.

5-*Methylalk*-4-*en*-1-*ols from* 2-*Alkyl*-3,3-*dichloro*-2-*methyltetrahydropyrans*

2,3,3-*Trichloro*-2-*methyltetrahydropyran*.—2-Methyltetrahydropyran (200 g, 2 mol) was chlorinated with sulphuryl chloride (270 g, 2 mol) at 65—70 °C, using a Nersasion type procedure[34] to yield 2,3,3-trichloro-2-methyltetrahydropyran in low yield (30 g, 15%), b.p. 95—99 °C/19 mmHg, *m/z* 202, 204, 206, and 208, (M^+) 167, 169, and 171 (9:6:1) (M^+ − Cl); δ($CDCl_3$) 4.35—3.82 (2 H, m, 6-H_a and 6-H_e), 2.97 (1 H, m), 2.40 (2 H, m), 2.10 (3 H, s, Me), and 1.66 (1 H, m). (Normant[35] reports the trichloride to be an unstable solid, m.p. 111—112 °C. In our hands the trichloride did not crystallise).

2-*Alkyl*-3,3-*dichloro*-2-*methyltetrahydropyrans*.—Grignard substitution (RMgBr; R = Et and Ph) of the trichloride (*cf.* the general procedure) afforded 3,3-dichloro-2-ethyl-2-methyltetrahydropyran (R = Et) (45%), b.p. 100—105 °C/15 mmHg, (lit.,[20] b.p. 107—108 °C/18 mmHg); *m/z* 196, 198, 200 (9:6:1) (M^+) 181, 183, 185 (9:6:1) and 167, 169, 171 (9:6:1) (M^+ − Me and M^+ − Et respectively); δ($CDCl_3$) 3.65 (2 H, t, *J* 6 Hz, 6-H), 2.60 (2 H, t, *J* 6 Hz), 1.98 (4 H, m), 1.41 (3 H, s, Me), and 0.91 (3 H, t, *J* 7 Hz, $MeCH_2$), and 3,3-*dichloro*-2-*methyl*-2-*phenyltetrahydropyran* (R = Ph) (12%), b.p. 114—116 °C/1 mmHg, m.p. 93—95 °C [Found: C, 59.5; H, 5.2%; M^+ 244, 246, and 248 (9:6:1). $C_{12}H_{14}Cl_2O$ requires C, 58.8; H, 5.7%; *M*, 244, 246, and 248 (9:6:1)]; *m/z* 229, 231, and 233 (9:6:1) (M^+ − Me); δ($CDCl_3$), 7.80 (2 H, m, ArH), 7.36 (3 H, m, ArH), 3.98 (2 H, dd, second order, 6-H), 2.70 (2 H, m), 2.35 (1 H, m), 1.90 (3 H, s, Me), and 1.69 (1 H, m). Both the dichlorides were unstable and rapidly darkened on standing.

Ring Scission.—Ring scissions with powdered sodium in ether were very sluggish. Scission of 3,3-dichloro-2-ethyl-2-

methyltetrahydropyran (48 h ether reflux over powdered sodium) afforded a mixture (43%) of (*Z*)- and (*E*)-(ratio 50:50 by n.m.r.) 5-methylhept-4-en-1-ols. Scission of 3,3-dichloro-2-methyl-2-phenyltetrahydropyran was exceedingly slow with sodium metal, but proceeded satisfactorily with potassium (48 h, ether reflux) to give a mixture (31%) of (*Z*)-5-phenylhex-4-en-1-ol [51% by g.l.c. (SE30)], 5-phenylhexan-1-ol (13%), and (*E*)-5-phenylhex-4-en-1-ol (36%).

Reaction of 3-Chloro-2-methyltetrahydrofuran with Tributyltin Hydride.—*cis*- and *trans*-3-Chloro-2-methyltetrahydrofurans (*ca.* 50:50) (1.2 g) and tributyltin hydride[38] (2.9 g) were heated in the presence of dibenzoyl peroxide (120 mg) at 120 °C for 12 h. G.l.c. analysis (PEGA, 60 °C) of the crude product showed 2-methyltetrahydrofuran (25% yield; 2-methyltetrahydropyran internal standard) in admixture with starting material; no (*Z*)- or (*E*)-pent-3-en-1-ol was detected.

