# Intramolecular Diels–Alder Reactions of Vinylfurans leading to Furanodecalins

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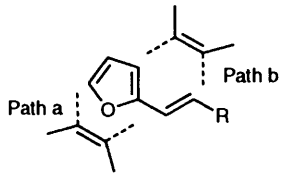
Thermolysis of the (2*E*,8*Z*)-9-(2-furyl)nonadienoate **25** at 290 °C leads to an essentially quantitative yield of a single furanodecalin **26**, whereas the corresponding (2*E*,8*E*)-isomer **34** undergoes a non-stereoselective cyclisation leading to the furanodecalins **26** and **35**. (*Z*)-Alkenoate functions undergo partial isomerisation prior to cyclisation and so lead to mixtures of isomers. Alkyl groups can be incorporated around the reaction sites, but this can result in overwhelming competition from side reactions. The corresponding 3-furyl analogues **56** and **59** display very similar reactivities.

In principle, a vinylfuran function **1** can act as a Diels–Alder diene in two ways, either by the addition of a dienophile across the furan nucleus (path a) or by reaction with the diene which includes the exocyclic alkene (path b). As one of the first Diels–Alder reactions to be recognised was between furan itself and maleic anhydride *via* path a,[1] it is perhaps not surprising that such transformations have been widely exploited in many elegant syntheses, especially those based upon intramolecular versions of such cycloadditions.[2–4] In contrast, cycloadditions *via* path b are much less common and, in general, have been restricted to simple models involving reactive dienophiles such as maleic anhydride and acetylenedicarboxylates. The intermolecular versions of such additions are often relatively inefficient and can give rise to products from both pathways; products from path a are favoured in some cases either when acetylenedicarboxylates are the dienophiles or the furan is highly substituted.[4,5] By contrast, other vinyl substituted heterocyclic dienes including vinylthiophenes,[6] vinylpyrroles,[7] vinylisoxazoles[8] and vinylpyrazoles[9] undergo cycloadditions to the diene function which includes the exocyclic alkene, presumably due to the reluctance of the central heteroaromatic ring to participate in Diels–Alder reactions in general. These reactions are sometimes complicated by a second addition of the dienophile to the initial Diels–Alder adducts *via* an ene reaction.

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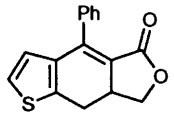


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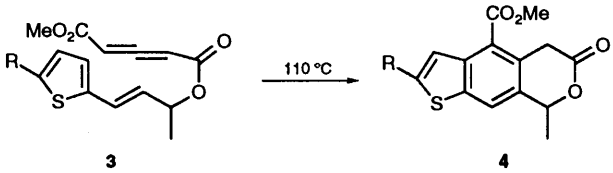
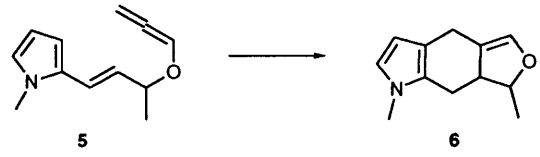
The idea that intramolecular Diels–Alder reactions of vinylheteroaromatics **1**, *via* path b, could provide useful entries into a variety of annulated heterocyclic systems was first realised nearly 30 years ago when the tricyclic lactones **2** were successfully prepared, albeit in poor yield, from the corresponding phenylalkynoates.[10] Related cyclisations of the allenyl carboxylates **3**




3 4

lead to the homologous benzothiophene lactones **4**, again in poor yields.[11] Much more efficient is a similar cyclisation of the allenyl ether **5** which leads to the annulated pyrrole **6** in 87% yield.[12] The corresponding prop-2-ynylic ether from which the allene **5** was derived underwent a similar cyclisation but much less efficiently. Examples of Diels–Alder reactions involving vinylindoles are much more numerous and an intramolecular version (the secodine route) has been suggested as a key step in pathways leading to various aspidosperma alkaloids such as those having the tabersonine skeleton.[13] A biomimetic synthesis based on this transformation has been reported in which the intermediate **7** cyclises at ambient temperature to the alkaloid vincadifformine **8**;[14] it is, however, questionable whether such cyclisations, which occur under unusually mild conditions, are true Diels–Alder reactions or rather sequential Michael additions initiated by the enamine function followed by an intramolecular Mannich-type ring closure.[15] More conventional Diels–Alder reactions of both 2- and 3-vinylindoles with typical examples of reactive dienophiles have been extensively studied mainly by Pindur and his colleagues;[16] this group have recently reported the first asymmetric examples of such reactions in which the source of chirality is an acrylamide derived from Oppolzer's sultam.[17] The excellent diastereoselectivities achieved in these reactions are somewhat compromised by the rather modest chemical yields. Intramolecular versions involving both 2-vinyl-[18] and 3-vinylindoles[19] have been reported, the latter method being a useful route to various annulated tetrahydrocarbazoles. Intramolecular Diels–Alder reactions have also been carried out using 5-vinylisoxazoles as the diene components; in these examples, trifluoroacetic acid was used as a catalyst.[20] The first examples of such reactions involving vinylfuran dienes were generally efficient preparations of the tricyclic lactones **9** by thermolysis of the corresponding fumaroyl esters.[21] In contrast, similar cyclisations of the furan analogues of the vinylthiopenes **3** led to very poor yields of the desired annulated products (**4**, O in place of S).[11] Prop-2-ynylic ethers [*e.g.* **10**] have also been used as dienophiles in combination with vinylfuran dienes, but much more efficient

