Stereoselective Synthesis of Alcohols containing (*Z*)- and (*E*)-Olefins, Dienes, Enynes and Styrenes: Cyclic β-Halogeno Ether Scissions using Samarium Diiodide as the Electron-transfer Agent

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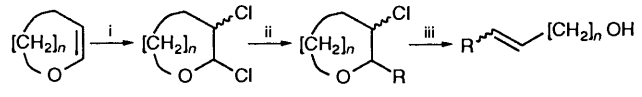
In contrast to the sodium-mediated ring scission of 2-substituted 3-chloro ethers of the tetrahydrofuran series, samarium diiodide gives olefins of high (*E*)-stereoselectivity and provides (*E*)-conjugated and unconjugated dienes, styrenes and enynes in good yield without appreciable over-reduction. Whilst the SmI_2 scission of 3-chloro-2-alkyltetrahydropyrans gives (*Z*)-rich (*Z*)/(*E*) olefin mixtures, the 2-(alk-1′-ynyl) members give (*Z*)-enyne alcohols with high stereoselectivity, providing a valuable complement to the (*E*)-enyne synthesis employing the tetrahydrofuran series.

In electron-transfer scissions using sodium, the stereochemistry of the product alcohols is related to the ground-state conformation of the *cis*- and *trans*-pyrans and -furans. The slow SmI_2-mediated reactions appear to involve samarium-complexed intermediates having structures independent of the original conformation, or of the *cis*- or *trans*-geometry of the furan or pyran, and it is the transition states from these intermediates that determine the stereochemical outcome.

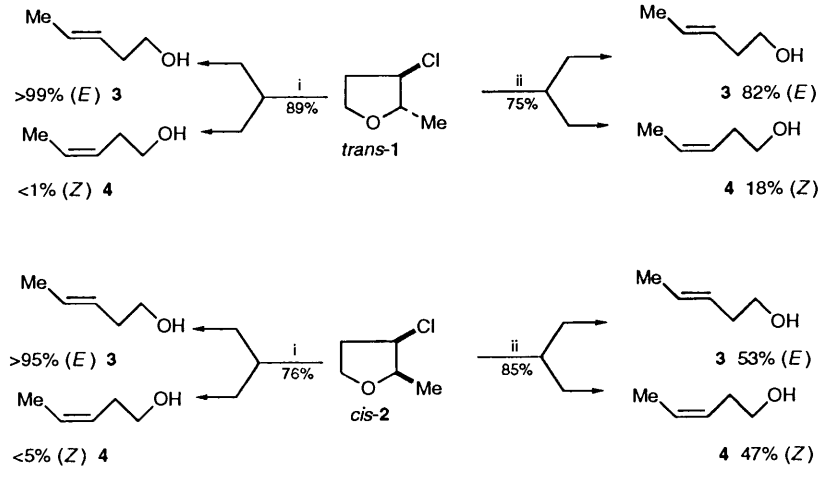
Scissions in the tetrahydrofuran series can be accelerated by addition of HMPA or DMPU with only a little deterioration in stereoselectivity, but in the tetrahydropyran series there are drastic changes in product stereochemistry when DMPU is added. Brief comment is made on the synthesis of tetrahydro-furan and -pyran precursors.

The stereochemistry of substituted cyclic β-halogeno ethers, and their cleavage using sodium in diethyl ether as the electron-transfer agent to form olefinic alcohols, has been examined in some detail in our earlier work[1] and is shown in generalised form in Scheme 1. The reaction provides an excellent regio-



Scheme 1 Generalised β-halogeno ether ring scission. *Reagents:* i, Cl_2; ii, RMgX; iii, Na.

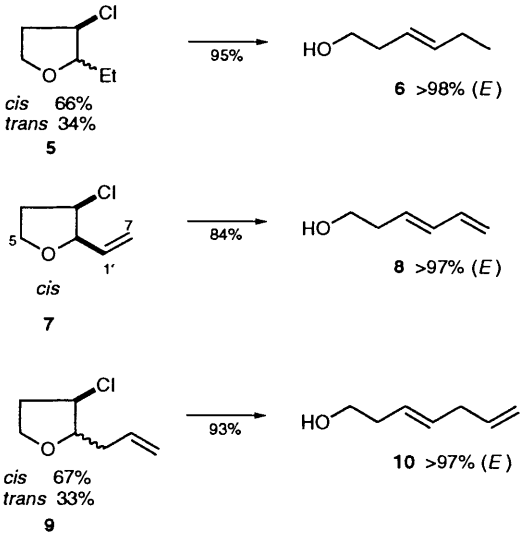
specific route to certain olefinic alcohols of defined stereochemistry, and its scope and limitations have been delineated.[1b] In particular we have been interested in the relationship between tetrahydropyran/tetrahydrofuran conformation and the geometry of the emergent olefinic alcohol. Such ring scissions have been carried out with an electropositive metal, usually sodium under diethyl ether, occasionally sodium/potassium alloy, magnesium[2] or zinc, as the electron-transfer agent. When the product is a conjugated olefin or a styrene, sodium can cause some over-reduction problems[1b] and we have therefore looked for more suitable electron-transfer agents, among them samarium diiodide.[3,4] From a synthetic point of view, the scission of 2-substituted 3-chlorotetrahydropyrans is of particular interest in that either the *trans*- or the *cis*-forms of the latter give almost stereochemically pure (>95%) (*E*)-olefinic alcohols in the sodium-mediated reaction.[1b] By contrast, the *trans*- and *cis*-forms of 2-substituted 3-chlorotetrahydrofurans each give (*E*)-/(*Z*)-alcohol mixtures of differing quantitative composition when treated with sodium, making the reaction of limited use from a synthetic point of view (Scheme 2). To our surprise the stereochemical position is quite different in these much slower samarium diiodide-mediated reactions.[5]



Scheme 2 Stereochemistry of ring scission of *trans*- and *cis*-3-chloro-2-methyltetrahydrofuran by using sodium in Et_2O and samarium diiodide in THF. *Reagents:* i, SmI_2; ii, Na.

Results

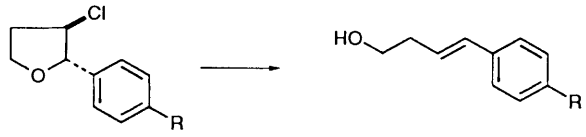
Scission of *trans*-3-chloro-2-methyltetrahydrofuran **1** with excess of samarium diiodide gives almost pure (*E*)-pent-3-en-1-ol **3** ($J_{3,4}$ 15.2 Hz) in good yield (Scheme 2) (baseline material in the ^{13}C NMR spectrum < 1%) as opposed to the (*E*)-/(*Z*)-mixtures encountered in the corresponding sodium reactions. The *cis*-isomer **2** (scission slower than the *trans*-) also gave almost stereochemically pure (*E*)-pent-3-en-1-ol, the (*Z*)-**4** impurity being less than 5%. Although the two geometrical isomers of the tetrahydrofuran formed by Grignard reaction between methylmagnesium halide and 2,3-dichlorotetrahydrofuran are easy to separate by distillation, there is thus no need to do this for ordinary preparative purposes. The mixed reaction product obtained from ethylmagnesium bromide and 2,3-dichlorotetrahydrofuran, *trans*- (34%) and *cis*- (66%) 3-chloro-2-ethyltetrahydrofuran **5**, gave hex-3-en-1-ol **6** of >98% (*E*)-purity in 95% yield on treatment with samarium diiodide. The small amount of (*Z*)-isomer could be detected in the baseline of the ^{13}C spectrum where, despite the closeness of other signals, the (*E*)- and (*Z*)-allylic carbons have substantially different chemical shifts [(*E*) δ_C 36.0 (C-2), 26.1 (C-5); (*Z*) δ_C 31.0 (C-2), 20.5 (C-5)]. These highly stereoselective findings for (*E*)-3-enols provide a useful complement to the formation of (*E*)-4-enols by the highly stereoselective sodium scission of 2-substituted 3-chlorotetrahydropyrans.



Reagent: SmI_2

Apart from the stereochemical inhomogeneity of the product diene alcohol, over-reduction of the exposed diene system of the alcohol formed causes particular problems in the sodium-promoted ring scission of 3-chloro-2-vinyltetrahydrofuran.[1b] When electron transfer is effected by samarium diiodide, there is no over-reduction of the diene in the slow reaction, and the product from *cis*-3-chloro-2-vinyltetrahydrofuran **7**, (*E*)-hexa-3,5-dien-1-ol **8**, is obtained in excellent yield (84%) with high stereoselectivity [>97% (*E*)]. Even after refluxing with SmI_2 for many hours there was no evidence of over-reduction. The mixed *trans*- (33%) and *cis*- (67%) 2-allyl-3-chlorotetrahydrofurans **9** gave, again in high yield and excellent stereochemical purity, >97% (*E*), the methylene-interrupted vinyl diene (*E*)-hepta-3,6-dien-1-ol **10**. The allylic carbons at C-2 and C-5 resonated at δ_C 35.96 and 36.78 respectively and traces of (*Z*)-isomer were indicated by resonances at δ 30.70 and 31.59 in the baseline of the ^{13}C NMR spectrum, though over-reduction products were not detected. Again, on monitoring of the reaction by GLC, the scission of the *cis*-isomer was found to be more sluggish than that of the *trans* one.

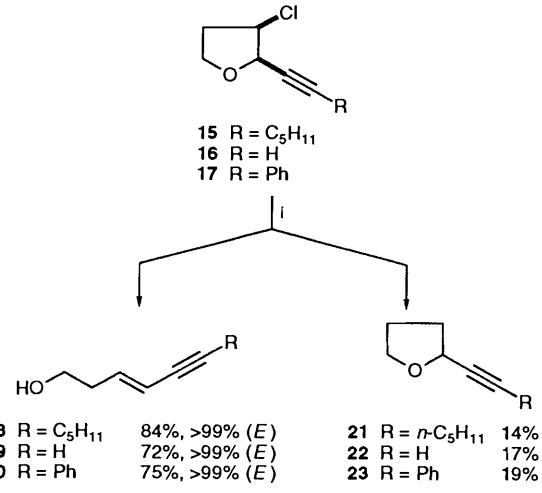
2-Aryl-3-chlorotetrahydrofurans are normally formed almost entirely as the *trans*-isomers ($J_{2a,3a}$ 9.8 Hz) in their preparation by the Grignard method, presumably because of steric compression in the S_Ni *cis*-forming reaction.[1a] The alcohol produced on ring scission is styrenoid, and over-reduction is again a difficulty during sodium-mediated reactions. However, as shown for the 2-phenyl **11** and 2-*p*-tolyl **13** cases, with samarium diiodide (*E*)-styrenoid alcohols **12** and **14** were obtained, stereochemically pure and in very high yield. No over-reduction of the styrenoid olefin was observed and the traces of (*Z*)-material were < 2%.



11 *trans* R = H — 95% yield — **12** >98% (*E*)
13 *trans* R = Me — ~100% yield — **14** >98% (*E*)

Reagent: SmI_2

In view of these satisfactory results with the olefinic and aromatic substituted tetrahydrofuran systems, attention was turned to acetylenic systems and an excellent (*E*)-enyne synthesis emerged (Scheme 3). Thus samarium diiodide



18 R = C_5H_{11} — 84%, >99% (*E*)
19 R = H — 72%, >99% (*E*)
20 R = Ph — 75%, >99% (*E*)
21 R = *n*-C_5H_{11} 14%
22 R = H 17%
23 R = Ph 19%

Scheme 3 (*E*)-Enyne synthesis from 3-chloro-2-alkyl- or -2-aryltetrahydrofurans. *Reagent:* i, SmI_2

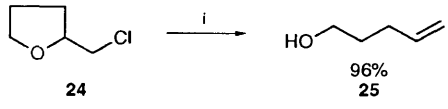
scission of *cis*-3-chloro-2-(hept-1'-ynyl)tetrahydrofuran **15**, from heptynylmagnesium bromide and 2,3-dichlorotetrahydrofuran, gave (*E*)-undec-3-en-5-yn-1-ol **18** with little over-reduction and in excellent yield (84%) and high stereochemical purity. The only evidence of over-reduction was a very small shoulder just visible on the main enynol GLC peak. This minor contaminant (estimated as < 1%) was collected by chromatography along with the enynol peak and was examined as a trace of baseline material in the ^{13}C NMR spectrum after many scans. Four $^{13}C(H)$ signals were detectable between δ_C 128 and 132 so it is likely to be a trace of dienol: there are low-intensity peaks in the mass spectrum at 168 (M^+ for $C_{11}H_{20}O$) and 167. The suspected dienol contaminant can be removed by careful chromatography as it runs ahead of the main enynol peak. A second major product (14%), fast running on silica gel chromatography, and easily separated, was the dechlorinated acetylenic furan **21**.

The shorter-chain example **16**, having a terminal acetylene linkage, required more careful adjustment of conditions. However, commencement of the reaction at 50 °C, and then gradually warming to a temperature just below reflux, gave (*E*)-hex-3-en-5-yn-1-ol **19** (^1H, $J_{3,4}$ 16 Hz and ^{13}C data) in 72% yield

on ring scission. The reaction proceeded with formation of a second, easily separable (chromatography) product which proved to be the dechlorinated furan **22** (17%). The purity of the major product was scrutinised by study of the baseline material in its ^{13}C NMR spectrum. Six small additional signals were discerned and were found to compare well with those of the hexa-3,5-dien-1-ol prepared above, so a small amount of over-reduction (< 5%) has been observed. The contaminant could be removed by careful chromatography.

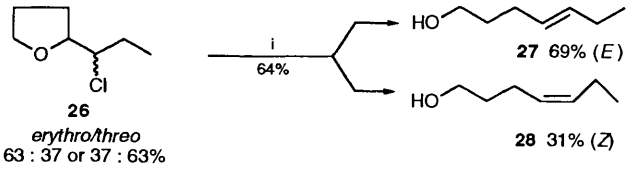
A phenyl-substituted acetylenic example was also investigated. The *cis*-isomer of 3-chloro-2-(phenylethynyl)tetrahydrofuran **17**, on treatment with samarium diiodide gave (*E*)-6-phenylhex-3-en-5-yn-1-ol **20** (^1H $J_{3,4}$ 15.8 Hz and ^{13}C spectrum) in good yield (75%). The product after chromatography was of high stereochemical purity, though it was noted that a small shoulder (< 3%) evident on GLC of the crude main product had been removed on purification and this probably signifies contaminating dienol. A second compound (19%), easily separated from the ring-scission product by silica gel chromatography, was again formed in this reaction. It proved to be the dechlorinated tetrahydrofuran **23**.

Methods for the synthesis of stereochemically pure (*E*)-enynes are scarce, and the present route using SmI_2 should prove to be generally valuable. Over-reduction, though observed, was not a serious problem since it represented at most 5% in the three examples. Furthermore, the over-reduced material could be removed by column chromatography and probably could be largely prevented from being formed by fine control of reaction time and conditions. In all these acetylene-containing examples the formation of dechlorinated starting tetrahydrofuran (14–19%) was a disadvantage, but it could very easily be removed by chromatography.



Reagent: i, SmI_2

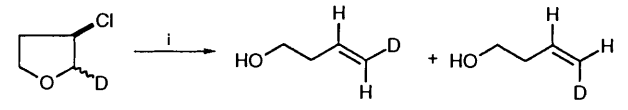
Tetrahydrofurfuryl chloride **24** gave pent-4-en-1-ol **25**, as in the familiar sodium-mediated reaction, and the *erythro*/*threo* mixture of 2-(1′-chloropropyl)tetrahydrofurans **26**[6] underwent successful ring scission in the presence of samarium diiodide to give hept-4-enols in reasonable yield (Scheme 4). However, the alcohol product was a mixture of (*E*) **27** and (*Z*) **28** forms. Analytical data for the starting tetrahydrofurans (63%/37% ratio, but it is uncertain which is the *erythro*, and which the



Scheme 4 Samarium diiodide ring scission of an *erythro*/*threo* mixture. *Reagent:* i, SmI_2.

threo) suggested that there may be a useful correlation between their stereochemistry and those of the *E* (69%) and *Z* (31%) hept-4-enols formed. This has not been established, since the diastereoisomers have not been separated and identified.