Reaction of 3-Chloro-2-methyltetrahydropyran with Tributyltin Hydride.—*cis*- and *trans*-3-Chloro-2-methyltetrahydropyrans (60% *cis*) (1.32 g) were subjected to the above treatment. G.l.c. analysis (PEGA, 60 °C) of the crude product showed 2-methyltetrahydropyran (23% yield; 2-methyltetrahydrofuran internal standard) in admixture with starting material; no (*E*)-hex-3-en-1-ol was detected.

Reaction of 3-Chloro-2-methyltetrahydro-pyrans and -furans with n-Butyl-lithium

Reaction of the Tetrahydrofurans.—*trans*-3-Chloro-2-methyltetrahydrofuran (3 g) was added to butyl-lithium (25 cm^3 of a 20—25% solution in hexane) whereupon the mixture immediately began to reflux and a yellow precipitate to separate. The mixture was stirred for 12 h and worked up as described for the sodium reaction. Distillation gave crude (*Z*)- and (*E*)-pent-3-en-1-ols (650 mg, 30%), b.p. 40—50 °C/16 mmHg. G.l.c. analysis (PEGA, 60 °C) showed the ratio of the (*Z*)- and (*E*)-pent-3-en-1-ols to be 20:80; other products were also found.

Similar reaction of *cis*-3-chloro-2-methyltetrahydrofuran produced (*Z*)- and (*E*)-pent-3-en-1-ols (ratio 47:53 by g.l.c.) in *ca.* 27% yield though other products were also formed.

Reaction of the Tetrahydropyrans.—Reaction of mixed *cis*- and *trans*-3-chloro-2-methyltetrahydropyrans (3 g) with an excess of n-butyl-lithium, followed by preparative g.l.c. isolation (PEGA), afforded (*E*)-hex-4-en-1-ol ($\nu_{max.}$ 970 cm^{-1}) in low yield. G.l.c. analyses (PEGA, ambient temp.) of the ether extracts containing the crude ring scission products showed the presence of butyl chloride.

2-Alkyl-3,3-dichlorotetrahydropyrans: Ring Scission.—*Reaction with 2 mol sodium.* Ring scissions of 2-alkyl-3,3-dichlorotetrahydropyrans (R = Et, Bu) (5 mmol) with powdered sodium (10 mmol) in THF (10 cm^3) were rapid. Each reaction after work-up and preparative g.l.c. (PEGA) afforded equal amounts of (*E*)-alk-4-en-1-ol and starting material. G.l.c. analyses of the crude reaction mixtures showed the absence of *cis*- or *trans*-2-alkyl-3-chlorotetrahydropyrans. Ring scission in benzene was sluggish but gave identical results.

Deuteriation studies with 4 mol Sodium. Ring scission [β-dihalide (5 mmol), powdered sodium (20 mmol), dry benzene (10 cm^3), in a dry nitrogen atmosphere] with a D_2O work-up, followed by preparative g.l.c. isolation of the alcohols (R = Et, Bu) produced alk-4-en-1-ols with no 4-D incorporation. Ring scission in C_6D_6 solvent with H_2O work-up, however, afforded (*E*)-[4-^{2}H]alk-4-en-1-ols. Relative integration of the ('2H') olefinic multiplet with respect to the (2H)CH_2OH triplet revealed D-incorporations in the range 30—45%.

Synthesis of Brevicomin

(E)-1-*Bromohept-4-ene.*—Phosphorus tribromide (112 g, 0.41 mol) was added dropwise, with stirring, to an ice-cold solution of (*E*)-hept-4-en-1-ol (70 g, 0.61 mol) in pyridine (28 g). Stirring was maintained for 2 h after which the crude bromide was distilled directly out of the flask under reduced pressure; it was diluted with light petroleum (b.p. 40—60 °C) and washed with aqueous acid, aqueous alkali, and water. Evaporation and distillation afforded (*E*)-1-bromo-hept-4-ene (86 g, 68%), b.p. 64—66 °C/21 mmHg, n_D^{22} 1.4685 (lit.,[36] 65%, b.p. 62—64 °C/11 mmHg, n_D^{17} 1.4706); $\nu_{max.}$ 970, 648 (C–Br), and 561 (C–Br) cm^{-1}.