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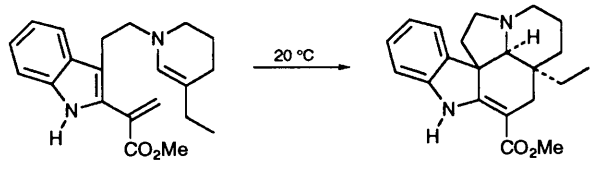


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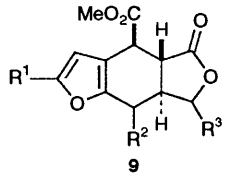

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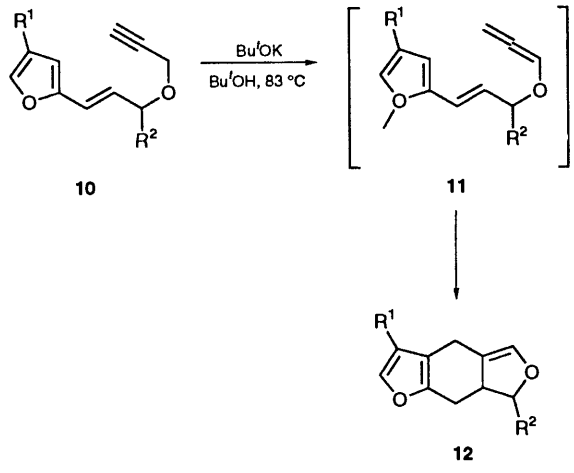
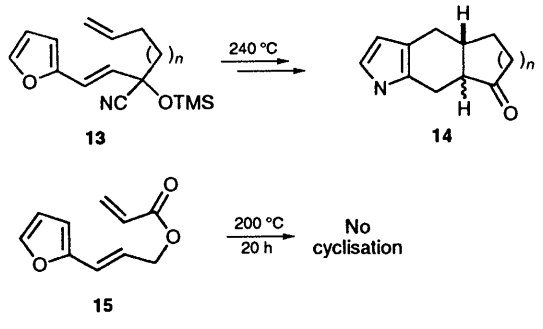
cyclisations have been developed by the Kanematsu group which involve the corresponding allenic ethers **11**, obtained by base-catalysed reorganisation of the initial acetylenes **10**, and



10 11 12

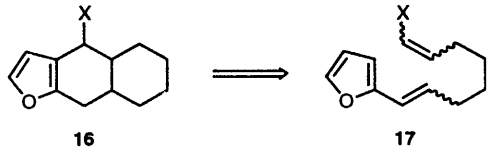
lead to nearly quantitative yields of the annulated furans **12**.[22] Finally, and while our own studies were in progress,[23] Fischer and Hunig reported the successful thermal cyclisation of the vinylfurans (**13**; $n$ = 1,2) at 240 °C in benzene to give, after deprotection, the tricyclic ketones **14** as stereochemical mix-



13 14 15

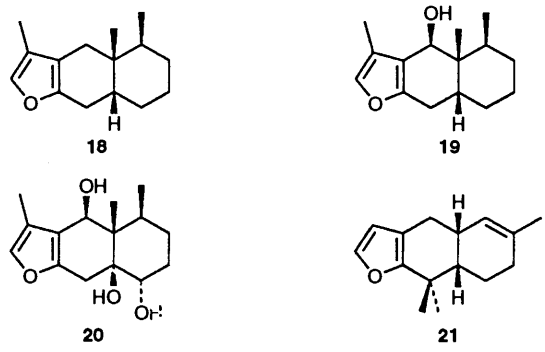
tures in which the *trans*-isomer predominated [*ca.* 70:30].[24] Remarkably, many of the foregoing cyclisations do not require activated (electron-deficient) dienophiles; this is in contrast with the reported failure of the activated substrate **15** to cyclise when heated to 200 °C.[21]