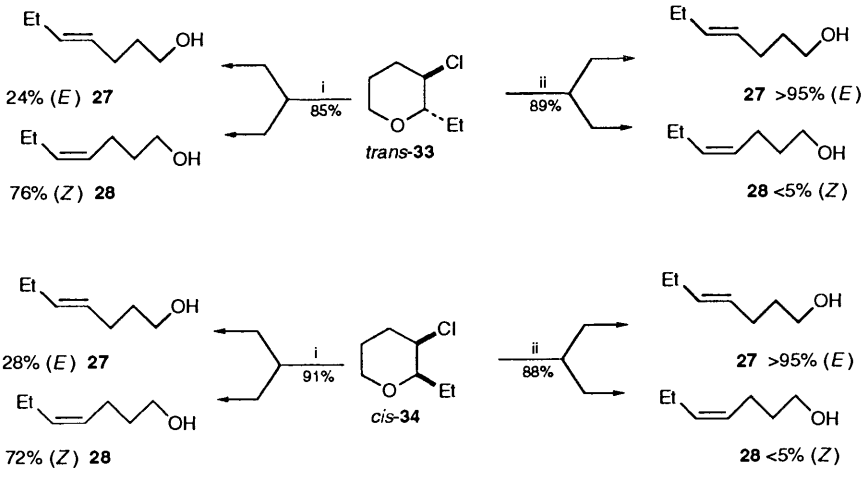
Samarium diiodide ring scission of a mixture of *trans*- **29** (22%) and *cis*- **30** (78%) 3-chloro-2-deuteriotetrahydrofurans gave a mixture of (*E*)- **31** and (*Z*)- **32** 4-deuteriobut-3-en-1-ols in almost exactly equal amounts (Scheme 5), so there is no



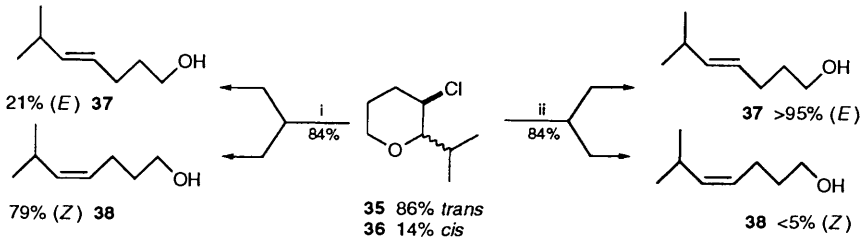
Scheme 5 Samarium diiodide ring scission of *cis*-/*trans*-3-chloro-2-deuteriotetrahydrofuran. *Reagent:* i, SmI_2.

correlation between the stereochemistry of the precursory deuteriotetrahydrofuran and the geometry of the deuterio alcohol formed: indeed, in view of the low conformational discrimination of H and D, the situation is suggestive of a common intermediate from substrates **29** and **30**.

Attention was now turned to samarium diiodide ring scissions in the tetrahydropyran series (Scheme 6). As mentioned earlier, the sodium ring scission of either pure *trans*-**33** or pure *cis*-**34** -3-chloro-2-ethyltetrahydropyran gave nearly pure (> 95%) (*E*)-hept-4-en-1-ol **27**, but with SmI_2 the *trans*-case gave a 24:76 (*E*)-**27**/(*Z*)-**28** ratio and the *cis*-case a 28:72 (*E*)-**27**/(*Z*)-**28** ratio, *i.e.* within probably experimental error the ratios are very similar from the two precursors having different geometries, again suggesting a common intermediate. From a preparative point of view, this degradation in stereospecificity by the employment of SmI_2 was disappointing, but it was confirmed by ring scission of the mixed (86:14) *trans*-**35** and *cis*-**36** -3-chloro-2-isopropyltetrahydropyrans when a 21:79 (*E*)-**37**/(*Z*)-**38** ratio for the resulting 6-methylhept-4-enols was

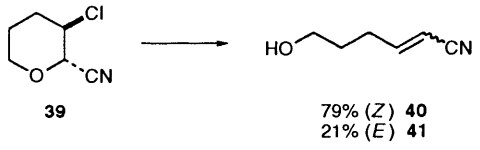


Scheme 6 Stereochemistry of ring scission of *trans*- and *cis*-3-chloro-2-ethyltetrahydropyran by using sodium in Et_2O[1b] and samarium diiodide in THF. *Reagents:* i, SmI_2; ii, Na.



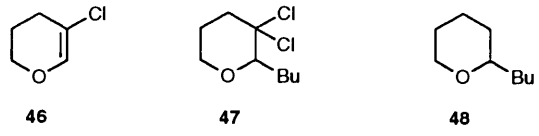
Scheme 7 Stereochemistry of ring scission of *trans*-/*cis*-3-chloro-2-isopropyltetrahydropyran by using sodium [1b] and samarium diiodide. *Reagents:* i, SmI_2; ii, Na.

found. With sodium, the same reaction is highly (*E*)-stereoselective (Scheme 7). SmI_2-initiated cleavage of *trans*-3-chloro-2-cyanotetrahydropyran **39** [7] under conditions specified in the Experimental section also gave a (*Z*)-**40**/(*E*)-**41** ratio of 79:21 for the 6-hydroxyhex-2-enonitriles formed, but in poor yield, with side-reactions apparently involving the conjugated nitrile: in aromatic and saturated alkyl cases, the nitrile group is reported to be stable to the reagent.[8]

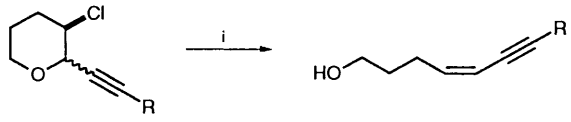


Ring scission of a *trans*-**42** (74%)/*cis*-**43** (26%) mixture of 3-chloro-2-deuteriotetrahydropyrans using SmI_2 (Scheme 8) gave a mixture of (*E*)-**44** and (*Z*)-**45** -5-deuteriopent-4-en-1-ols, in an approximately 1:1 ratio like the deuteriobut-3-enols above. This again suggests a common intermediate as between substrates **42**/**43** and the alcohol products, whereas in the sodium-initiated reaction there is an approximate correlation between pyran ground-state conformation and the geometrical isomers formed.[1b] 3-Chloro-5,6-dihydro-4*H*-pyran **46** was not cleaved by long treatment with the SmI_2 electron-transfer agent, and treatment of 2-butyl-3,3-dichlorotetrahydropyran **47** [9] resulted only in reduction of the chlorine substituents in a comparatively rapid reaction, giving 2-butyltetrahydropyran **48**.

When acetylenic cases were investigated in the tetrahydropyran series, the SmI_2 ring scission produced two surprises (Scheme 9). The examples were highly stereoselective for the enynes produced, and, unlike the similar tetrahydrofuran examples above, the stereoselectivity was for the (*Z*)- and not the (*E*)-form. Thus 3-chloro-2-(hept-1′-ynyl)tetrahydropyran **49** as a *cis*/*trans* mixture (20:80%) gave (*Z*)-dodec-4-en-6-yn-1-ol **52** (^{1}H, $J_{4,5}$ 10.6 Hz) in 93% yield; the *trans*-isomer reacted more rapidly than the *cis*-. Close examination by ^{13}C NMR spectroscopy suggested the presence of ~3% of an impurity but the chemical shifts indicated that this was due to formation of a small amount of (*E*)-isomer rather than over-reduction products. Surprisingly, in view of the results above on the acetylenic furans, no dechlorination product, 2-(hept-1′-ynyl)-tetrahydropyran, was found.



The lower homologue 3-chloro-2-(pent-1′-ynyl)tetrahydropyran **50** as a *cis*/*trans* mixture gave pure (*Z*)-dec-4-en-6-yn-1-ol **53** as expected, the *cis*-isomer reacting more sluggishly than the *trans*-. Examination of the specimen of enyne alcohol product gave no evidence of (*E*)-contamination or unwanted over-reduction, and it appeared to be >99% (*Z*)-isomer. Again, no dechlorinated pyran was found.



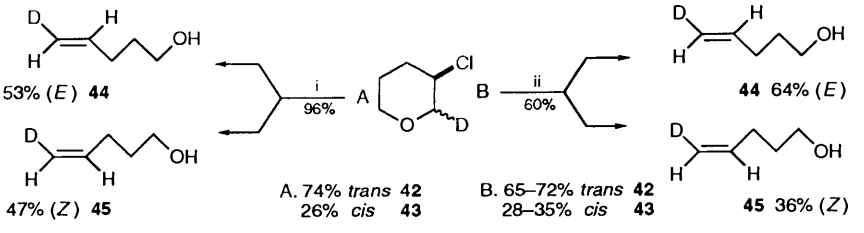
49 R = C_5H_{11} 80% *trans* 20% *cis*
50 R = Pr 70% *trans* 30% *cis*
51 R = H 100% *trans*

52 R = C_5H_{11} 93%; >97% (*Z*)
53 R = Pr 79%; >99% (*Z*)
54 R = H 72%; >95% (*Z*)

Scheme 9 Synthesis of (*Z*)-enynes from samarium diiodide scission of 3-chloro-2-ynetetrahydropyrans. *Reagent:* i, SmI_2.

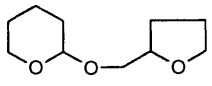
The third member of the acetylenic pyran series to be subjected to treatment with SmI_2 in refluxing tetrahydrofuran (THF) was the terminal acetylene *trans*-3-chloro-2-ethynyltetrahydropyran **51**. It was evident that this precursor was reacting more slowly than were the *trans*-alkylacetylene compounds **49** and **50** and the reaction was stopped after 91 h, though a little starting material remained. The product was (*Z*)-hept-4-en-6-yn-1-ol **54** (^{1}H, $J_{4,5}$ 10.8 Hz at δ 6.03) and scrutiny by ^{1}H and ^{13}C NMR spectroscopy indicated a little (*E*)-contamination (^{1}H, $J_{4,5}$ 15.9 Hz at δ 6.26) to the extent of < 5%. Together with the tetrahydrofuran cases mentioned above, we thus have complementary synthetic methods for producing enyne alcohols as either *E* or *Z* forms, both isomers being formed in reactions of high stereoselectivity and good yield.

Although the samarium diiodide-induced ring scission of tetrahydro-furans and -pyrans has given novel results of interest in synthesis, an obvious disadvantage of the reactions is the long time necessary for complete conversion of starting material into



Scheme 8 Stereochemistry of ring scission of *trans*-/*cis*-3-chloro-2-deuteriotetrahydropyran by using sodium [1b] and samarium diiodide. *Reagents:* i, SmI_2; ii, Na.

products. Some experiments were therefore initiated to explore the possibility of accelerating the reaction whilst maintaining stereocontrol over the alcohol produced. Initially it was hoped to use higher temperatures by replacing THF by 2(3)-tetrahydrofurfuryloxytetrahydropyran **55** ('T-solvent') as the solvent. However, the usual procedure for making SmI_2 in THF (Experimental section) failed with T-solvent even when the sonicated mixture was heated to 100 °C under nitrogen (no blue colour). Attention was then turned to the use of solvent additives. Inanaga and his colleagues[10] have observed marked accelerations in the rate of some SmI_2/THF-induced reactions on the addition of ~ 5% by volume of hexamethylphosphoric triamide **56** (HMPA), and the effects of this additive on a simple ring scission were therefore investigated.



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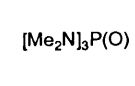

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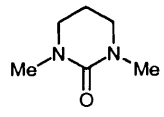

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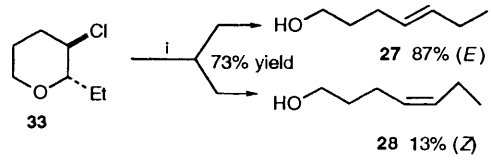
In the absence of HMPA, the ring scission of a *cis*/*trans* mixture (66%:34% respectively) of 3-chloro-2-ethyltetrahydrofuran **5** resulted in > 98% (*E*)-hex-3-en-1-ol **6** in 95% yield. The reaction took 76 h at reflux when using 5 mol equiv. of SmI_2 in THF. The same precursor mixture was then treated with 2.7 mol equiv. of SmI_2 in THF with HMPA as co-solvent (3.1% by volume), with monitoring by GLC. Within 4 h at reflux all of the *trans*-isomer and much of the *cis*- had been converted into a single product. The reaction was finally stopped after 9 h, when the product was isolated (95% GLC yield) and was shown to be hex-3-en-1-ol of > 92% (*E*)- **6**/< 8% (*Z*)-content as judged by the relative intensities of the C-2 ^{13}C NMR signals at δ_C 35.96 (*E*) and 30.71 (*Z*). This more than eight-fold diminution in reaction time at the expense of only limited deterioration in stereospecificity led us to try another additive to replace toxic HMPA.

Seebach and co-workers[11] have recommended the replacement of HMPA by the much less toxic 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one **57** (DMPU), though it is reported that larger amounts are required to give comparable effects. The same *cis*/*trans* mixture (66:34) of 3-chloro-2-ethyltetrahydrofuran **5** (above) was therefore refluxed with SmI_2 (2.6 mol equiv.) in THF containing 4.8% by volume DMPU. GLC monitoring showed that all of the *trans*-isomer, and most of the *cis*-, had been converted into product after 2.5 h and, after 5 h, with only a trace of starting material remaining, the reaction was worked up to give hex-3-en-1-ol **6** in 96% yield and > 93% (*E*)/< 7% (*Z*) stereochemical quality. Results are comparable, or slightly better than, with HMPA. In view of this, the influence of DMPU on an enyne-producing reaction was examined (*cf.* Scheme 3).

The SmI_2-mediated ring scission of *cis*-3-chloro-2-(hept-1'-ynyl)tetrahydrofuran **15** had given the (*E*)-enynol **18** in > 99% stereochemical purity at a yield of 84%, the reaction taking 22 h at reflux when using 5 mol equiv. of reagent (see above). In the present experiment the *cis*-tetrahydrofuran was refluxed with 2.6 mol equiv. of SmI_2 in THF with the addition of DMPU (4.6% by volume), and monitoring by GLC. After 3 h all the starting material had reacted and there was a slight shoulder on the main product peak (over-reduction). The product (83% yield) was shown to be undec-3-en-5-yn-1-ol **18** of > 94% (*E*)-purity, < 6% (*Z*). As in the absence of DMPU, there was a little over-reduction and this was < 2% of the total products. These accelerated reactions gave virtually unchanged alcohol yields with only slightly reduced stereoselectivity, and in view of the promise in the tetrahydrofuran series the investigation was extended to tetrahydropyrans.