(E)-*Non*-6-*en*-2-*one.*—Dry dimethylacetamide (23.5 g, 0.27 mol) in dry ether (50 cm^3) was added dropwise, with stirring, to a solution of (*E*)-hept-4-enylmagnesium bromide [from (*E*)-1-bromohept-4-ene (45 g, 0.25 mol) and magnesium turnings (8 g, 0.33 mol) in ether (50 cm^3)] maintained at −10 °C under nitrogen. After 1.5 h the mixture was allowed to attain room temperature and then poured into aqueous ammonium chloride–ice and thoroughly extracted with ether. The ether solution was washed with water, dried, and distilled to give (E)-*non*-6-*en*-2-*one* (23 g, 64%), b.p. 46—48 °C/1.5 mmHg, n_D^{27} 1.4355 (Found: C, 77.3; H, 11.2%; M^+, 140. $C_9H_{16}O$ requires C, 77.2; H, 11.4%; *M*, 140]; $\nu_{max.}$ 1 709 and 970 cm^{-1}; δ(CCl_4) 5.38 (2 H, m, olefinic), 2.34 (2 H, t, *J* 7 Hz, CH_2COMe), 2.20—1.40 (9 H, with *Me*CO, s, at 2.05), and 0.99 (3 H, t, *J* 7 Hz, *Me*CH_2), The 2,4-dinitrophenylhydrazone formed yellow flakes, m.p. 82—83 °C (EtOH).

(E)-*Non*-6-*en*-2-*one Ethylene Acetal.*—(*E*)-Non-6-en-2-one (11.3 g), ethylene glycol (7.4 g), and toluene-*p*-sulphonic acid (200 mg) in benzene (65 cm^3) were refluxed using a Dean-Stark water trap until no more water separated. The mixture was neutralised (Na_2CO_3) and distilled to give the *ethylene acetal* (12.7 g, 87%), b.p. 103—107 °C/4 mmHg [lit.,[37] (*cis* + *trans*) b.p. 110—116 °C/22 mmHg] (Found: C, 72.2; H, 10.7%; M^+, 184.1462. $C_{11}H_{20}O_2$ requires C, 71.7; H, 10.8%; *M*, 184.1463); $\nu_{max.}$ 970 cm^{-1}; δ(CCl_4) 5.36 (2 H, m, olefinic), 3.80 (4 H, s, OCH_2CH_2O), 1.95 (4 H, m), 1.48 (4 H, m), 1.20 (3 H, s, $MeCO_2$), and 0.95 (3 H, t, *J* 7 Hz, *Me*CH_2).

exo-*Brevicomin.*—Osmium tetraoxide (1 g) in dioxane (12 cm^3) was added to a stirred solution of (*E*)-non-6-en-2-one (550 mg) in dioxane (12 cm^3). A black osmate ester precipitated immediately. On further stirring (2 h) the mixture was thoroughly saturated with hydrogen sulphide and filtered through Supercel. The solvent was then distilled under partially reduced pressure and the residue purified by column chromatography [Al_2O_3; benzene–ethyl acetate (10:1)]. Removal of the solvent under partially reduced pressure followed by short path distillation of the residue (air-bath temp. 55 °C/18 mmHg) afforded *exo*-brevicomin (305 mg, 50%) (Found: C, 69.1; H, 10.3%; M^+, 156. Calc. for $C_9H_{16}O_2$: C, 69.2; H, 10.3%; *M*, 156); δ(CCl_4) 3.99 (1 H, s, $w_{\frac{1}{2}}$ 5 Hz), 3.80 (1 H, t, *J* 6 Hz, 1.90—1.15 (8 H, with 3 H, s, Me at 1.30), and 0.88 (3 H, distorted t, *J* 7 Hz, *Me*CH_2). The i.r., n.m.r., and mass spectra of the product were identical with those of the natural attractant.[18] G.l.c. analysis (Carbowax 20M) revealed the presence of *ca.* 4% of the *endo*-epimer (the *endo*-epimer has the longer retention time).