We were intrigued by the prospect of utilising such cyclisations to construct the furanodecalin ring system **16** from what



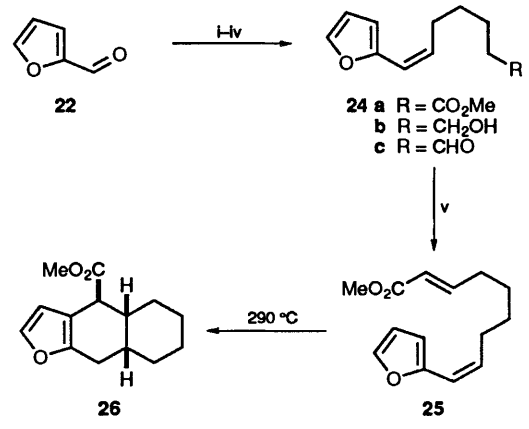
16 17

appeared to be readily obtainable acyclic precursors **17**; in addition, all possible geometric isomers should be available which would increase the versatility of the method, at least in stereochemical terms. The furanodecalin ring system **16** is the parent of naturally occurring sesquiterpenes of the furanoeremophilane group,[25] characterised by the presence of a *syn*-4a,5-dimethyl substitution pattern and *cis*-ring fusion, exemplified by furanoeremophilane itself **18**,[26] first isolated from coltsfoot *Petasites albus* and the more oxygenated metabolites petalsalbin **19**[26] from the same source and euryopsol **20** found in *Euryops floribundus*,[27] as well as various ketone derivatives.[28] Different substitution patterns are also common as is the presence of further unsaturation, features exemplified in furodysin **21**, a metabolite of a *Dysidea* coral species.[29]



18 19 20 21

We began our studies with one of the simplest examples, the (2*E*,8*Z*)-dienoate **25** (Scheme 1). This was prepared by an initial

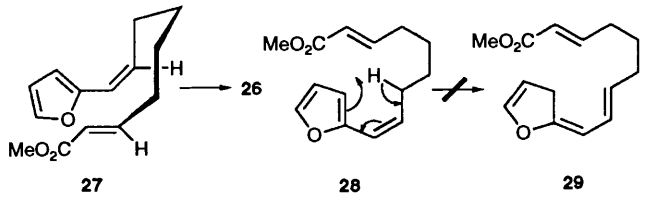


22 24 a R = $CO_2Me$ b R = $CH_2OH$ c R = CHO 26 25

**Scheme 1** *Reagents:* i, $Ph_3P^+CH^-(CH_2)_4CO_2Na$ **23**, DMSO; ii, $CH_2N_2$; iii, $LiAlH_4$, $Et_2O$; iv, PCC, $CH_2Cl_2$; v, $Ph_3PCHCO_2Me$, $CH_2Cl_2$

Wittig condensation between furan-2-carbaldehyde **22** and the phosphorylide **23** derived from 6-bromohexanoic acid;[30] subsequent esterification followed by careful chromatography separated the (*Z*)-alkenoate **24a**, which was subsequently converted into the corresponding aldehyde **24c** by way of the alcohol **24b**. A second Wittig condensation then secured the desired Diels–Alder precursor **25**. We were somewhat surprised to find that thermolysis of this compound in dry, degassed toluene in a sealed tube at temperatures of up to 220 °C resulted in neither cycloaddition nor any significant decomposition of the sensitive vinylfuran. Remarkably, however, thermolysis at 290 °C for 16 h led to an essentially quantitative conversion into the *cis*-furanodecalin **26**. The only detectable impurity was a trace (*ca.* 5%) of the corresponding *trans*-fused isomer **35** which may well have arisen by some isomerisation of the (8*Z*)-alkene function in dienoate **25** to give the (2*E*,8*E*)-isomer **34**, prior to cyclisation (*vide infra*). The expected *cis* disposition of the ester and the adjacent 4a-ring junction proton was evident from the appearance of a resonance at $\delta_H$ 3.41 (br d, $J$ ~ 3.8 Hz) due to the 4-proton, α-to the ester group. The *cis*-ring fusion in the furanodecalin **26** was indicated by the relative narrowness of the methylene envelope, especially when compared with the corresponding *trans*-isomer **35**.[31] Further definitive information could not be elicited from the $^1H$ NMR data owing to