The ring scission of *trans*-3-chloro-2-ethyltetrahydropyran **33** using 4 mol equiv. of SmI_2 in refluxing THF had been very slow, taking 142 h and giving, in 85% yield, an (*E*)-**27**/(*Z*)-**28** mixture (24%:76% respectively) of hept-4-en-1-ols (Scheme 6). The same precursor was treated with 2.5 mol equiv. of SmI_2 in refluxing THF containing 4.7% by volume of DMPU and the course of the reaction was followed by GLC (Scheme 10). The reaction, though accelerated,

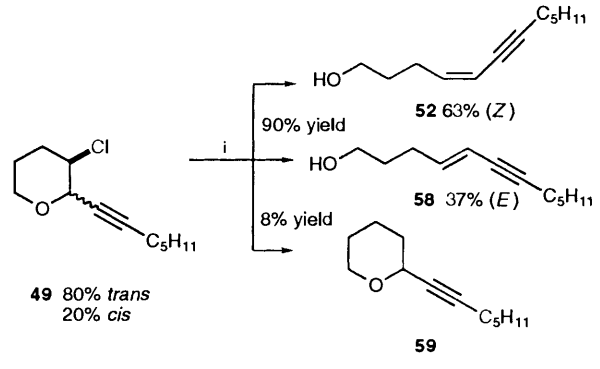


33

Scheme 10 Influence of DMPU on product stereochemistry from SmI_2 scission of 3-chloro-2-ethyltetrahydropyran. *Reagents:* i, SmI_2, THF–DMPU.

remained more sluggish than for the corresponding tetrahydrofuran. After 27 h, the majority of the starting material had reacted and the remainder was diminishing slowly: the reaction was stopped and worked up after 43 h, and the product alcohol, formed in 73% yield, was shown now to consist of an (*E*)-rich mixture of hept-4-en-1-ols: (*E*)-**27**, 87%; (*Z*)-**28** 13%. The addition of DMPU had therefore brought about a surprising reversal of isomer predominance. The stability of (*Z*)-hex-4-en-1-ol **28** under these SmI_2/DMPU/THF conditions was tested, but after 52 h of reflux it was unchanged and there was no conversion into the (*E*)-isomer **27**.

A second example of the strong stereochemical effects of solvent additive in the pyran series was found in the ring scission of *cis*- (20%)/*trans*- (80%) -3-chloro-2-(hept-1'-ynyl)tetrahydropyran **49**, which, when using 5.6 mol equiv. of SmI_2 in THF under reflux for 94 h, gave (*Z*)-dodec-4-en-6-yn-1-ol **52** of > 97% purity in 93% yield (Scheme 9). Using the same *cis*/*trans* mixture and 3.6 mol equiv. of SmI_2 in THF–DMPU (3.6% by volume), reaction under reflux was complete in 25 h (GLC), but three products were now isolated on chromatography (Scheme 11). These were dodec-4-en-6-yn-1-ol (90% yield), 63% as (*Z*)-



49 80% *trans*
20% *cis*

59

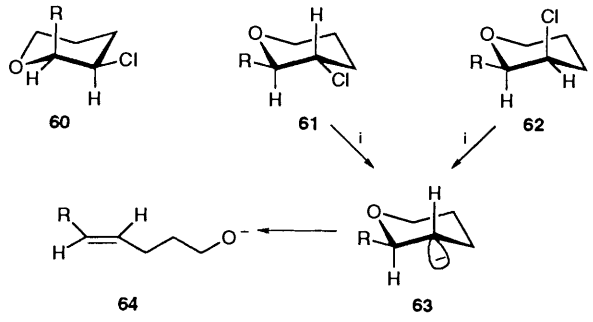
Scheme 11 Influence of DMPU on product stereochemistry from SmI_2 scission of 3-chloro-2-(hept-1'-ynyl)tetrahydropyran. *Reagents:* i, SmI_2, THF–DMPU.

form **52** and 37% as (*E*)-isomer **58**, along with 2-(hept-1'-ynyl)tetrahydropyran **59** (8% yield). The price paid for diminution of reaction time was thus a large loss of stereoselectivity.

Discussion

In earlier work we have studied the stereochemistry and conformation of 2-substituted 3-chlorotetrahydro-furans and -pyrans and their relationships to the stereochemistry of the

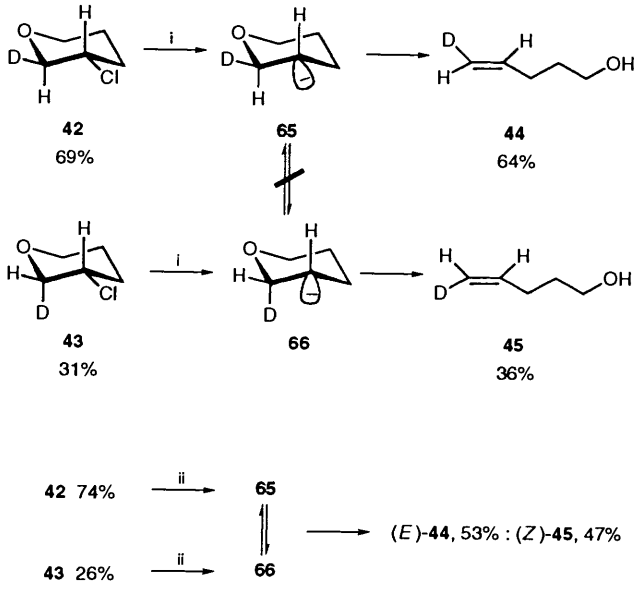
olefinic alcohols formed on ring scission employing sodium metal in diethyl ether as the electron-transfer agent.[1] ^{1}H NMR evidence indicates a 2_e3_a **62** rather than a 2_a3_e **60** conformation for *cis*-3-chloro-2-alkyl- or -aryltetrahydropyrans[1a,12] with both the *cis* **62** and *trans* **61** compounds undergoing fast electron transfer to form the rapidly inverting carbanion **63** which then undergoes scission in a fast reaction to give the anion **64** of the (*E*)-alcohol (Scheme 12). Overall, the scission



Scheme 12 Formation of (*E*)-olefinic alcohols in the sodium-in-Et_2O ring scission of *trans*- and *cis*-3-chloro-2-substituted tetrahydropyrans (for 2-substituent without anomeric effect). *Reagent:* i, Na.

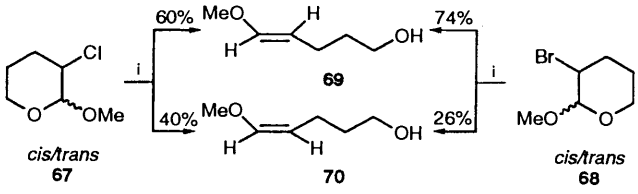
involves three fast processes which take place on a time-scale which does not permit ring inversion (see below) and the conformation of the ground state of the *cis*- or *trans*-3-chloro-2-alkyl- or aryltetrahydropyrans relates to the product stereochemistry.[1b]

Scheme 13 shows that in the 3-chloro-2-deuterio compounds



Scheme 13 Comparison of ring scissions of *trans*- and *cis*-3-chloro-2-deuteriotetrahydropyran with sodium in Et_2O[1b] and with samarium diiodide in THF. *Reagents:* i, Na; ii, SmI_2.

trans-**42** and *cis*-**43**, in which the large chlorine atom is equatorial and the deuterium atom of low conformational discrimination is, in the one case, equatorial, and in the other axial, sodium-promoted ring scission gives, within experimental error, *E*-olefin **44** correlating with the equatorial deuterium of compound **42** and *Z*-olefin **45** correlating with the axial deuterium of compound **43**. There is no equilibration (which requires ring inversion) between the carbanions **65** and **66**. A second example which supports the lack of equilibration of similar carbanions in the sodium-mediated cleavage is shown in Scheme 14.[1] Unlike the examples of Scheme 13, here there is,

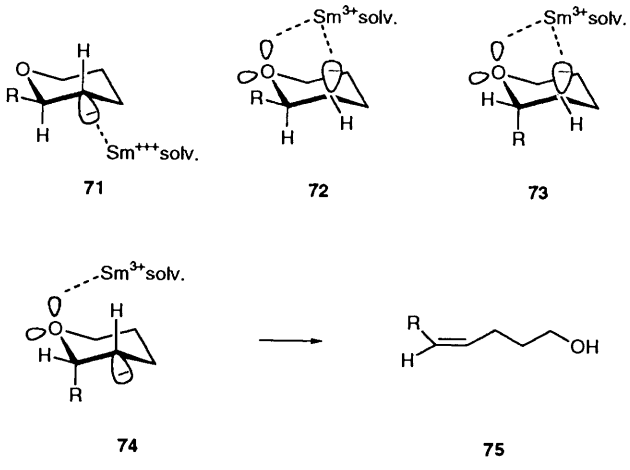


Scheme 14 Evidence against a common intermediate in the Na–Et_2O ring scission. *Reagent:* i, Na.

in both *trans* and *cis* cases, a strong time-averaged anomeric effect. Should there be a common equilibrated carbanion intermediate, the scission of both the chloro (**67**) and the bromo (**68**) compounds should lead to the same stereoisomeric mixture of olefinic alcohols **69** and **70**: it is clear that they do not.

By contrast, there is evidence that the much slower samarium diiodide scission can proceed through a common equilibrated carbanion intermediate. Thus the approximately 1:1 mixture of (*E*)- and (*Z*)-deuterio olefinic alcohols **44** and **45** does not correlate with the 74:26 ground-state mixture of *trans*- and *cis*-chlorotetrahydropyran **42** and **43** in Scheme 13. The varying *cis*:*trans* ratios of 2-alkynyl-3-chlorotetrahydropyrans **49–51** in Scheme 9, all leading to olefinic alcohols of >95% (*Z*)-purity, are also consistent with there being a common equilibrated intermediate lying beyond the *cis*- and *trans*-form of each pyran type.

These differences in behaviour, as between the use of sodium in diethyl ether and samarium diiodide in THF, appear to indicate the formation of longer lived, complexed samarium anions with conformations different from those of the ground states. At present there is little experimental information on the nature of such complexes but a system such as **73**, decomposing to (*Z*)-alcohol **75** *via* the anion-inverted form **74** [and in some cases equilibrating with species **71** or **72**, leading to the (*E*)-alcohol], presents a simplified view of the systems involved (see Scheme 15). Species **73** has an axial 2-R grouping as required to



Scheme 15 Samarium-complexed anion models for the tetrahydropyran series

account for the (*Z*)-enyne series **52–54**. The *cis*- and *trans*-3-chloro-2-alkyl- or -aryl-tetrahydropyrans which gave >95% (*E*)-isomers on treatment with sodium (*e.g.*, Schemes 6 and 7) gave (*Z*)-rich *Z*/*E* mixtures when samarium diiodide was the electron-transfer agent, indicating involvement by both axial and equatorial 2-alkyl transition states.

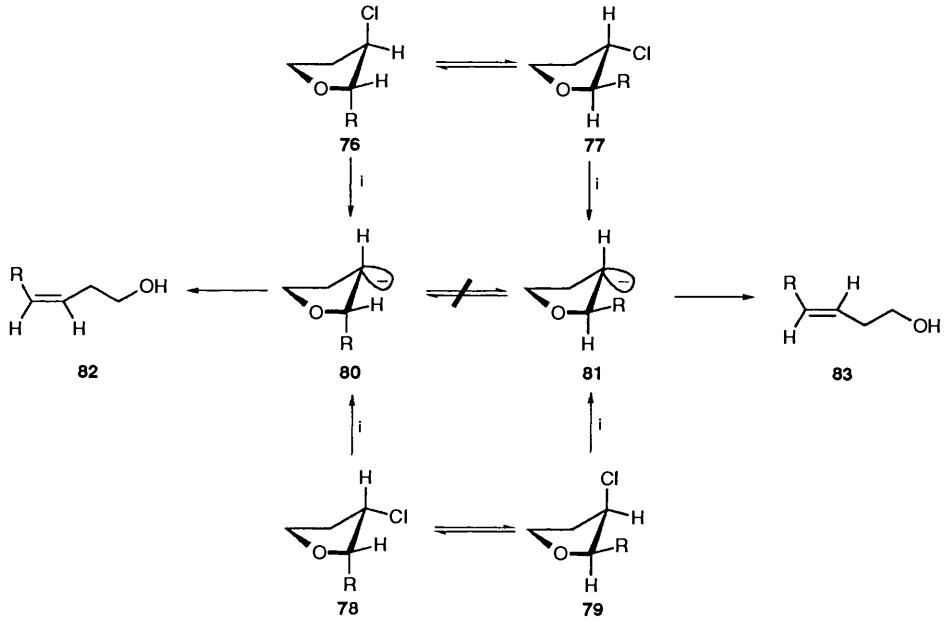
It is clear that DMPU has a substantial effect on the formation and conformation of such samarium complexes in solution. The 76% (*Z*)-**28**/24% (*E*)-**27** ratio of the hept-3-en-1-ols from 3-chloro-2-ethyltetrahydropyran (Scheme 6) was changed to 13% (*Z*)-**28**/87% (*E*)-**27** when DMPU was added

(Scheme 10). Similarly the >97% (*Z*)-dodec-4-en-6-yn-1-ol **52** formed by ring scission of 3-chloro-2-(hept-1′-ynyl)tetrahydropyran **49** (Scheme 9) became stereochemically degraded to a 63% *Z*/37% *E* mixture (Scheme 11).

The sodium-in-diethyl ether ring scission of 2-substituted 3-chlorotetrahydrofurans is more complex than in the tetrahydropyran cases because of conformational uncertainties resulting from pseudorotation (Scheme 16), and this has been discussed in some detail by us earlier.[1b] When R is not an electronegative substituent, the magnitude of $J_{2,3}$ (averaged) in the ^{1}H NMR spectrum suggests that the *trans*-isomers favour a diequatorially biased equilibrium, and the *cis*-isomers an equilibrium in which the 3-chlorine is axial. *cis*- and *trans*-Forms each gave different *Z*/*E* mixtures of alk-3-en-1-ols (see Scheme 2, and Table 2 of our earlier publication[1b] for a series of examples), and whilst ring inversion of both *trans*- (**76**, **77**) and *cis*- (**78**, **79**) forms occurs there is no evidence for conformational equilibration between the anions (**80**, **81**) which decompose to give (*Z*)-**82** and (*E*)-**83** olefinic alcohols.

As in the pyran series, the samarium diiodide-mediated scission of the 2-substituted 3-chlorotetrahydrofurans appears to involve equilibrated anions stabilised by samarium complexation. Thus the mixture of *cis*- (**30**) (78%) and *trans*- (**29**) (22%) -3-chloro-2-deuteriotetrahydrofuran led to a 1:1 mixture of olefinic alcohols (*E*)-**31** and (*Z*)-**32** (Scheme 5). In addition, eight examples of 3-chloro-2-alkyl- or -2-aryl-tetrahydrofurans (above) underwent scission with samarium diiodide to give olefinic alcohols having >95% (*E*)-content. This high stereoselectivity suggests that the products arise from complexed transition states having the 2-R equatorial. Unlike the pyran cases, additives such as DMPU, whilst speeding the reaction, have little effect on the stereochemical nature of the alcohols formed in the furan examples examined. Further work on the involvement of samarium ions in the conformation of ring-scission intermediates, and the transition states leading from them, is obviously needed.

Precursors for Ring Scission.—The majority of the ring-scission precursors employed in this work (Tables 1 and 2) were made by the Grignard method from mixed *cis*-/*trans*-2,3-dichloro compounds obtained by addition of chlorine to dihydrofuran or dihydropyran as in Scheme 17. The stereochemistry of the dichloride mixtures does not noticeably influence the stereochemistry of the products (S_N1 reaction).[1a] One or two points deserve mention. As commented on by us previously, there is, except where the entering substituent is large (aryl), a strong tendency for Grignard attack to produce *cis*-rich mixtures in the tetrahydrofuran series (Table 1) and this can be

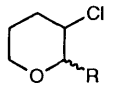


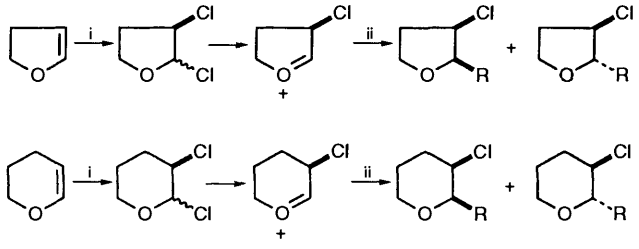
Scheme 16 Formation of (*Z*)- and (*E*)-olefinic alcohols in the Na–Et_2O ring scission of *trans*- and *cis*-3-chloro-2-substituted tetrahydrofurans. *Reagent:* i, Na.