Similar reaction of osmium tetraoxide (1 g) with (*E*)-non-6-en-2-one ethylene acetal (726 mg) afforded *exo*-brevicomin (340 mg) in 55% yield.

trans-6,7-*Epoxynonan*-2-*one*.—*m*-Chloroperbenzoic acid (2 g, 11.5 mmol) in chloroform (100 cm^3) was added dropwise, with stirring, to an ice-cold solution of (*E*)-non-6-en-2-one (1.1 g, 7.8 mmol) in chloroform (20 cm^3). The following day aqueous sodium hydroxide (10%) was added and the chloroform solution washed with water and dried. Evaporation of the solvent followed by purification of the residue by column chromatography [Al_2O_3, benzene–ether (10:1)] gave *trans*-6,7-epoxynonan-2-one (1.15 g, 94%). The epoxide was converted into *endo*-brevicomin without further purification. A portion of the product was distilled (short path, air-bath temp. 70 °C/15 mmHg) (Found: C, 69.25; H, 10.0%; M^+, 156. Calc. for $C_9H_{16}O_2$: C, 69.25; H, 10.25%; *M*, 156); $\nu_{max.}$ 1 712 cm^{-1}; $\delta(CCl_4)$ 2.49 (4 H, m, CH·CHO and CH_2COMe), 2.07 (3 H, s, MeCO), 1.51 (6 H, br, CH_2), and 0.98 (3 H, distorted t, *J* 7 Hz).

trans-6,7-*Epoxynonan*-2-*one Ethylene Acetal*.—Following the procedure above, (*E*)-non-6-en-2-one ethylene acetal (1 g, 5.4 mmol) was epoxidised with *m*-chloroperbenzoic acid (830 mg, 6 mmol) in benzene (100 cm^3) to yield *trans*-6,7-epoxynonan-2-one ethylene acetal (1 g, 92%). A portion of the product was distilled (short path) *m/z* 200 (M^+); $\delta(CCl_4)$ 3.80 (4 H, s, OCH_2CH_2O), 2.49 (2 H, m, CH–CHO), 1.50 (8 H, br, CH_2), and 0.97 (3 H, distorted t, *J* 7 Hz, CH_2Me). The n.m.r. spectrum was essentially the same as that described by Silverstein [37] (there is a discrepancy of 2H in Silverstein's reported data). G.l.c. analysis (Carbowax 20M) failed to reveal the presence of any *cis*-epoxide (the isomers are known to separate on this column [37]).

endo-*Brevicomin*.—*trans*-6,7-Epoxynonan-2-one (1 g, 6.4 mmol) was dissolved in aqueous acetone [acetone (50 cm^3) + water (7 cm^3)]. A catalytic amount of sulphuric acid (1 drop) was added and the mixture gently refluxed for 2 h. When cool, the mixture was poured into aqueous sodium hydrogen carbonate (1%), extracted with ether, washed with water, dried, and the ether distilled through a short column. The residue was then distilled (short path, air-bath temp. 60 °C/20 mmHg) to give *endo*-brevicomin (820 mg, 82%) (Found: C, 69.2; H, 10.3%; *m/z* 156. Calc. for $C_9C_{16}O_2$: C, 69.2; H, 10.3%; *M*, 156); $\delta(CCl_4)$ 4.02 (1 H, br, $w_{\frac{1}{2}}$ *ca.* 7 Hz), 3.85 (1 H, m, OC*H*Et), 1.60 (6 H, br), 1.35 (3 H, s, Me), and 0.98 (3 H, t, *J* 7 Hz, CH_2Me). The i.r., n.m.r. and mass spectra of the synthetic material were identical with those of the inactive component isolated from frass.[18] G.l.c. analysis revealed the presence of *ca.* 5% of the *exo*-isomer [Carbowax 20M, 120 °C, N_2 26 cm^3 min^{-1}; *endo*-(R_t 6.8 min), *exo*-(R_t 5.2 min)].

Similar reaction of *trans*-6,7-epoxynonan-2-one ethylene acetal (1 g) afforded *endo*-brevicomin (618 mg) in 79% yield [Silverstein *et al*[37] report a 91% yield for this reaction using a *cis*/*trans* mixture of the acetal].

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