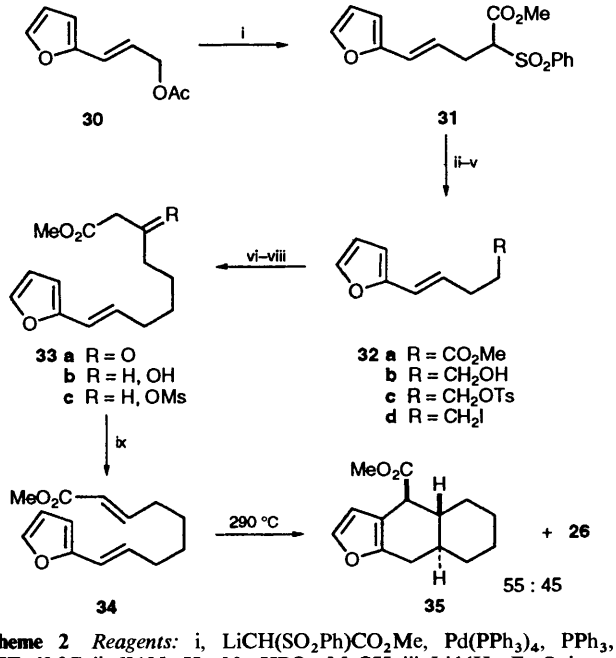
resonance coincidence but, fortunately, the $^{13}C$ NMR data provided confirmatory evidence. It has been established that *trans*-fused decalins exhibit consistently higher chemical shifts relative to the corresponding *cis*-isomers,[32] especially in the cases of the ring junction carbons.[33] In the present examples, the *cis*-furanodecalin showed $\delta_C$ 37.63 (C-4a) and 32.75 (C-8a) as compared to $\delta_C$ 41.55 (C-4a) and 38.20 (C-8a) in the *trans*-isomer **35**; a similar pattern was observed when a comparison was made of the remaining, similarly positioned ring carbons in these two isomers (see Experimental section). Similar reasoning has been employed by others to evaluate structural assignments in this area.[21,24] The probably stereospecific cyclisation of the (*Z*)-dienoate **25** is consistent with other examples involving this diene geometry which all give rise to *cis*-fused products.[3] This is because the geometry of a (*Z*)-diene strongly favours cyclisation *via* the *anti* (*endo*) transition state **27**.[3] This has been observed in




**27** **28** **29**

all reported examples of cyclisations of dienes with this geometry which are, however, rather rare[2,3,15] owing to competition from [1.5]-hydride shifts.[34] Such a process, **28**, presumably does not interfere in the case of the dienoate **25** as this would involve an additional energy cost in disruption of the furan ring aromaticity. The essentially quantitative yield of the decalin **26** which was obtained indicates that the potentially unstable alternative product **29** is not formed to any appreciable extent.

The corresponding (2*E*,8*E*)-dienoate **34** was prepared (Scheme 2) starting from the readily available (*E*)-allylic acetate **30**.[35] Palladium-catalysed alkylation[36] of the sodium salt of methyl phenylsulphonylacetate by this electrophile led smoothly to the sulphonyl ester **31** which was desulphurised using 6% sodium amalgam[37] to give the ester **32a**. Subsequent reduction to the corresponding alcohol **32b**, conversion into the

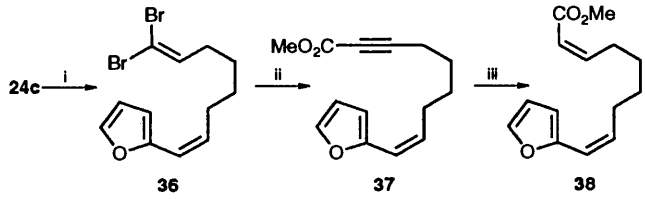



**30** **31** **33** a R = O, b R = H, OH, c R = H, OMs **32** a R = $CO_2Me$, b R = $CH_2OH$, c R = $CH_2OTs$, d R = $CH_2I$ **34** **35**

**Scheme 2** *Reagents:* i, $LiCH(SO_2Ph)CO_2Me$, $Pd(PPh_3)_4$, $PPh_3$, THF, 60 °C; ii, 6% Na-Hg, $Na_2HPO_4$, MeOH; iii, $LiAlH_4$, $Et_2O$; iv, *p*-TsCl, pyridine; v, NaI, $Me_2CO$; vi, $LiCH_2C(O)CH(Li)CO_2Me$, THF; vii, $NaBH_4$, MeOH; viii, MsCl, pyridine; ix, DBU, $C_6H_6$