Table 1 Data for tetrahydrofurans used in the ring scission

Reagent for 2,3-dichlorotetrahydrofuran		Yield (%)	*cis* (%)	^{1}H NMR $J_{2,3}$ Hz	*trans* (%)	^{1}H NMR $J_{2,3}$ Hz	GLC Conditions
$MeMgBr/Et_2O$	R = Me	55	63	3.3	37	5.6	PEGA/102 °C
$EtMgBr/Et_2O$	R = Et	63	66		34		Carbowax 20M/84 °C
$CH_2{=}CHMgBr/Et_2O$	R = $CH_2{=}CH$	58		3.3		4.5	OV-17/114 °C
$CH_2{=}CHCH_2MgBr/Et_2O$	R = $CH_2{=}CHCH_2$	62	67	3.6	33	5.9	OV-17/117 °C
$PhMgBr/Et_2O$	R = Ph	65	0		100	4.5	Carbowax 20M/184 °C
$p\text{-}MeC_6H_4MgBr/Et_2O$	R = $p\text{-}MeC_6H_4$	54	0		100	4.5	Apiezon L/179 °C
$Am^nC{\equiv}CMgBr/Et_2O$	R = $Am^nC{\equiv}C$	69	100	2.4	0		Apiezon L/203 °C
$HC{\equiv}CMgBr/THF$	R = $HC{\equiv}C$	64	100	2.2	0		Apiezon L/114 °C
$PhC{\equiv}CMgBr/THF$	R = $PhC{\equiv}C$	48	100	2.4	0		Apiezon L/242 °C
$LiAlD_4/THF$	R = D	71	78	2.5	22		

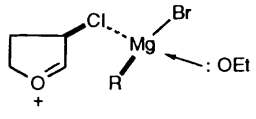
Table 2 Data for tetrahydropyrans used in the ring scissions

Reagent for 2,3-dichlorotetrahydropyrans		Yield (%)	*cis* (%)	^{1}H NMR $J_{2,3}$ Hz	*trans* (%)	^{1}H NMR $J_{2,3}$ Hz	GLC Conditions
$EtMgBr/Et_2O$	R = Et	70	48	1.5	52	9.6	Carbowax 20M/104 °C
Pr^iMgBr/Et_2O	R = Pr^i	60	34	1.4	66	9.8	PEGA/142 °C
Cu^ICN	R = CN	63	0		100	7.1	
$LiAlD_4/Et_2O$	R = D	76	26		74		
$Am^nC{\equiv}CMgBr/Et_2O$	R = $Am^nC{\equiv}C$	65	20		80	7.3	Apiezon L/206 °C
$Pr^nC{\equiv}CMgBr/Et_2O$	R = $Pr^nC{\equiv}C$	71	30		70	7.3	Apiezon L/188 °C
$HC{\equiv}CMgBr/THF$	R = $HC{\equiv}C$	66	0		100	7.4	Carbowax 20M/138 °C



Scheme 17 Grignard synthesis of 3-chloro-2-alkyltetrahydro-furans and -pyrans. *Reagents:* i, Cl_2; ii, RMgBr.

attributed to the directing effect of the chlorine towards *syn*-face substitution **84**.[1a] The effect is most marked in 1′-acetylene-containing cases. In the tetrahydropyran series the effect is less marked, the *trans*-isomer being the more plentiful product. This is so even in the 1′-acetylene-containing group (Table 2).



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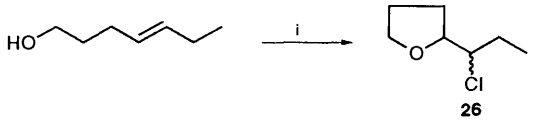
When combined with the examples previously prepared[1a] (Tables 10 and 11 of that paper) the following coupling-constant ranges are found:

2-R-3-chlorotetrahydrofurans $J_{2,3}$ *cis* 2.2–3.6 Hz
$J_{2,3}$ *trans* 4.3–5.9 Hz
2-R-3-chlorotetrahydropyrans $J_{2,3}$ *cis* 1.4–1.5 Hz
$J_{2,3}$ *trans* 9.6–9.8 Hz

There are two exceptions. When the 2-R substituent possesses a 1′-triple bond in the tetrahydropyran series, $J_{2,3}$ *trans* falls to 7.1–7.3 Hz, and when there is a time-averaged anomeric effect (solvent dependent) there are considerable changes (see ref. 1*a*).

The *erythro*/*threo* mixture of 2-(1′-chloropropyl)tetrahydrofurans [26] was made by the method of Srebnik and Mechoulam[6] (Scheme 18).



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Scheme 18 Synthesis of 2-(1′-chloropropyl)tetrahydrofuran diastereoisomers. *Reagents:* i, NaCl, MCPBA, 18-crown-6, CH_2Cl_2.

Experimental

M.p.s were determined using a Kofler hot-stage microscope and are uncorrected. UV–VIS spectra were recorded on a Pye Unicam SP-700 or a Philips PU 8720 spectrophotometer. ^{1}H NMR spectra were recorded at 80 MHz on a Bruker WP80 SY PFT instrument, at 90 MHz on a Perkin-Elmer R32 instrument, at 250 MHz on a Bruker WM250 PFT instrument, and at 400 MHz on a Bruker AM400 PFT instrument, using tetramethylsilane as internal standard. *J*-Values are given in Hz. ^{13}C NMR spectra were recorded at 100 MHz on the Bruker AM400 PFT spectrometer, and distortionless enhancement by polarisation transfer (DEPT) sequences were employed to assist assignments. Mass spectra were obtained using an AEI MS902 or a VG 7070E spectrometer. TLC plates were visualised with anisaldehyde, potassium permanganate or sulfuric acid in methanol. Analysis by gas chromatography (GLC) was carried out on a Pye Unicam 104 machine, with flame ionisation detection, using glass or stainless steel columns (5′ × 0.25″) packed with 10% stationary phase (as quoted) supported on Chromosorb W or Diatomite C. High-performance liquid chromatography (HPLC) employed a Waters Associates chromatograph consisting of a 6000a pump, 440 absorbance detector, and an R401 differential refractometer. For column chromatography, silica gel refers to Woelm dry-column silica, and alumina to BDH grade 1 aluminium oxide. Ultrasonic irradiation was provided by a Decon FS100 ultrasonic bath with a minimum continuous power output of 100 W.

2,3-*Dichlorotetrahydrofuran*.—Dry (conc. sulfuric acid-scrubbed) chlorine gas was bubbled through a solution of 2,3-dihydrofuran (5 g, 0.07 mol) in dry diethyl ether (30 cm^3) at 0 to −5 °C (ice–salt) until the solution acquired a green tinge. Sufficient dihydrofuran was added to decolourise (just) the solution, which for most experiments was not distilled but was freshly prepared and used directly.

cis- *and* trans-3-*Chloro*-2-*methyltetrahydrofuran* **2** *and* **1**.—A Grignard reagent was prepared by bubbling bromomethane through a slurry of magnesium turnings (14.58 g, 0.60 mol) in dry diethyl ether (300 cm^3) and was then treated as below with 2,3-dichlorotetrahydrofuran [from 2,3-dihydrofuran (28 g, 0.40 mol)]. Work-up (as below) and distillation gave a mixture of *cis* and *trans* compounds (26.42 g, 55%) (37% *trans*/63% *cis* by GLC on PEGA column), b.p. 31–48 °C/20 mmHg (lit.,[1a] b.p. 32–43 °C/14 mmHg). Separation by spinning-band distillation at atmospheric pressure gave the *trans*-isomer **1**, b.p. 132–134 °C (lit.,[1a] 129–131 °C) and the *cis*-isomer **2**, b.p. 145–146 °C (lit.,[1a] 146–147 °C). The *cis*-isomer (longer retention time on GLC) had ν_{max}(film)/cm^{-1} 2980s, 1445, 1385, 1120, 1070s (C–O), 1020, 995 and 845. The *trans*-isomer had ν_{max}(film)/cm^{-1} 2990s, 1450, 1390, 1070br (C–O), 1020 and 870.

cis- *and* trans-3-*Chloro*-2-*ethyltetrahydrofuran* **5**.—Ethylmagnesium bromide was prepared from bromoethane (11.67 g,

0.11 mol) and magnesium turnings (2.73 g, 0.11 mol) in dry diethyl ether (40 cm^3). The stirred Grignard reagent was cooled in ice and 2,3-dichlorotetrahydrofuran solution [prepared as above using 2,3-dihydrofuran (5 g, 0.07 mol)] was added dropwise, and the mixture was then stirred overnight before being poured cautiously into ice–water and acidified with conc. hydrochloric acid. The resulting solution was extracted with diethyl ether and the extracts were united and washed successively with saturated aq. sodium hydrogen carbonate, water and brine, and dried ($MgSO_4$). Evaporation under reduced pressure and distillation *in vacuo* gave the *cis*-/*trans*-3-chloro-2-ethyltetrahydrofuran mixture **5** (5.91 g, 63%), b.p. 55–62 °C/17 mmHg [lit.,[13] *trans* b.p. 150 °C, *cis* b.p. 165 °C]. GLC analysis (Carbowax 20M) showed the *cis*-isomer (longer retention time) to constitute 66% of the mixture.

cis-2-*Vinyl*- **7**, cis-/trans-2-*Allyl*- **9**, trans-2-*Phenyl*- **11** *and* trans-2-p-*Tolyl*- **13** -3-*Chlorotetrahydrofuran*.—The specimens used originated from our earlier investigation,[1a] where their preparation and characterisation is described, and were re-purified and reanalysed before use.

cis-3-*Chloro*-2-(*hept*-1′-*ynyl*)*tetrahydrofuran* **15**.—A solution of hept-1-yne (9.62 g, 0.1 mol) in dry diethyl ether (15 cm^3) was added to stirred ice-cold ethylmagnesium bromide prepared from bromoethane (10.90 g, 0.1 mol), magnesium turnings (2.43 g, 0.1 mol) and diethyl ether (40 cm^3), and the mixture was then refluxed (1 h). The acetylenic Grignard reagent was cooled (ice) and 2,3-dichlorotetrahydrofuran [from dihydrofuran (5 g, 0.07 mol)] was added dropwise: the mixture was then stirred overnight. Work-up in the usual manner gave cis-3-*chloro*-2-(*hept*-1′-*ynyl*)*tetrahydrofuran* **15** (9.88 g, 69%), b.p. 62–69 °C/0.03 mmHg (Found: M^+, 202.090/200.089. $C_{11}H_{17}ClO$ requires M, 202.094/200.097). The material was also purified by chromatography on silica gel, with hexane–diethyl ether (95 : 5) as eluent and monitoring by GLC (Apiezon L); ν_{max}(film)/cm^{-1} 2950s, 2260w (C≡C) and 1040s (C–O); δ_H(400 MHz; $CDCl_3$) 4.66 (1 H, d, *J* 2.4, 2-H), 4.36 (1 H, td, *J* 6.1 and 2.4, 3-H), 4.08 (2 H, m, 5-H_2), 2.58 (1 H, m, 4-H), 2.17 (3 H, m, 4-H and 3′-H_2), 1.50 (2 H, m, 4′-H_2), 1.33 (4 H, m, 5′- and 6′-H_2) and 0.90 (3 H, t, *J* 6.5, 7′-H_3); δ_C(100 MHz; C_6D_6) 87.42 (C, C-1′), 77.89 (C, C-2′), 76.95 (CH, C-2), 66.33 (CH_2, C-5), 62.62 (CH, C-3), 35.67 (CH_2, C-4), 31.20 (CH_2, C-5′), 28.41 (CH_2, C-4′), 22.42 (CH_2, C-6′), 18.85 (CH_2, C-3′) and 14.07 (Me, C-7′); *m*/*z* (+ve, EI) 202/200 (M^+, 5/19%) and 123 (100).

cis-3-*Chloro*-2-*ethynyltetrahydrofuran* **16**.—Dry (H_2SO_4) acetylene was bubbled through THF (35 cm^3) for several minutes. A solution of ethylmagnesium bromide [from bromoethane (10.79 g, 0.10 mol) and magnesium (2.19 g, 0.10 mol)] in THF (55 cm^3) was then added dropwise during 2 h, whilst a rapid flow of acetylene and vigorous stirring were maintained. The solution of ethynylmagnesium bromide[14] was vigorously stirred and cooled (ice), a solution of 2,3-dichlorotetrahydrofuran [from dihydrofuran (4.21 g, 0.06 mol)] in diethyl ether was added, and the mixture was stirred overnight. Work-up and distillation gave the *cis*-furan **16** (5.01 g, 64%), b.p. 57–62 °C/7 mmHg (lit.,[15] b.p. 56–62 °C/12 mmHg). The product was further purified by chromatography on silica gel, with hexane–diethyl ether (95 : 5) as eluent and monitoring by GLC (Apiezon L); ν_{max}(film)/cm^{-1} 3300s (≡CH), 2950, 2900, 2130w (C≡C), 1440, 1080, 1050br (C–O) and 820s; δ_H(400 MHz; $CDCl_3$) 4.68 (1 H, t, *J* 2.3 and 2.2, 2-H), 4.44 (1 H, dt, *J* 6.2, 2.3 and 2.3, 3-H), 4.12 (2 H, m, 5-H_2), 2.61 (1 H, m, 4-H), 2.56 (1 H, d, *J* 2.2, 2′-H) and 2.20 (1 H, m, 4-H); δ_C(100 MHz; $CDCl_3$) 80.42 (C, C-1′), 76.02 (CH, C-2), 75.04 (CH, C-2′), 66.85 (CH_2, C-5), 61.80 (CH, C-3) and 35.53 (CH_2, C-4).

cis-3-*Chloro*-2-(*phenylethynyl*)*tetrahydrofuran* **17**.—A solution of phenylacetylene (10.21 g, 0.1 mol) in dry THF (20 cm^3) was added dropwise to an ice-cold solution of ethylmagnesium bromide in THF (40 cm^3) [from bromoethane (10.90 g, 0.1 mol) and magnesium turnings (2.43 g, 0.1 mol)] and the mixture was then refluxed (1 h). The phenylacetylene Grignard was cooled (ice), a solution of 2,3-dichlorotetrahydrofuran [from dihydrofuran (5 g, 0.07 mol) and chlorine] was added, and the mixture was stirred overnight at room temperature and then worked up. Distillation gave cis-3-*chloro*-2-(*phenylethynyl*)*tetrahydrofuran* **17** (7.10 g, 48%), b.p. 90–95 °C/0.02 mmHg (Found: C, 69.8; H, 5.4%; M^+, 208.045/206.050. $C_{12}H_{11}ClO$ requires C, 69.7; H, 5.4%; M, 208.047/206.050). The material was also purified by chromatography on silica gel, with hexane–diethyl ether (92 : 2) as eluent and monitoring by GLC (Apiezon L); λ_{max}(EtOH)/nm 205 (ε 20 400 dm^3 mol^{-1} cm^{-1}), 233infl (14 000), 240 (18 000) and 251 (16 000); ν_{max}(film)/cm^{-1} 2230w (C≡C), 1490 (arom), 1445, 1080, 1050s (C–O), 760s and 695s; δ_H(400 MHz; $CDCl_3$) 7.43 (2 H, m, ArH), 7.30 (3 H, m, ArH), 4.91 (1 H, d, *J* 2.5, 2-H), 4.52 (1 H, dt, *J* 6.2, 2.5 and 2.5, 3-H), 4.16 (2 H, m, 5-H_2), 2.65 (1 H, m, 4-H) and 2.23 (1 H, m, 4-H); δ_C(100 MHz; $CDCl_3$) 131.81 (CH, C-4′ and -8′), 128.84 (CH, C-6′), 128.37 (CH, C-5′ and -7′), 122.05 (C, C-3′), 86.79 (C, C-1′), 85.52 (C, C-2′), 76.91 (CH, C-2), 66.87 (CH_2, C-5), 62.10 (CH, C-3) and 35.78 (CH_2, C-4); *m*/*z* (+ve, EI) 208/206 (M^+, 18/56%) and 102 (100).