tosylate **32c** and finally an exchange reaction then led to the iodide **32d**. This was then used to alkylate the dianion of methyl acetoacetate[38] leading to the keto ester **33a** and thence to the required (*E*,*E*)-dienoate **34**, following borohydride reduction to the corresponding hydroxy ester **33b**, conversion into the mesylate **33c** and finally base-catalysed elimination. Thermolysis of the (2*E*,8*E*)-dienoate **34** under the same conditions used for the corresponding (2*E*,8*Z*)-isomer **25** afforded an excellent 90% isolated yield of the cyclised products **26** and the *trans*-fused isomer **35** as an inseparable mixture in a ratio of 45:55. The latter *trans*-isomer **35** was distinguishable from the *cis*-isomer **26** by a relatively broad methylene envelope[31] and a resonance at $\delta_H$ 3.22 (1 H, ddd, *J* 9.9, 3.0 and 1.6) due to the 4-H adjacent to the ester function. This latter feature, amongst others, closely resembles those reported for the related *trans*-fused lactone **9**.[21] In addition, the relatively higher chemical shifts observed in the $^{13}C$ NMR spectrum, especially for the ring junction and adjacent carbons,[21,24] were also consistent with this assignment (*vida supra*).[32,33] It is most likely[3] that these two isomers arise by the intermediacy of the *syn* (*exo*) and *anti* (*endo*) transition states leading to the *cis*- and *trans*-fused products **26** and **35**, respectively. A similar pattern of stereoselectivity has been found in intramolecular Diels–Alder cyclisations of various trienoate systems which usually result in a slight preference for the *trans*-fused isomers.[39] Milder reaction conditions usually favour the product(s) formed by way of *endo* transition states in this type of cyclisation. Therefore, in an effort to increase the proportion of the *trans*-isomer **35** which was formed, we examined the thermal behaviour of the dienoate **34** in the presence of various Lewis acids; these were uniformly unsuccessful, possibly due to competing complexation with the furan oxygen. As an alternative, the dienoates **25** and **34**, the corresponding carboxylic acids and their sodium salts were all heated in water or water–methanol mixtures at temperatures up to 80 °C in order to try and take advantage of the enormous rate acceleration which these conditions can impart upon such cyclisations.[40] In no case was the formation of any cyclised product observed.

This sequence was completed by the preparation (Scheme 3) of the (2*Z*,8*Z*)-dienoate **38**, starting from the previously obtained (*Z*)-aldehyde **24c**. Homologation using the Corey–Fuchs procedure[41] led, *via* the dibromoalkene **36**, to the alkynoate **37** and thence to the target compound **38** following

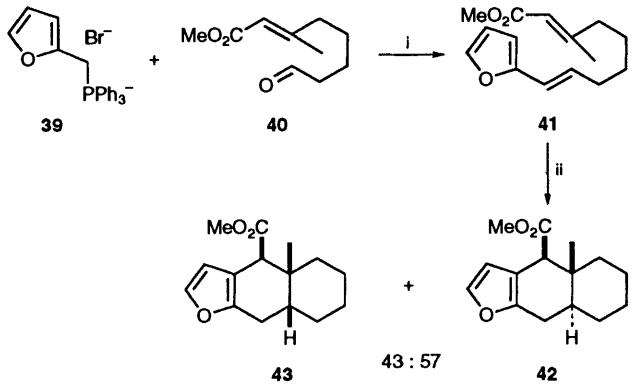



**36** **37** **38**

**Scheme 3** *Reagents:* i, Zn, $PPh_3$, $CBr_4$, $CH_2Cl_2$; ii, 2 BuLi, LiBr, $ClCO_2Me$; iii, $H_2$, 5% $Pd\text{-}BaSO_4$, quinoline, MeOH

Lindlar partial hydrogenation. Unfortunately, thermolysis of this substrate at 290 °C led to an excellent yield of furanodecalins but as a gross stereochemical mixture. Examination of a sample of the thermolysate partway through the reaction by $^1H$ NMR spectroscopy and using the data from the dienoate **25** for comparison, clearly showed that this was due to extensive isomerisation of the (2*Z*)-alkene function to the corresponding (2*E*)-isomer prior to cyclisation. Further examples of (*Z*)-alkenoates as dienophiles were therefore not investigated.

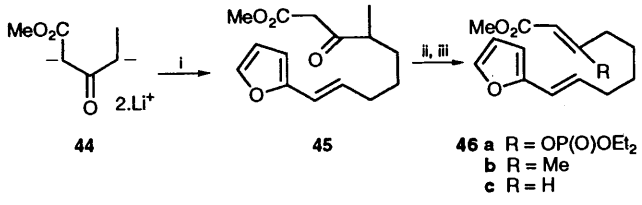
Similar cyclisations of some more highly substituted dienoates were also examined. Thus, a Wittig condensation between the furylmethylphosphonium salt **39**[42] and the aldehydo ester **40**, obtained from the corresponding hydroxy ester[43] by PCC