2-(1′-*Chloropropyl*)*tetrahydrofuran* **26**.—(*E*)-Hept-4-en-1-ol **27** (1.14 g, 10 mmol), sodium chloride (2.92 g, 50 mmol) and 18-crown-6 (0.26 g, 1 mmol) were stirred together for 5 min at room temperature in dry dichloromethane (25 cm^3).[6] After cooling (ice–salt) of the stirred mixture, an ice-cold solution of *m*-chloroperbenzoic acid (MCPBA) (1.90 g, 11 mmol) in dichloromethane (20 cm^3) was added during 2 h. The mixture was stirred at 0 to −5 °C for a further 2 h. After storage at 0 °C overnight, the product was washed successively with saturated aq. sodium sulfite, saturated aq. sodium hydrogen carbonate, water, and brine, and dried ($MgSO_4$). Evaporation of the organic layer and chromatography of the residue on silica gel with hexane–diethyl ether (98 : 2) as eluent, gave the title product **26** (0.18 g, 12%) as a mixture of diastereoisomers.[16] The *erythro* : *threo* ratio was determined by GLC (Carbowax 20M) as 63 : 37 or 37 : 63, as stereochemical assignment was not available; ν_{max}(film)/cm^{-1} 2920s, 2830, 2810, 1460, 1440, 1295, 1280, 1260, 1070s (C–O) and 755; δ_H(400 MHz; $CDCl_3$) 3.93–3.05 (4 H, m, 5-H_2, 2- and 1′-H), 2.28–1.33 (6 H, m, 4-, 3- and 2′-H_2), 0.99 (1.9 H, t, *J* 7.3, 3′-H_3) and 0.90 (1.1 H, t, *J* 7.4, 3′-H_3).

cis- *and* trans-3-*Chloro*-2-*deuteriotetrahydrofuran* **30** *and* **29**.—A slurry of lithium aluminium deuteride (0.5 g, 0.01 mol) in dry diethyl ether (20 cm^3) was added to a solution of 2,3-dichlorotetrahydrofuran [from 2,3-dihydrofuran (3.5 g, 0.05 mol)] in diethyl ether (20 cm^3) so as to maintain gentle reflux. The mixture was then refluxed (40 min), cooled, and wet diethyl ether was cautiously added to decompose excess of reagent. Water and dil. sulfuric acid were added, and the ethereal phase was separated, and dried over anhydrous magnesium sulfate. Distillation gave the *cis*-/*trans*-3-chloro-2-deuteriotetrahydrofuran mixture **30**/**29** (3.80 g, 71%), b.p. 62–65 °C/40 mmHg (lit.,[1a] 54–58 °C/25 mmHg). From the decoupled ^2H NMR spectrum, which had a large singlet at δ 4.09 and a smaller one at δ 3.94, by expansion and integration of several scans, the product was found to be a 78% *cis*- **30**/22% *trans*- **29** mixture; ν_{max}(film)/cm^{-1} 2950s, 2910s, 2850s, 2110w (C–D), 1445, 1095s, 1070s (C–O) and 900; δ_H(400 MHz; $CDCl_3$) 4.49 (1 H, dt, *J* 6.0 and 2.5, 3-H), 4.04 (1.22 H, m, 5-H and 2-H_{trans}), 3.95 (1 H, td, m, 5-H), 3.91 (0.78 H, br s, 2-H_{cis}), 2.35 (1 H, m, 4-H)

and 2.19 (1 H, m, 4-H); δ_D(38 MHz; $CHCl_3$) 4.09 (0.78 D, br s, 2-D_{cis}) and 3.94 (0.22 D, br s, 2-D_{trans}).

2,3-*Dichlorotetrahydropyran*.—By using 2,3-dihydro-4*H*-pyran, this was prepared by a method analogous to that for 2,3-dichlorotetrahydrofuran (above).

cis-2-*Ethyl*- **34**, trans-2-*Ethyl*- **33**, *and* cis- **36**/trans- **35** -*Isopropyl*-3-*chlorotetrahydropyran*.—The specimens used originated from our earlier investigations, where their preparation and characterisation is described, and were repurified and reanalysed before use.

trans-3-*Chlorotetrahydropyran*-2-*carbonitrile* **39**.—Ethereal 2,3-dichlorotetrahydropyran was prepared by chlorination of 2,3-dihydro-4*H*-pyran (2.80 g, 0.03 mol) and the solvent was evaporated off under reduced pressure and copper(I) cyanide (4.45 g, 0.05 mol) was added. The mixture was stirred on a steam-bath (3 h), cooled, diethyl ether was added, and the product was filtered through a pad of Kieselguhr, which was washed with diethyl ether. The combined ethereal solutions were dried ($MgSO_4$) and evaporated, and the residue was distilled to give the *trans*-pyran **39** (3.04 g, 63%), b.p. 108–110 °C/7 mmHg (lit.,[7] 118–119 °C/21 mmHg). It formed a single peak on GLC (Apiezon L); ν_{max}(film)/cm^{-1} 2940s, 2860s, 2320w (C≡N), 1100s (C–O), 940s and 790; δ_H(400 MHz; $CDCl_3$) 4.35 (1 H, d, *J* 7.1, 2-H), 4.07 (1 H, m, 6-H), 3.99 (1 H, m, 3-H), 3.64 (1 H, m, 6-H), 2.41 (1 H, m, 4-H), 1.91 (2 H, m, 4- and 5-H) and 1.73 (1 H, m, 5-H).

cis- *and* trans-3-*Chloro*-2-*deuteriotetrahydropyran* **43**/**42**.—A slurry of lithium aluminium deuteride (0.5 g, 0.01 mol) in dry diethyl ether (20 cm^3) was added to 2,3-dichlorotetrahydropyran in diethyl ether [from 2,3-dihydro-4*H*-pyran (4.21 g, 0.05 mol)] so as to maintain gentle reflux. The mixture was refluxed for a further 40 min and was then worked up as for the furan case. Distillation gave the mixed *cis*- and *trans*-pyran (4.61 g, 76%), b.p. 43–45 °C/7 mmHg (lit.,[1a] 52–55 °C/14 mmHg). As determined by ^1H NMR spectroscopy [1a] the mixture was 74% *trans* **42**/26% *cis* **43**; ν_{max}(film)/cm^{-1} 2930s, 2830s, 2175w (C–D), 1440, 1205, 1100s (C–O), 1060, 820 and 755; δ_H(80 MHz; $CDCl_3$) 4.09–3.70 (2.26 H, m, 2-H_e and 6-H_2), 3.61–3.31 (1.74 H, m, 2-H_a and 3-H) and 2.50–1.20 (4 H, m, 4- and 5-H_2).

2-*Butyl*-3,3-*dichlorotetrahydropyran* **47**.—Ethereal 2,3,3-trichlorotetrahydropyran was prepared by addition of chlorine to 3-chloro-5,6-dihydro-4*H*-pyran **46** [9] (4.00 g, 0.03 mol) as described for 2,3-dichlorotetrahydropyran. The diethyl ether was removed under reduced pressure and was replaced by dry benzene (25 cm^3). A vigorously stirred solution of butylmagnesium bromide [from bromobutane (7.81 g, 0.06 mol), magnesium (1.39 g, 0.06 mol) and diethyl ether (30 cm^3)] was cooled (ice) during the addition of crushed dry cadmium(II) chloride (6.51 g, 0.03 mol) in portions. The mixture was refluxed (3 h), when the diethyl ether was distilled off and replaced by benzene (30 cm^3). The solution of dibutylcadmium was cooled (ice) and the 2,3,3-trichlorotetrahydropyran was added dropwise, the mixture then being stirred overnight. The product was poured into water, acidified with conc. hydrochloric acid, and the benzene layer was separated. The aqueous phase was extracted with diethyl ether and the combined organic extracts were washed successively with saturated aq. sodium hydrogen carbonate, water, and brine, and dried over anhydrous magnesium sulfate. Evaporation and distillation gave the title pyran **47** (3.65 g, 51%), b.p. 39–42 °C/0.1 mmHg (lit.,[9] 121–123 °C/18 mmHg); ν_{max}(film)/cm^{-1} 2970s, 2940s, 2870s, 1460, 1435, 1100s (C–O) and 800s; δ_H(90 MHz; $CDCl_3$) 4.11–3.26 (3 H, m, 2-H and 6-H_2), 2.90–1.10 (10 H, m, 4-, 5-, 1′-, 2′- and 3′-H_2) and 0.85 (3 H, t, *J* 6, 4′-H_3).

cis- *and* trans-3-*Chloro*-2-(*hept*-1′-*ynyl*)*tetrahydropyran* **49**.—Hept-1-ynylmagnesium bromide was prepared in a manner analogous to that below from hept-1-yne (7.69 g, 0.08 mol) in diethyl ether (10 cm^3), bromoethane (8.75 g, 0.08 mol) and magnesium (2.05 g, 0.08 mol) in diethyl ether (30 cm^3). 2,3-Dichlorotetrahydropyran [from 2,3-dihydro-4*H*-pyran (4.22 g, 0.05 mol)] was added to the cooled Grignard reagent and the mixture was stirred overnight. Work-up and distillation gave *cis*- and *trans*-3-chloro-2-(hept-1′-ynyl)tetrahydropyran **49** (6.94 g, 65%), b.p. 85–86 °C/0.2 mmHg (lit.,[17] 150 °C/14 mmHg). GLC (Apiezon L) and ^1H NMR analysis showed the *trans*-isomer (longer retention time) to constitute 80% of the mixture; ν_{max}(film)/cm^{-1} 2965s, 2935s, 2870, 2255w (C≡C), 1070s (C–O), 940 and 775; δ_H(400 MHz; $CDCl_3$): For *trans*-isomer: 4.18 (1 H, d, *J* 7.3, 2-H), 3.99 (1 H, m, 6-H_e), 3.89 (1 H, m, 3-H), 3.53 (1 H, m, 6-H_a), 2.35 (1 H, m, 4-H), 2.24 (2 H, td, *J* 7.2 and 1.9, 3′-H_2), 1.81 (2 H, m, 4- and 5-H), 1.65 (1 H, m, 5-H), 1.54 (2 H, m, 4′-H_2), 1.34 (3 H, m, 5′- and 6′-H_2) and 0.90 (3 H, t, *J* 7.1, 7′-H_3). For *cis*-isomer: 4.62 (1 H, unresolved d, 2-H), 4.07 (1 H, dt, m, 3-H), 3.62 (1 H, dt, *J* 11.4 and 4.6, 6-H_e) and 2.27 (2 H, dt, *J* 7.0 and 2.0, 3′-H_2) (other signals masked by *trans*-isomer); δ_C(100 MHz; $CDCl_3$): For *trans*-isomer: 87.76 (C, C-1′), 76.41 (C, C-2′), 72.58 (CH, C-2), 66.15 (CH_2, C-6), 58.70 (CH, C-3), 32.10 (CH_2, C-4), 31.02 (CH_2, C-5′), 28.16 (CH_2, C-4′), 24.54 (CH_2, C-5), 22.17 (CH_2, C-6′), 18.68 (CH_2, C-3′) and 13.99 (CH_3, C-7′), For *cis*-isomer: 89.38 (C, C-1′), 74.56 (C, C-2′), 70.42 (CH, C-2), 63.30 (CH_2, C-6), 57.22 (CH, C-3), 31.02 (CH_2, C-5′), 30.13 (CH_2, C-4), 28.25 (CH_2, C-4′), 24.54 (CH_2, C-5), 22.17 (CH_2, C-6′), 18.68 (CH_2, C-3′) and 13.99 (CH_3, C-7′).

cis- *and* trans-3-*Chloro*-2-(*pent*-1′-*ynyl*)*tetrahydropyran* **50**.—A solution of pent-1-yne (7.29 g, 0.11 mol) in dry diethyl ether (11 cm^3) was added dropwise to an ice-cold solution of ethylmagnesium bromide in diethyl ether (30 cm^3) [from bromoethane (11.6 g, 0.11 mmol) and magnesium (2.60 g, 0.11 mmol)] and the mixture was refluxed (1 h). The resulting stirred solution of pent-1-ynylmagnesium bromide was cooled in ice, 2,3-dichlorotetrahydropyran [from chlorination of 2,3-dihydro-4*H*-pyran (6 g, 0.07 mol)] added dropwise, and the mixture was stirred overnight. The product was poured cautiously into ice–water, acidified with hydrochloric acid, and extracted with diethyl ether. The extracts were washed successively with saturated aq. sodium hydrogen carbonate, water, and brine, and dried over anhydrous magnesium sulfate. Evaporation and distillation gave cis- and trans-3-*chloro*-2-(*pent*-1′-*ynyl*)-*tetrahydropyran* **50** (9.4 g, 71%), b.p. 72–77 °C/0.2 mmHg (Found: M^+, 188.080/186.076. $C_{10}H_{15}ClO$ requires M, 188.078/186.081). The mixture was further purified by chromatography on silica gel, with hexane–diethyl ether (97 : 3) as eluent. GLC analysis (Apiezon L) showed the *trans*-isomer (longer retention time) to constitute 70% of the mixture; ν_{max}(film)/cm^{-1} 3010s, 2920s, 2290w (C≡C) and 1080s (C–O); δ_H(400 MHz; $CDCl_3$): For *trans*-isomer: 4.18 (1 H, d, *J* 7.3, 2-H), 3.99 (1 H, m, 6-H_e), 3.90 (1 H, m, 3-H), 3.53 (1 H, m, 6-H_a), 2.36 (1 H, m, 4-H), 2.23 (2 H, td, *J* 6.8 and 2.0, 3′-H_2), 1.81 (2 H, m, 4- and 4-H), 1.65 (1 H, m, 5-H), 1.57 (2 H, m, 4′-H_2) and 1.00 (3 H, t, *J* 7.4, 5′-H_3). For *cis*-isomer: 4.63 (1 H, unresolved d, 2-H), 4.05 (1 H, m, 3-H), 3.99 (1 H, m, 6-H_a), 3.61 (1 H, dt, *J* 11.6 and 4.5, 6-H_e), 2.26 (2 H, td, *J* 6.9 and 2.0, 3′-H_2), 2.08 (3 H, m, 4-H_2 and 5-H), 1.81 (1 H, m, 5-H), 1.57 (2 H, m, 4′-H_2) and 1.02 (3 H, t, *J* 7.4, 5′-H_3); δ_C(100 MHz; $CDCl_3$): For *trans*-isomer: 87.54 (C, C-1′), 76.61 (C, C-2′), 72.58 (CH, C-2), 66.15 (CH_2, C-6), 58.70 (CH, C-3), 32.10 (CH_2, C-4), 24.55 (CH_2, C-5), 21.92 (CH_2, C-4′), 20.68 (CH_2, C-3′) and 13.48 (CH_3, C-5′). For *cis*-

isomer: 89.18 (C, C-1'), 74.73 (C, C-2'), 70.41 (CH, C-2), 63.28 (CH_2, C-6), 57.22 (CH, C-3), 30.13 (CH_2, C-4), 24.55 (CH_2, C-5), 22.04 (CH_2, C-4'), 20.73 (CH_2, C-3') and 13.48 (CH_3, C-5').

trans-3-*Chloro*-2-*ethynyltetrahydropyran* **51**.—Ethynylmagnesium bromide[14] (0.09 mol) as a solution in THF (95 cm^3) was prepared as described for the tetrahydrofuran analogue, and the solution was cooled to 0 °C. 2,3-Dichlorotetrahydropyran [from dihydropyran (5.05 g, 0.06 mol)] was added and the product was worked up as before. Distillation gave the *trans*-pyran **51** (5.72 g, 66%), b.p. 75–78 °C/7 mmHg (lit.,[15] 80–84 °C/11 mmHg). The material was further purified by chromatography on silica gel, with hexane–diethyl ether (95:5) as eluent, monitoring by GLC (PEGA); ν_{max}(film)/cm^{-1} 3300s (≡CH), 2970s, 2880s, 2140w (C≡C), 1080s (C–O), 950 and 780; δ_H(400 MHz; $CDCl_3$) 4.21 (1 H, dd, *J* 7.4 and 2.1, 2-H), 4.03–3.92 (2 H, m, 3- and 6-H), 3.55 (1 H, m, 6-H), 2.57 (1 H, d, *J* 2.2, 2'-H), 2.39 (1 H, m, 4-H), 1.90–1.77 (2 H, m, 4- and 5-H) and 1.69 (1 H, m, 5-H); δ_C(100 MHz; $CDCl_3$) 80.01 (C, C-1'), 74.81 (CH, C-2'), 72.06 (CH, C-2), 66.31 (CH_2, C-6), 57.84 (CH, C-3), 31.94 (CH_2, C-4) and 24.34 (CH_2, C-5).

Samarium Diiodide.[3]—In a typical preparation a slurry of samarium powder (1 g, 6.65 mol) in dry THF (20 cm^3) was sonicated for 15 min and a solution of 1,2-diiodoethane (1.7 g, 6.03 mmol) in THF (40 cm^3) was then added with vigorous stirring of the mixture. The mixture was alternately stirred and sonicated until an intense blue colour had fully developed (~1–15 h). Throughout the preparation a fairly fast flow of dry nitrogen was maintained. The air- and moisture-sensitive reducing agent was freshly prepared just prior to use in each case.

(E)-*Hex*-3-*en*-1-*ol* **6**.—Mixed *cis*- and *trans*-3-chloro-2-ethyltetrahydrofuran (above) (169 mg, 1.25 mmol) as a solution in dry THF (7 cm^3) were added to a vigorously stirred mixture of samarium diiodide in THF (0.1 mol dm^{-3}; 5.0 mol equiv.) under nitrogen. The mixture was heated to reflux and the course of the reaction was monitored by GLC (PEGA). After 76 h at reflux virtually all of the furans had reacted, and the reaction vessel was opened to the air to oxidise any remaining Sm^{2+} to Sm^{3+}. Dil. hydrochloric acid was added to dissolve Sm^{3+} species and the resulting solution was extracted with diethyl ether. The extracts were washed successively with saturated aq. sodium thiosulfate, water, and brine, and dried ($MgSO_4$). The product yield (95%) was determined by GLC (PEGA) using heptan-2-one as internal standard. After evaporation of the extracts, the title alcohol **6** was purified by bulb-to-bulb distillation at 70 °C (oven)/15 mmHg (lit.,[18] b.p. 51–53 °C/9 mmHg); ν_{max}(film)/cm $^{-1}$ 3340br s (OH), 2980s, 2940s, 2880s, 1045br s, (C–O) and 970s [(*E*)-CH=CH]; δ_H(80 MHz; $CDCl_3$) 5.49 (2 H, m $J_{3,4}$ 15.4, 3- and 4-H), 3.62 (2 H, t, *J* 6.3, 1-H_2), 2.40–1.82 (4 H, m, 2- and 5-H_2), 1.73 (1 H, br s, OH), 0.98 (3 H, t, *J* 7.4, 6-H_3); δ_C(100 MHz; $CDCl_3$) 135.00 (CH, C-3), 124.85 (CH, C-4), 62.08 (CH_2, C-1), 35.96 (CH_2, C-2), 25.69 (CH_2, C-5) and 13.80 (CH_3, C-6).

(E)-*Pent*-3-*en*-1-*ol* **3**.—A solution of *trans*-3-chloro-2-methyltetrahydrofuran **1** (204 mg, 1.69 mmol) in THF (8 cm^3) was added to a mixture of samarium diiodide in THF (0.1 mol dm^{-3}; 4.5 mol equiv.) under nitrogen. The reaction mixture was heated under reflux (N_2) for 54 h, when GLC (PEGA) showed that complete utilisation of the starting material had occurred. Work-up was as described previously and the yield (89%) was evaluated from an internal standard (heptan-1-ol). Bulb-to-bulb distillation gave (*E*)-pent-3-en-1-ol **3**, b.p. 40 °C (oven)/20 mmHg (lit.,[18] 136–137 °C); ν_{max}(film)/cm^{-1} 3350br s (OH), 2970s, 2895s, 1050br s(C–O) and 970 [(*E*)-CH=CH]; δ_H(400 MHz; $CDCl_3$) 5.56 (1 H, m, 3-H), 5.40 (1 H, m, $J_{3,4}$ 15.2, 4-H), 3.62 (2 H, t, *J* 6.3, 1-H_2), 2.25 (2 H, m, 2-H_2), 1.85 (1 H, br s, OH) and 1.69 (3 H, dd, *J* 6.3 and 1.4, 5-H_3); δ_C(100 MHz; $CDCl_3$) 128.50 (CH, C-3), 127.15 (CH, C-4), 62.03 (CH_2, C-1), 35.96 (CH_2, C-2) and 18.05 (CH_3, C-5).

The procedure was repeated using *cis*-3-chloro-2-methyltetrahydrofuran **2** (200 mg, 1.66 mmol) and samarium diiodide (0.1 mol dm^{-3}; 7.1 mol equiv.), heating under reflux (N_2) for 72 h, and monitoring by GLC (PEGA). Work-up was followed by GLC evaluation of yield (76%) using an internal standard (heptan-1-ol). Bulb-to-bulb distillation gave (*E*)-pent-3-en-1-ol, b.p. (oven) 40 °C/20 mmHg. NMR data [^{1}H (400 MHz) and ^{13}C (100 MHz')] were identical with those reported above.

(E)-*Hexa*-3,5-*dien*-1-*ol* **8**.—A solution of *cis*-3-chloro-2-vinyltetrahydrofuran **7** (131 mg, 0.99 mmol) in THF (5 cm^3) was refluxed (N_2) with samarium diiodide in THF (0.1 mol dm^{-3}; 5.0 equiv.) for 165 h, when GLC analysis (OV 17) showed that all the starting furan had reacted (~80% of the furan had reacted in 45 h). The GLC yield using heptan-1-ol as internal standard was 84%. Isolation gave the (*E*)-dienol **8**, purified by bulb-to-bulb distillation at 70 °C (oven)/15 mmHg (lit.,[20] 79–80 °C/20 mmHg); λ_{max}(EtOH)/nm 222infl (ε 21 200), 225 (22 300) and 232infl (15 500); ν_{max}(film)/cm^{-1} 3350br s (OH), 2940s, 2890s, 1645w, 1600w, 1420, 1045br s (C–O), 1000s, 960s [(*E*)-CH=CH] and 900s; δ_H(80 MHz; $CDCl_3$) 6.78–4.90 (5 H, m, $J_{3,4}$ 16.6, 3-, 4- and 5-H and 6-H_2), 3.68 (2 H, t, *J* 6.3, 1-H_2), 2.35 (2 H, q, *J* 6.5, 2-H_2) and 1.71 (1 H, br s, OH); δ_C(100 MHz; $CDCl_3$) 136.84 (CH, C-3), 133.64 (CH, C-4), 130.70 (CH, C-5), 115.91 (CH_2, C-6), 61.85 (CH_2, C-1) and 35.90 (CH_2, C-2).

(E)-*Hepta*-3,6-*dien*-1-*ol* **10**.—Mixed *cis*- and *trans*-2-allyl-3-chlorotetrahydrofuran **9** (127 mg, 0.87 mmol) were refluxed (N_2; 59 h) in THF (6 cm^3) with samarium diiodide in THF (0.1 mol dm^{-3}; 5.0 mol equiv.), with monitoring by GLC (OV-17). Use of an internal standard (heptan-1-ol) gave the yield as 93%. Bulb-to-bulb distillation gave (*E*)-hepta-3,6-dien-1-ol **10** (oven 50 °C/7 mmHg) (lit.,[2] b.p. 79–82 °C/17 mmHg); ν_{max}(film)/cm^{-1} 3340br s (OH), 3080, 2930s, 2895s, 1640, 1430, 1050br s (C–O), 970s [(*E*)-CH=CH] and 910; δ_H(80 MHz; $CDCl_3$) 5.86 (1 H, ddt, *J* 17, 10 and 6, 6-H), 5.54 (2 H, m, 3- and 4-H), 5.02 (1 H, d, *J* 17, 7-H), 5.00 (1 H, d, *J* 10, 7-H), 3.63 (2 H, t, *J* 6, 1-H_2), 2.77 (2 H, m, 5-H_2), 2.30 (2 H, m, 2-H_2) and 1.80 (1 H, br s, OH); δ_C(100 MHz; $CDCl_3$) 136.93 (CH, C-3), 131.07 (CH, C-4), 127.28 (CH, C-6), 115.17 (CH_2, C-7), 36.78 (CH_2, C-5) and 35.96 (CH_2, C-2).

(E)-4-*Phenylbut*-3-*en*-1-*ol* **12**.—A solution of *trans*-3-chloro-2-phenyltetrahydrofuran **11** (124 mg, 0.68 mmol) in THF (6 cm^3) was added to a mixture of samarium diiodide in THF (0.1 mol dm^{-3}; 4.7 mol equiv.) and heated under reflux (N_2) for 52 h, with monitoring by GLC (Carbowax 20M). The product yield (95%) following work-up was evaluated using (*E*)-4-phenylbut-2-en-2-one as GLC standard. Distillation (bulb-to-bulb) at 100 °C (oven)/0.3 mmHg gave (*E*)-4-phenylbut-3-en-1-ol **12** (lit.,[19] b.p. 134–140 °C/12 mmHg); ν_{max}(film)/cm^{-1} 3350br s (OH), 3020, 2940s, 2890s, 1600, 1500 (Ar), 1050br s (C–O), 965s [(*E*)-CH=CH], 745s and 695s; δ_H(90 MHz; $CDCl_3$) 7.35 (5 H, m, Ph), 6.50 (1 H, d, *J* 16, 4-H), 6.17 (1 H, dt, *J* 16 and 6, 3-H), 3.69 (2 H, t, *J* 6, 1-H_2), 2.42 (2 H, q, *J* 6, 2-H_2) and 2.32 (1 H, br s, OH); δ_C(100 MHz; $CDCl_3$) 137.26 (C, C-5), 132.48 (CH, C-4), 128.49 (CH, C-6 and -10), 127.17 (CH, C-3), 126.45 (CH, C-8), 126.03 (CH, C-7 and -9), 61.91 (CH_2, C-1) and 36.33 (CH_2, C-2).

(E)-4-p-*Tolylbut*-3-*en*-1-*ol* **14**.—A solution of *trans*-3-chloro-2-*p*-tolyltetrahydrofuran **13** (117 mg, 0.59 mmol) in

THF (6 cm^3) was refluxed (N_2; 48 h) with samarium diiodide in THF (0.1 mol dm^{-3}; 5.1 mol equiv.) with GLC monitoring (Apiezon L). The yield, as measured by an internal standard [(*E*)-4-phenylbut-3-en-2-one], was almost theoretical. The product **14** on work-up crystallised from pentane in needles, m.p. 54–55 °C (lit.,[2] 52 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 2920s, 1605, 1500 (Ar), 1020br s (C–O) and 970s [(*E*)-CH=CH]; δ_H(80 MHz; $CDCl_3$) 7.17 (4 H, m, ArH), 6.48 (1 H, d, *J* 16, 4-H), 6.09 (1 H, dt, *J* 16 and 6, 3-H), 3.72 (2 H, t, *J* 6, 1-H_2), 2.45 (2 H, q, *J* 6, 2-H_2), 2.32 (3 H, s, 8-Me) and 1.77 (1 H, br s, OH); δ_C(100 MHz; $CDCl_3$) 136.92 (C, C-5), 134.46 (C, C-8), 132.46 (CH, C-4), 129.19 (CH, C-6 and -10), 125.94 (CH, C-7 and -9), 125.27 (CH, C-3), 61.98 (CH_2, C-1), 36.34 (CH_2, C-2) and 21.12 (CH_3, Me).

(E)-*Undec*-3-*en*-5-*yn*-1-*ol* **18**.—A solution of *cis*-3-chloro-2-(hept-1′-ynyl)tetrahydrofuran **15** (200 mg, 1 mmol) in THF (7 cm^3) was refluxed (N_2) with samarium diiodide in THF (0.1 mol dm^{-3}; 5.1 mol equiv.) for 22 h, after which all the starting furan had reacted to form two products in 84 and 14% yield as determined by GLC (Apiezon L, internal standard hexadecane). These were separated by chromatography on silica gel, with hexane–diethyl ether (70 : 30) as eluent and monitoring fractions by GLC. The major product (longer GLC retention time) was (E)-*undec*-3-*en*-5-*yn*-1-*ol* **18** (Found: M^+, 166.134. $C_{11}H_{18}O$ requires M, 166.136); λ_{max}(EtOH)/nm 229 (ε 15 500) and 235infl (13 600); ν_{max}(film)/cm^{-1} 3350br s(OH), 2960s, 2940s, 2870, 2220w (C≡C), 1050br s (C–O) and 960 [(*E*)-CH=CH]; δ_H(400 MHz; $CDCl_3$) 5.95 (1 H, dt, *J* 15.8 and 7.2, 3-H), 5.50 (1 H, d, *J* 15.8, 4-H), 3.59 (2 H, t, *J* 6.4, 1-H_2), 2.27 (2 H, q, *J* 6.2, 2-H_2), 2.21 (2 H, td, *J* 7.1 and 2.0, 7-H_2), 1.90 (1 H, br s, OH), 1.45 (2 H, m, *J* 7.2, 8-H_2), 1.25 (4 H, m, 9- and 10-H_2) and 0.83 (3 H, t, *J* 7, 11-H_3); δ_C(100 MHz; $CDCl_3$) 138.62 (CH, C-3), 112.91 (CH, C-4), 89.76 (C, C-5), 78.78 (C, C-6), 61.62 (CH_2, C-1), 36.30 (CH_2, C-2), 31.12 (CH_2, C-9), 28.49 (CH_2, C-8), 22.56 (CH_2, C-10), 19.31 (CH_2, C-7) and 13.98 (CH_3, C-11). The minor product was identified as the dechlorinated furan **21**.

(E)-*Hex*-3-*en*-5-*yn*-1-*ol* **19**.—A solution of *cis*-3-chloro-2-ethynyltetrahydrofuran **16** (118 mg, 0.90 mmol) in THF (51 cm^3) was added to a mixture of samarium diiodide in THF (0.1 mol dm^{-3}; 4.1 mol equiv.) and the mixture was warmed to 50 °C for 5 h, with monitoring by GLC (Carbowax 20M). The temperature was raised to 58 °C for 18 h, then to 68 °C for 5 h, by which time virtually no starting material was present and two products were observed by GLC, 72% and 17% as evaluated by using hexadecane as internal standard. Separation on silica gel gave 2-ethynyltetrahydrofuran **22** as the minor product and (*E*)-hex-3-en-5-yn-1-ol **19** as the major product (longer GLC retention time); $\nu_{max}(CHCl_3)/cm^{-1}$ 3580, 3410br s (OH), 3300s (≡CH), 2920s, 2870s, 2110w (C≡C), 1380, 1105s, 1030br s (C–O), 965s [(*E*)-CH=CH] and 905; δ_H(400 MHz; $CDCl_3$) 6.24 (1 H, dt, *J* 15.9 and 7.3, 3-H), 5.58 (1 H, dd, *J* 15.9 and 2.0, 4-H), 3.69 (2 H, t, *J* 6.3, 1-H_2), 2.83 (1 H, d, *J* 2.0, 6-H), 2.39 (2 H, m, 2-H_2) and 1.98 (1 H, br s, OH); δ_C(100 MHz; $CDCl_3$) 142.48 (CH, C-3), 111.28 (CH, C-4), 82.04 (C, C-5), 76.46 (CH, C-6), 61.33 (CH_2, C-1) and 36.29 (CH_2, C-2).