**Scheme 4** *Reagents:* i, BuLi, THF; ii, 280 °C, toluene

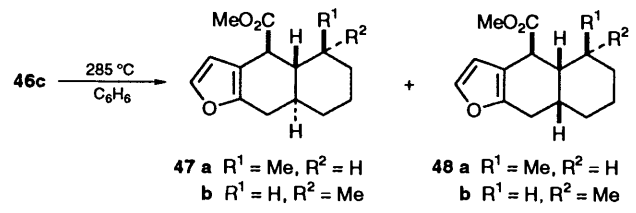
oxidation, followed by careful chromatography separated the (2*E*,8*E*)-dienoate **41** in good yield (Scheme 4). Thermolysis led to a lower 63% isolated yield, relative to the foregoing examples, of the cyclised products **42** and **43**. In other respects, the outcome was essentially the same as the cyclisation of the demethyl analogue **34**. The two products were identified on exactly the same basis as above and were formed in a very similar ratio of 57:43, in favour of the *trans*-fused isomer **42**. It would, therefore, seem reasonable to assume that the transition states involved were also the same.

A more highly substituted example did not behave so well (Scheme 5). Thus alkylation of the dianion derived from methyl 3-oxopentanoate **44**,[38] with the (*E*)-iodide **32d** led to the keto ester **45**. This was then converted into the enol phosphate **46a**

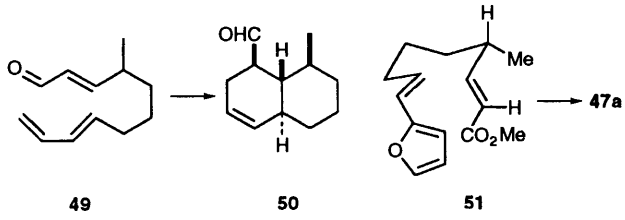



**Scheme 5** *Reagents:* i, **32d**, THF; ii, NaH, $(EtO)_2P(O)Cl$, $Et_2O$; iii, $Me_2CuLi$, $Et_2O$

followed by displacement of the latter leaving group by a tandem Michael addition–elimination reaction using lithium dimethylcuprate.[43] The expected product **46b** was accompanied by a substantial amount of the demethyl compound **46c**, which fortunately could be separated using HPLC. The origin of this latter, unexpected product was not further investigated; a possible mechanism for its formation could be by a single-electron transfer from the cuprate reagent followed by β-elimination of phosphate from the resulting radical anion and finally protonation. Unfortunately, thermolysis of the 3,4-dimethylnonadienoate **46b** in toluene at 290 °C resulted in decomposition. At the lower temperature of 260 °C (heptane, 16 h), partial conversion (*ca.* 35%) to what appeared to be a single furanodecalin was observed; this proved difficult to separate from the remaining starting material and, as prolonged heating led to further decomposition, cyclisations of this substrate were not further investigated. The 4-methyl analogue **46c** did, however, undergo cyclisation in benzene at 285 °C and gave, in 68% combined isolated yield, a mixture of four furanodecalins in a ratio of 20:14:4:3. The major component was separated using HPLC and was found to be the *trans*-isomer **47a** by comparisons between its NMR spectral data and those displayed by the related furanodecalins **26** and **35**. Similarly, the second major product, which was not separated from the two minor products, was clearly the *cis*-isomer **48a** using the same arguments. The slight preponderance of the *trans*-isomer **47a** is

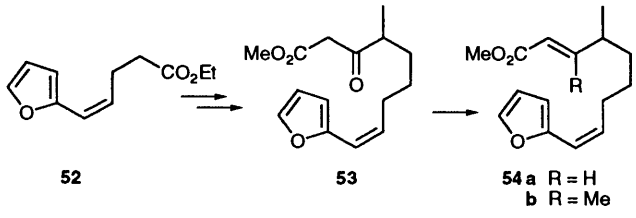



as expected from the foregoing observations, especially as cyclisation of the dienoate **34** gave a 45:55 mixture of the decalins **26** and **35**. The stereochemistry of the 5-methyl group was derived both from literature precedent together with a consideration of the likely transition state involved. For example, the trienal **49** undergoes smooth cyclisation in the presence of a Lewis acid to give only the decalin **50**;[44] presumably, a related *anti* (*endo*) transition state **51**, in which



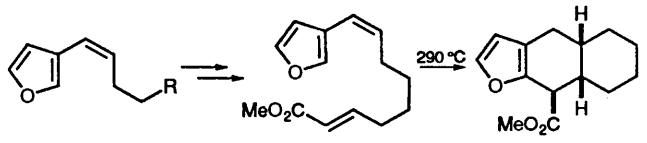

the methyl group occupies a pseudo-equatorial position is also involved in the present example.[3] For the same reasons, we have assigned structure **48a** to the major *cis*-isomer. It follows that the two minor isomers (**47b** and **48b**) are those in which the 5-methyl groups are positioned α and which arise *via* transition states in which this group occupies a pseudoaxial orientation.