(E)-6-*Phenylhex*-3-*en*-5-*yn*-1-*ol* **20**.—A solution of *cis*-3-chloro-2-(phenylethynyl)tetrahydrofuran **17** (192 mg, 0.93 mmol) in THF (8 cm^3) was refluxed (N_2) with samarium diiodide in THF (0.1 mol dm^3; 4.2 mol equiv.) for 22 h, and monitoring by GLC (Azpiezon L). Two products were formed, in 75 and 19% yield (GLC, eicosane internal standard), and these were separated by chromatography on silica gel, with hexane–diethyl ether (70 : 30) as eluent. The major product (longer GLC retention time) was (E)-6-*phenylhex*-3-*en*-5-*yn*-1-*ol* **20** (Found: M^+, 172.089. $C_{12}H_{12}O$ requires M, 172.089); λ_{max}(EtOH)/nm 216infl (ε 14 500), 259infl (17 000), 273 (25 600) and 289 (20 000); ν_{max}(film)/cm^{-1} 3360br s (OH), 3050, 2955s, 2900s, 2200w (C≡C), 1600, 1490s (Ar), 1445, 1055br s (C–O), 960s [(*E*)-CH=CH], 765s and 700s; δ_H(400 MHz; $CDCl_3$, aided by COSY) 7.42 (2 H, m, ArH), 7.30 (3 H, m, ArH), 6.22 (1 H, td, *J* 15.8 and 7.4, 3-H), 5.81 (1 H, d, *J* 15.8, 4-H), 3.72 (2 H, t, *J* 6.3, 1-H_2), 2.42 (2 H, q, *J* 6.3, 2-H_2) and 1.76 (1 H, br s, OH); δ_C(100 MHz) 140.25 (CH, C-3), 131.21 (CH, C-8 and -12), 128.05 (CH, C-9 and -11), 127.83 (CH, C-10), 123.09 (C, C-7), 112.18 (CH, C-4), 88.42 (C, C-5), 87.53 (C, C-6), 61.30 (CH_2, C-1) and 36.25 (CH_2, C-2).

The first eluted product was identified as 2-(phenylethynyl)-tetrahydrofuran **23**; δ_H(80 MHz; $CDCl_3$) 7.32 (5 H, m, Ph), 4.82 (1 H, m, 2-H), 3.93 (2 H, m, 5-H_2), 2.09 (4 H, m, 3- and 4-H_2); *m*/*z* (+ve EI) 172 (M^+, 100%).

Pent-4-*en*-1-*ol* **25**.—A solution of tetrahydrofurfuryl chloride **24** (152 mg, 1.26 mmol) in THF (7 cm^3) was refluxed (N_2) with samarium diiodide in THF (0.1 mol dm^{-3}; 4.9 mol equiv.) for 93 h with GLC monitoring (PEGA). The yield was 96% (GLC, heptan-1-ol internal standard). Work-up and bulb-to-bulb distillation (oven 60 °C/55 mmHg) (lit.,[13] b.p. 134–137 °C) gave pent-4-en-1-ol **25** spectroscopically identical with authentic material; ν_{max}(film)/cm^{-1} 3330br s (OH), 3080, 2940s, 1640, 1065br s (C–O), 990 [(*E*)-CH=CH] and 910; δ_H(80 MHz; $CDCl_3$) 5.86 (1 H, ddt, *J* 17, 10 and 6, 4-H), 5.03 [1 H, d, *J* 17, 5-H(*E*)], 5.00 [1 H, d, *J* 10, 5-H(*Z*)], 3.65 (2 H, t, *J* 6, 1-H_2) and 2.31–1.48 (5 H, m, including at δ 1.92 a br s, OH, and 2- and 3-H_2).

(E)- *and* (Z)-*Hept*-4-*en*-1-*ol* **27**/**28** *from* erythro-/threo-2-(1′-*Chloropropyl*)*tetrahydrofuran* **26**.—A solution of *erythro*-/*threo*-**26** (75 mg, 0.5 mmol) (above) in THF (5 cm^3) was refluxed (N_2) for 30 h with samarium diiodide in THF (0.1 mol dm^{-3}; 4.3 mol equiv.). GLC (Carbowax 20M) showed that reaction was essentially complete. After work-up, the GLC yield (hexadecane internal standard) was 64%. Chromatography on silica gel, with hexane–diethyl ether as eluent, gave hept-4-en-1-ol, a 69% (*E*)-**27**/31% (*Z*)-**28** mixture as determined by NMR spectroscopy; ν_{max}(film)/cm^{-1} 3355br s (OH), 2985s, 2955s, 2895s, 1455, 1065br s(C–O) and 965 [(*E*)-CH=CH]; δ_H(400 MHz; $CDCl_3$) 5.50 [0.69 H, dt, *J* 15.3 and 6.1, 4-H(*E*)], 5.44–5.32 [1.31 H, m, 4-H(*Z*) and 5-H(*Z* + *E*)], 3.64 (2 H, t, *J* 6.5, 1-H_2), 2.04 (4 H, m, 3- and 6-H_2), 1.77 (1 H, br s, OH), 1.63 (2 H, m, *J* 6.9, 2-H_2) and 0.97 (3 H, t, *J* 7.4, 7-H_3); δ_C(100 MHz; $CDCl_3$): For (*E*)-isomer: 132.26 (CH, C-4), 127.94 (CH, C-5), 62.04 (CH_2, C-1), 31.98 (CH_2, C-2), 28.38 (CH_2, C-3), 25.07 (CH_2, C-6) and 13.40 (CH_3, C-7). For (*Z*)-isomer: 131.92 (CH, C-4), 127.81 (CH, C-5), 62.10 (CH_2, C-1), 32.17 (CH_2, C-2), 23.00 (CH_2, C-3), 20.00 (CH_2, C-6) and 13.81 (CH_3, C-7).

[4-^{2}H]*But*-3-*en*-1-*ol* **31**/**32**.—*cis*-/*trans*-3-chloro-2-deuteriotetrahydrofuran **29**/**30** (78% *cis*/22% *trans*) (100 mg, 0.93 mmol) in THF (5 cm^3) was refluxed (N_2) for 69 h with samarium diiodide in THF (0.1 mol dm^{-3}; 5.5 mol equiv.), when GLC monitoring (Carbowax 20M) showed no furan remained. Work-up with diethyl ether gave the title material (29 mg, 43%) after purification by bulb-to-bulb distillation (oven 115 °C) (lit.,[1b] b.p. 112–114 °C). From the ^{1}H NMR data (from expanding and integrating several times in the δ 5.12–5.14 region) the product was found to be an (*E*)-**31**/(*Z*)-**32** mixture of 49/51%, respectively; $\nu_{max}(CHCl_3)/cm^{-1}$ 3590, 3430br s (OH), 2925s, 2250w (C–D), 1040br s (C–O) and 985 [(*E*)-CH=CH]; δ_H(400 MHz; $CDCl_3$) 5.81 (1 H, m, 3-H), 5.14 [dt, *J* 17.2 and 1.4, 4-H(*E*)], 5.12 [d, *J* 10.2, 4-H(*Z*)], 3.75 (2 H, t, *J* 6.6, 1-H_2), 2.34 (2 H, q, *J* 6.5, 2-H_2) and 1.45 (1 H, br s, OH).

(E)- *and* (Z)-*Hept*-4-*en*-1-*ol* **27**/**28** *from* trans-3-*Chloro*-2-*ethyltetrahydropyran* **33**.—A solution of the pyran **33** (200 mg,

1.35 mmol) in THF (6 cm^3) was refluxed (N_2) with samarium diiodide in THF (0.1 mol dm^{-3}; 4.2 mol equiv.) for 142 h, when GLC (Carbowax 20M) showed the disappearance of most of the pyran. The product was worked up as usual [yield (hexadecane as internal GLC standard) 85%], and chromatographed on silica gel, with hexane–diethyl ether (70:30) as eluent, to give a 24% (*E*)-**27**/76% (*Z*)-**28** mixture of hept-4-en-1-ols (^{1}H NMR); ν_{max}(film)/cm^{-1} 3390br s (OH), 3070, 3030s, 3000s, 2930s, 1455, 1065br s, (C–O), 970w [(*E*)-CH=CH]; δ_H(400 MHz; $CDCl_3$] 5.50 [0.24 H, dt, *J* 15.3 and 6.0, 4-H(*E*)], 5.44–5.30 [1.76 H, m, 4-H(*Z*) + 5-H(*E*)], 3.64 (2 H, t, *J* 6.6, 1-H_2), 2.15–1.96 (5 H, m, 3- and 6-H_2, OH), 1.63 (2 H, m, *J* 7.0, 2-H_2) and 0.96 (3 H, t, *J* 7.5, 7-H_3); δ_C(100 MHz; $CDCl_3$): For (*E*)-isomer: 132.73 (CH, C-4), 128.44 (CH, C-5), 62.49 (CH_2, C-1), 32.47 (CH_2, C-2), 28.89 (CH_2, C-3), 25.58 (CH_2, C-6) and 13.92 (CH_3, C-7). For (*Z*)-isomer: 132.40 (CH, C-4), 128.33 (CH, C-5), 62.54 (CH_2, C-1), 32.65 (CH_2, C-2), 23.50 (CH_2, C-3), 20.51 (CH_2, C-6) and 14.33 (CH_3, C-7).

cis-3-Chloro-2-ethyltetrahydropyran **34** (160 mg, 1.08 mmol) was refluxed for 93 h with samarium diiodide in THF (N_2), and the product was worked up, and examined by GLC and spectroscopically, as above, to give hept-4-en-1-ols (91%) as a 28% (*E*)-/72% (*Z*)-isomer mixture.

(E)- *and* (Z)-6-*Methylhept*-4-*en*-1-*ol* **37**/**38**.—A solution of 3-chloro-2-isopropyltetrahydropyran **35**/**36** (86% *trans*/14% *cis*) (200 mg, 1.23 mmol) in THF (5 cm^3) was refluxed with samarium diiodide in THF (0.1 mol dm^{-3}; 5.6 mol equiv.) for 125 h, when GLC (PEGA) analysis showed that all starting pyran had reacted, though the stereoisomeric alcohols were not separated by this column. Work-up was followed by estimation of product yield (84%) with hexadecane as internal standard. The product was chromatographed on silica gel and eluted with hexane–diethyl ether (75:25), and was a 21% (*E*)-**37**[21]/79% (*Z*)-**38** mixture as determined by ^{1}H NMR spectroscopy; ν_{max}(film)/cm^{-1} 3340br s (OH), 3020, 2980s, 2950s, 2890s, 1460, 1065br s (C–O), 965w [(*E*)-CH=CH] and 745; δ_H(400 MHz; $CDCl_3$) 5.43 [0.21 H, AB, dd, *J* 15.6 and 5.9, 5-H(*E*)], 5.37 [0.21 H, AB, dd, *J* 15.3 and 5.9, 4-H(*E*)], 5.32–5.19 [1.58 H, m, 4- and 5-H(*Z*)], 3.67 (2 H, t, *J* 6.5, 1-H_2), 2.62 (1 H, m, 6-H), 2.26–2.04 (2 H, m, 3-H_2), 1.63 (3 H, br p, *J* 6.8, 2-H_2 and OH), and 0.95 (6 H, d, *J* 6.5, 7- and 8-H_3); δ_C(100 MHz; $CDCl_3$). For (*E*)-isomer: 138.12 (CH, C-4), 126.10 (CH, C-5), 62.40 (CH_2, C-1), 32.28 (CH_2, C-2), 30.75 (CH, C-6), 28.62 (CH_2, C-3) and 22.37 (CH_3, C-7 and -8). For (*Z*)-isomer: 138.12 (CH, C-4), 126.23 (CH, C-5), 62.40 (CH_2, C-1), 32.59 (CH_2, C-2), 26.22 (CH, C-6), 23.47 (CH, C-3) and 22.91 (CH_3, C-7 and -8).

(E)- *and* (Z)-6-*Hydroxyhex*-2-*enonitrile* **41**/**40**.—A solution of *trans*-3-chlorotetrahydropyran-2-carbonitriles **39** (149 mg, 1.02 mmol) in THF (5 cm^3) was stirred at room temperature with samarium diiodide in THF (0.1 mol dm^{-3}; 3.0 mol equiv.) for 3 h, then was warmed to 45 °C for 20 h, with monitoring by TLC. After a further increase in temperature to 55 °C for a further 23 h, and finally to 65 °C for 20 h, the mixture was worked up under neutral conditions. The crude product was chromatographed on silica gel, and eluted with hexane–ethyl acetate (50:50) to yield (E)- and (Z)-6-*hydroxyhex*-2-*enonitrile* **41**/**40** (14 mg, 12%) (Found: M^+, 111.066. C_6H_9NO requires M, 111.068). ^{1}H NMR analysis, using the relative integrals for the 3-(*E*) and 3-(*Z*) protons, showed the (*Z*)-**40** isomer to constitute 79% of the mixture; ν_{max}($CHCl_3$)/cm^{-1} 3610, 3460br s (OH), 2870s, 2170s (C≡N), 1620, 1055br s, (C–O) and 970w [(*E*)-CH=CH]; δ_H(400 MHz; $CDCl_3$) 6.76 [0.2 H, td, *J* 16.3 and 7.0, 3-H(*E*)], 6.54 [0.8 H, td, *J* 10.9 and 7.7, 3-H(*Z*)], 5.37 [0.2 H, d, *J* 16.4, 2-H(*E*)], 5.35 [0.8 H, d, *J* 10.9, 2-H(*Z*)], 3.70 (1.6 H, t, *J* 6.3, 6-H_2(*Z*)], 3.67 [0.4 H, t, *J* 6.2, 6-H_2(*E*)], 2.54 [1.6 H, q, *J* 7.6, 4-H_2(*Z*)], 2.35 [0.4 H, q, *J* 7.3, 4-H_2(*E*)], 1.85–1.68 (2 H, m, 5-H_2) and 1.26 (1 H, br s, OH); δ_C(100 MHz; $CDCl_3$): For (*E*)-isomer: 155.44 (CH, C-3), 117.45 (C, C-1), 100.17 (CH, C-2), 61.54 (CH_2, C-6), 29.70 (CH_2, C-5) and 30.43 (CH_2, C-4). For (*Z*)-isomer: 154.62 (CH, C-3), 115.97 (C, C-1), 99.96 (CH, C-2), 61.75 (CH_2, C-6), 31.00 (CH_2, C-5) and 28.44 (CH_2, C-4).

Treatment of 2-*Butyl*-3,3-*dichlorotetrahydropyran* **47** *with Samarium Diiodide*.—A solution of 2-butyl-3,3-dichlorotetrahydropyran **47** (249 mg, 1.18 mmol) in THF (7 cm^3) was refluxed (N_2) for 4 h with samarium diiodide in THF (0.1 mol dm^{-3}; 5.0 mol equiv.), when monitoring by GLC (OV-17) showed that all the starting material had reacted. The major product was formed in 51% GLC yield (internal standard hexadecane) and was purified by bulb-to-bulb distillation (oven 90 °C/18 mmHg) and identified as 2-butyltetrahydropyran **48** (Found: M^+, 142. Calc. for $C_9H_{18}O$: M, 142); δ_H(400 MHz; $CDCl_3$, aided by COSY) 3.96 (1 H, m, 6-H_e), 3.41 (1 H, td, *J* 11.5 and 2.4, 6-H_a), 3.21 (1 H, m, 2-H), 1.85–1.20 (12 H, m, 3-, 4-, 5-, 1′-, 2′- and 3′-H_2), 0.89 (3 H, t, *J* 7.3, 4′-H_3); δ_C(100 MHz; $CDCl_3$) 78.02 (CH, C-2), 68.58 (CH_2, C-6), 36.42 (CH_2, C-1′), 32.01 (CH_2, C-3), 27.79 (CH_2, C-5), 26.32 (CH_2, C-4), 23.69 (CH_2, C-2′), 22.87 (CH_2, C-3′) and 14.13 (CH_3).

Treatment of 3-*Chloro*-5,6-*dihydro*-4H-*pyran* **46** *with Samarium Diiodide*.—A solution of the pyran (178 mg, 1.5 mmol) in THF (7 cm^3) was refluxed (N_2) with samarium diiodide in THF (0.1 mol dm^{-3}, 4.1 mol equiv.) for 166 h, but GLC analysis (Carbowax 20M) indicated no change in the starting material.

[5-^{2}H]*Pent*-4-*en*-1-*ol* **44**/**45**.—A solution of 3-chloro-2-deuteriotetrahydropyran, mixed *cis*-**43** (26%) and *trans*-**42** (74%) isomers (206 mg, 1.69 mmol) in THF (6 cm^3) was refluxed with samarium diiodide in THF (0.1 mol dm^{-3}; 4.0 mol equiv.) for 70 h, when GLC analysis (Carbowax 20M) showed that all the pyran had reacted. The GLC yield after work-up was 96% (internal standard heptan-1-ol). The product was chromatographed over silica gel, and eluted with hexane–diethyl ether to give the title alcohol as a 53% (*E*)-**44**/47% (*Z*)-**45** mixture by ^{1}H NMR analysis; ν_{max}($CHCl_3$)/cm^{-1} 3600, 3440br s (OH), 2930s, 2895s, 2250w (C–D), 1620, 1045br s (C–O), 985s [(*E*)-CH=CH]; δ_H(400 MHz; $CDCl_3$) 5.82 (1 H, m, 4-H), 5.03 [0.53 H, dt, *J* 17.1 and 1.5, 5-H(*E*)], 4.96 [0.47 H, d, *J* 10.3, 5-H(*Z*)], 3.65 (2 H, t, *J* 6.5, 1-H_2), 2.14 (3 H, br q, *J* 7.0, 3-H_2 and OH) and 1.67 (2 H, p, *J* 7.0, 2-H_2); δ_C(100 MHz; $CDCl_3$) 138.18 (CH, C-4), 114.63 (CH, C-5), 62.33 (CH_2, C-1), 31.78 (CH_2, C-2) and 30.04 (CH_2, C-3). The isomer composition was determined by expansion and integration of the ^{1}H (*E*)-signal (δ 5.03, $J_{4,5}$ 17.1) and the (*Z*)-signal (δ 4.96, $J_{4,5}$ 10.3).

(Z)-*Dodec*-4-*en*-6-*yn*-1-*ol* **52**.—A solution of 3-chloro-2-(hept-1′-ynyl)tetrahydropyran as a *cis*/*trans* mixture **49** (80% *trans*/20% *cis*) (131 mg, 0.61 mmol) in THF (5 cm^3) was refluxed with samarium diiodide in THF (0.1 mol dm^{-3}; 5.6 mol equiv.) for 94 h and worked up. The GLC yield (Apiezon L, hexadecane standard) was 93% and the product was purified by bulb-to-bulb distillation at 70 °C (oven)/0.1 mmHg to give (Z)-*dodec*-4-*en*-6-*yn*-1-*ol* **52** (Found: M^+, 180.154. $C_{12}H_{20}O$ requires M, 180.151); λ_{max}(EtOH)/nm 218infl (ε 6900), 227 (10 400) and 234infl (8400); ν_{max}(film)/cm^{-1} 3340br s (OH), 3030, 2940s, 2870s, 2220w (C≡C), 1470, 1065br s (C–O) and 740; δ_H(400 MHz; $CDCl_3$, aided by COSY) 5.83 (1 H, dt, *J* 10.6 and 7.6, 4-H), 5.50 (1 H, dd, *J* 10.6 and 1.2, 5-H), 3.66 (2 H, t, *J* 6.4, 1-H_2), 2.40 (2 H, q, *J* 7.2, 3-H_2), 2.33 (2 H, td, *J* 7.1 and 2.1, 8-H_2), 1.74 (1 H, br s, OH), 1.68 (2 H, m, *J* 6.8, 2-H_2), 1.55 (2 H, m, *J* 7.2, 9-H_2), 1.36 (4 H, m, 10- and 11-H_2) and 0.91 (3 H, t, *J* 7.1,

12-H_3); δ_C(100 MHz; $CDCl_3$) 141.25 (CH, C-4), 110.40 (CH, C-5), 95.19 (C, C-6), 77.16 (C, C-7), 62.08 (CH_2, C-1), 31.53 (CH_2, C-3), 31.12 (CH_2, C-10), 28.59 (CH_2, C-9), 26.16 (CH_2, C-2), 22.21 (CH_2, C-11), 19.49 (CH_2, C-8) and 14.00 (CH_3, C-12).

(Z)-*Dec*-4-*en*-6-*yn*-1-*ol* **53**.—A solution of 3-chloro-2-(pent-1′-ynyl)tetrahydropyran **50** as a *cis*/*trans* mixture (70% *trans*/30% *cis*) (187 mg, 1 mmol) in THF (7 cm^3) was refluxed with samarium diiodide in THF (0.1 mol dm^{-3}; 4.0 mol equiv.) for 93 h, with monitoring by GLC (Apiezon L). On work-up the yield was 79% by GLC (internal standard hexadecane). The product was chromatographed on silica gel and eluted with hexane–diethyl ether (60:40) to give (Z)-*dec*-4-*en*-6-*yn*-1-*ol* **53** (70% isolated yield) (Found: M^+, 152.119. $C_{10}H_{16}O$ requires M, 152.120); λ_{max}(EtOH)/nm 219infl (ε 10 900), 227 (14 400) and 234infl (11 800); ν_{max}(film)/cm^{-1} 3360br s(OH), 3040, 2980s, 2955s, 2895s, 2230w (C≡C), 1450, 1065br s (C–O) and 755; δ_H(400 MHz; $CDCl_3$) 5.83 (1 H, dt, *J* 10.7 and 7.6, 4-H), 5.50 (1 H, d, *J* 10.6, 5-H), 3.65 (2 H, t, *J* 6.4, 1-H_2), 2.39 (2 H, q, *J* 7.3, 3-H_2), 2.32 (2 H, td, *J* 7.0 and 2.2, 8-H_2), 1.68 (2 H, m, *J* 6.8, 2-H_2), 1.57 (2 H, m, *J* 7.2, 9-H_2) and 1.01 (3 H, t, *J* 7.4, 10-H_3); δ_C(100 MHz; $CDCl_3$) 141.32 (CH, C-4), 110.34 (CH, C-5), 94.97 (C, C-6), 77.32 (C, C-7), 62.04 (CH_2, C-1), 31.52 (CH_2, C-3), 26.17 (CH_2, C-2), 22.32 (CH_2, C-9), 21.52 (CH_2, C-8) and 13.55 (CH_3, C-10).

(Z)-*Hept*-4-*en*-5-*yn*-1-*ol* **54**.—A solution of *trans*-3-chloro-2-ethynyltetrahydropyran **51** (200 mg, 1.38 mmol) in THF (5 cm^3) was refluxed for 91 h (N_2) with samarium diiodide in THF (0.1 mol dm^{-3}, 4.1 mol equiv.) for 91 h, after which time GLC (Carbowax 20M) showed that reaction was essentially complete. After work-up the GLC yield (geraniol internal standard) was 72% and the product was chromatographed on silica gel, and eluted with hexane–diethyl ether (70:30) to give (Z)-*hept*-4-*en*-6-*yn*-1-*ol* **54** (Found: M^+, 110.075. $C_7H_{10}O$ requires M, 110.073); λ_{max}(EtOH)/nm 216infl (ε 9800), 223 (11 300) and 229infl (9000); ν_{max}(film)/cm^{-1} 3340br s (OH), 3300s (≡CH), 3040, 2955s, 2890s, 2110w (C≡C), 1445, 1060br s (C–O) and 745; δ_H(400 MHz; $CDCl_3$) 6.03 (1 H, dt, *J* 10.8 and 7.6, 4-H), 5.49 (1 H, dd, *J* 10.9 and 1.5, 5-H), 3.65 (2 H, t, *J* 6.5, 1-H_2), 3.13 (1 H, s, 7-H), 2.42 (3 H, br q, *J* 7.4, 3-H_2 and OH) and 1.69 (2 H, m, *J* 6.9, 2-H_2); δ_C(100 MHz; $CDCl_3$) 145.12 (CH, C-4), 108.79 (CH, C-5), 81.77 (CH, C-7), 80.36 (C, C-6), 61.94 (CH_2, C-1), 31.42 (CH_2, C-3) and 26.54 (CH_2, C-2).

Samarium Diiodide in THF–HMPA.—A solution of samarium diiodide in THF (0.1 mol dm^{-3}; 2.5 mol equiv. for 1 mol equiv. of pyran or furan) was prepared as described above. Dry HMPA (~5 mol equiv. per 1 mol equiv. of pyran or furan) was added with vigorous stirring of the mixture to afford a deep purple solution. The reagent was prepared just prior to use.

Samarium Diiodide in THF–DMPU.—A solution of samarium diiodide in THF (0.1 mol dm^{-3}; 2.5 mol equiv. to 1 mol equiv. of pyran or furan) was prepared. Dry DMPU (~10 mol equiv. per 1 mol equiv. of pyran or furan) was added to afford a deep purple solution: it was used immediately.

(E)-*Hex*-3-*en*-1-*ol* **6** *by using the THF–HMPA Reagent*.—A solution of *cis*- and *trans*-3-chloro-2-ethyltetrahydrofuran **5** (162 mg, 1.2 mmol) in THF (5 cm^3) was refluxed with samarium diiodide in THF (0.1 mol dm^{-3}; 2.7 mol equiv.) and HMPA (1 cm^3, 5.3 mol equiv.) for 9 h, when GLC (PEGA) showed that almost all of the furan had reacted. The GLC yield (hexadecane as internal standard) of (E)-hex-3-en-1-ol **6** was 95%. Spectral data were as reported above.

(E)-*Hex*-3-*en*-1-*ol* **6** *by using the THF–DMPU Reagent*.—Replacing the HMPA in the above experiment by DMPU (1.5 cm^3, 10.3 mol equiv.) gave complete reaction in 5 h, with a GLC yield of the (*E*)-alcohol **6** of 96%, and with ^1H and ^{13}C NMR spectral data as reported above.

(E)-*Undec*-3-*en*-5-*yn*-1-*ol* **18** *by using the THF–DMPU Reagent*.—A solution of *cis*-3-chloro-2-(hept-1′-ynyl)tetrahydrofuran **15** (200 mg, 1 mmol) in THF (5 cm^3) was added to a mixture of samarium diiodide in THF (0.1 mol dm^{-3}; 2.6 mol equiv.) and DMPU (1.2 cm^3, 9.9 mol equiv.) and refluxed for 3 h, by which time all the furan had reacted. The GLC yield was 83% (Apiezon L, hexadecane standard) and isolation and distillation gave the (*E*)-enynol **18** (118 mg, 71%) with ^1H and ^{13}C NMR data as reported above.

(E)- *and* (Z)-*Hept*-4-*en*-1-*ol* **27**/**28** *by using the THF–DMPU Reagent*.—A solution of *trans*-3-chloro-2-ethyltetrahydropyran **33** (300 mg, 2.02 mmol) in THF (5 cm^3) was refluxed with samarium diiodide in THF (0.1 mol dm^{-3}; 2.5 mol equiv.) and DMPU (2.4 cm^3, 9.8 mol equiv.). GLC analysis (PEGA) showed that, after 43 h, virtually all starting material had been used and the reaction mixture was worked up. The GLC yield (hexadecane standard) was 73%. Isolation of the hept-4-en-1-ol and analysis of the stereochemical composition by ^1H NMR spectroscopy showed 87% (*E*)-**27**/13% (*Z*)-**28**; δ_H(400 MHz; $CDCl_3$) 5.50 [0.87 H, dt, *J* 15.3 and 6.0, 4-H(*E*)] and 5.44–5.30 [1.13 H, m, 3-H(*E*), 3-H(*Z*) and 4-H(2)]. The ^{13}C NMR spectrum showed the resonances for both the (*E*)- and (*Z*)-form (as listed above).

(E)- **58** *and* (Z)- **52** -*Dodec*-4-*en*-6-*yn*-1-*ol by using the THF–DMPU Reagent*.—A solution of *cis*- (20%)/*trans*- (80%) -3-chloro-2-(hept-1′-ynyl)tetrahydropyran **49** (300 mg, 1.4 mmol) in THF (5 cm^3) was refluxed with samarium diiodide in THF (0.1 mol dm^{-3}; 3.6 mol equiv.) and DMPU (1.8 cm^3, 10.6 mol equiv.) for 25 h, when GLC monitoring (Apiezon L) showed that all the starting chloride had reacted. On work-up three products were observed by GLC (standard hexadecane): (*Z*)-dodec-4-en-6-yn-1-ol **52** (57%), (*E*)-dodec-4-en-6-yn-1-ol **58** (33%) and 2-(hept-1′-ynyl)tetrahydropyran **59** (8%). Retention times were in the order: (*E*) > (*Z*) > the dechlorinated pyran. The three products were isolated by chromatography on silica gel, and elution with hexane–diethyl ether. Spectral data for the (*Z*)-isomer were identical with those given above, and data for the (*E*)-isomer follow: ν_{max}(film)/cm^{-1} 3345br s (OH), 2940s, 2875s, 2230w (C≡C), 1465, 1455, 1430, 1375, 1330, 1055br s (C–O) and 960 [(*E*)-CH=CH]; δ_H(400 MHz; $CDCl_3$) 6.05 (1 H, dt, *J* 15.8 and 7.5, 4-H), 5.50 (1 H, d, *J* 15.8, 5-H), 3.65 (2 H, t, *J* 6.4, 1-H_2), 2.28 (2 H, t, *J* 6.8, 8-H_2), 2.18 (2 H, q, *J* 7.2, 3-H_2), 1.66 (3 H, br p, *J* 7.0, 2-H_2 and OH), 1.52 (2 H, p, *J* 7.2, 9-H_2), 1.34 (4 H, m, 10- and 11-H_2) and 0.90 (3 H, t, *J* 6.9, 12-H_3); δ_C(100 MHz; $CDCl_3$) 142.15 (CH, C-4), 110.60 (CH, C-5), 89.21 (C, C-6), 78.95 (C, C-7), 62.20 (CH_2, C-1), 31.76 (CH_2, C-3), 31.12 (CH_2, C-10), 29.24 (CH_2, C-2), 28.54 (CH_2, C-9), 22.24 (CH_2, C-11), 19.33 (CH_2, C-8) and 13.99 (CH_3, C-12).

Spectral data for 2-(hept-1′-ynyl)tetrahydropyran **59** were as follows: ν_{max}(film)/cm^{-1} 2935s, 2860s, 2250w (C≡C), 1470, 1445, 1365, 1340, 1205, 1090s, 1045s (C–O) and 870; δ_H(80 MHz; $CDCl_3$) 4.30–3.35 (3 H, m, 2-H and 6-H_2), 2.17 (2 H, m, 5-H_2), 1.90–1.00 (12 H, m) and 0.90 (3 H, t, *J* 5.8, 7′-H_3).

Treatment of (Z)-*Hex*-3-*en*-1-*ol with Samarium Diiodide and DMPU*.—A solution of (*Z*)-Hex-3-en-1-ol (100 mg, 1 mmol) in THF (5 cm^3) was refluxed with samarium diiodide in THF (0.1 mol dm^{-3}; 2.6 mol equiv.) and DMPU (1.2 cm^3, 9.9 mol equiv.) for 52 h and worked up by chromatography on silica gel, and elution with hexane–diethyl ether (60:40). As judged by the

^1H and ^{13}C NMR spectra the (*Z*)-alcohol was completely unchanged, no trace of the (*E*)-isomer **6** being found. (*Z*)-Hex-4-en-1-ol behaved similarly.

Acknowledgements

One of us (L. J. R.) thanks the SERC for a postgraduate award.

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Paper 3/05983I
Received 6*th October* 1993
Accepted 4*th November* 1993