Our final substrates in the 2-vinylfuran series were the 4-methyl and 3,4-dimethylnonadienoates **54a** and **54b**, respectively. These were prepared starting with a Wittig reaction between furan-2-carbaldehyde and (3-ethoxycarbonylpropyl)-triphenylphosphonium bromide using KHMDS as base in THF at −78 °C. The resulting (*Z*)-enoate **52** was converted into the




corresponding iodide, as described above for the preparation of the isomeric (*E*)-iodide **32d**. Subsequent coupling with dianion **44** led to the keto ester **53** and thence to the two unsaturated esters **54a** and **54b** exactly as described in the preparation of the corresponding (*E*)-isomers **46a** and **46b**. Attempts to effect cyclisation of these over a range of temperatures between 260 and 295 °C in toluene uniformly met with failure as the substrates underwent partial or total decomposition. In view of the foregoing results, this was something of a surprise. Perhaps the additional methyl substituents add significantly to the energy required to attain the *anti* (*endo*) transition state (*cf.* **27**) and allow ene reactions and/or [1.5]-hydride shifts to compete successfully with the desired Diels–Alder process.

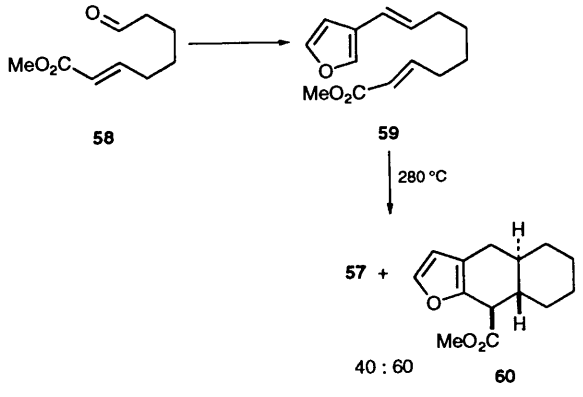
We have also examined the possibilities of extending this type of Diels–Alder cyclisation to 3-vinylfurans. The (2*E*,8*Z*)-dienoate **56** was prepared in a fashion identical with that outlined in Scheme 1 for the synthesis of the corresponding 2-furyl isomer **25**. Thus, a Wittig condensation between furan-3-carbaldehyde and the phosphorane **23** followed by esterification led to the ester **55a** which was converted into the aldehyde **55c** *via* the




**55a** R = $CO_2Me$
**b** R = $CH_2OH$
**c** R = CHO

**56** **57**

corresponding alcohol **55b**; a second Wittig reaction then secured the required precursor **56**. We found that cyclisation of this material proceeded in a fashion very similar to that of the 2-furyl isomer **25** and gave an essentially quantitative yield of the *cis*-furanodecalin **57**, the structure of which was proven as outlined above in the case of the 2-furan isomer **26**. Finally, the corresponding (2*E*,8*E*)-dienoate **59**, obtained in moderate yield by a Wittig condensation between 3-furyl(triphenyl)phosphonium bromide[45] and the aldehydo ester **58**,[46] also followed the pattern of the related 2-furyl analogue **34** in that cyclisation was also very efficient but resulted in the formation of the two possible isomers **57** and **60**, with a slight preference for the




*trans*-isomer. It seems highly likely that the features controlling these cyclisations are much the same as in the 2-furyl series.

In summary, we have shown that intramolecular Diels–Alder reactions can be used to prepare furanodecalins from both 2- and 3-furylnonadienoates in often excellent yields. However, the high temperatures required will undoubtedly be a limiting factor with respect to a variety of additional substituents and functional groups which would not tolerate such conditions. The incorporation of alkyl groups around the reaction centres can also result in poor yields probably due to the intervention of ene and related processes.

## Experimental

$^1H$ NMR spectra were recorded using a Perkin-Elmer R32 instrument unless otherwise stated. Other spectra were determined using a Bruker WP 80 SY (80 MHz), WM 250 (250 MHz) or an AM 400 (400 MHz) instrument. The last two instruments were used to measure $^{13}C$ NMR spectra at 62.8 and 100 MHz respectively. All reactions were carried out under dry nitrogen. Ether refers to diethyl ether and light petroleum refers to the fraction with b. p. 40–60 °C. All organic solutions from work-up procedures were dried using anhydrous magnesium sulphate.

*Methyl* (6Z)-7-(2-*Furyl*)*hept*-6-*enoate* **24a**.—Dry dimethyl sulphoxide (DMSO) (160 ml) was added to sodium hydride (60% suspension in oil; 3.50 g, 87.4 mmol) and the resulting suspension stirred under nitrogen at 70–75 °C for 2 h. The resulting solution was cooled to ambient temperature and treated dropwise during 5 min with a solution of 5-carboxypentyl(triphenyl)phosphonium bromide (20.0 g, 44 mmol)[30] in DMSO (60 $cm^3$). The resulting crimson solution of the ylide **23** was cooled until the solvent began to crystallise (~ 5–10 °C) and stirred at this temperature for 0.5 h; it was then treated dropwise with freshly distilled furan-2-carbaldehyde **22** (3.52 $cm^3$, 44 mmol). The cooling bath was removed and the mixture stirred overnight before being poured into water (500 $cm^3$) containing potassium hydroxide (0.5 g). The aqueous mixture was washed with ether (4 × 200 $cm^3$), acidified to pH 3 using concentrated hydrochloric acid and extracted with chloroform (3 × 300 $cm^3$). The combined organic extracts were washed with brine (200 $cm^3$), dried and evaporated. The residue (~ 9 g) was stirred with ether (200 $cm^3$) and methanol (10 $cm^3$), while cooled in an ice bath, and treated with an ethereal solution of diazomethane (500 $cm^3$). The cooling bath was removed and stirring continued for 2 h. Excess of diazomethane was removed in a stream of nitrogen and the resulting solution washed with water (300 $cm^3$) and brine (250 $cm^3$) and then dried and evaporated. The residual brown oil was separated by column chromatography over alumina (Woelm grade III) eluted with 30% ether in light petroleum to give the *ester* **24a** (4.6 g, 49%) as a colourless oil, $\nu_{max}/cm^{-1}$ 1738; $\delta_H$ 7.43 (1 H, m, furan 5-H), 6.45 (1 H, dd, *J* 3.0 and 2.0, furan 4-H), 6.35–6.14 (2 H, m, furan 3-H and 7-H), 5.57 (1 H, dt, *J* 12.0 and 6.8, 6-H), 3.80 (3 H, OMe), 2.66–2.07 (4 H, m, 2- and 5-$CH_2$) and 1.91–1.31 (4 H, m, 3- and 4-$CH_2$); *m/z* 208 ($M^+$, 53%), 177 (24), 176 (32), 148 (11), 134 (18), 133 (11), 121 (19), 120 (30), 107 (100), 94 (57), 91 (20), 81 (39), 79 (31) and 77 (26) (Found: $M^+$, 208.1090. $C_{12}H_{16}O_3$ requires *M*, 208.1099).

(6Z)-7-(2-*Furyl*)*hept*-6-*en*-1-*ol* **24b**.—Lithium aluminium hydride (0.55 g, 14.5 mmol) was added to a vigorously stirred solution of the ester **24a** (3.01 g, 14.5 mmol) in dry ether (100 $cm^3$) maintained at 0 °C. After 0.5 h, TLC showed completion of reaction; aqueous 0.5 mol $dm^{-3}$ sodium hydroxide (4 $cm^3$) was cautiously added followed by ether (50 $cm^3$). After being stirred for a further 10 min, the mixture was filtered and the solid residue washed with ether (50 $cm^3$). The combined filtrates were washed with brine (100 $cm^3$), dried, filtered through a pad of silica gel and evaporated to leave the *alcohol* **24a** (2.03 g, 78%) as a colourless oil, $R_f$ 0.15 ($CH_2Cl_2$); $\nu_{max}/cm^{-1}$ 3600–3100, 3030, 2940, 2870 and 1495; $\delta_H$ 7.35 (1 H, br, s, furan 5-H), 6.36 (1 H, dd, *J* 3.0 and 2.0, furan 4-H), 6.31–6.07 (2 H, m, furan 3-H and 7-H), 5.51 (1 H, dt, *J* 12.0 and 7.0, 6-H), 3.59 (2 H, t, *J ca.* 6, 1-$CH_2$), 2.62–2.30 (2 H, m, 5-$CH_2$) and 1.77–1.27 (6 H, m, 2-, 3- and 4-$CH_2$); *m/z* 180 ($M^+$, 50%), 120 (14), 113 (8), 108 (10), 107 (78), 95 (44), 94 (100), 91 (18), 82 (12), 81 (29), 79 (34), 77 (30) and 53 (8) (Found: $M^+$, 180.1151. $C_{11}H_{16}O_2$ requires *M*, 180.1150).

(6Z)-7-(2-*Furyl*)*hept*-6-*enal* **24c**.—A solution of the foregoing alcohol **24b** (1.82 g, 10.1 mmol) in dry dichloromethane (30 $cm^3$) was added dropwise to a vigorously stirred suspension of pyridinium chlorochromate (PCC; 4.77 g, 22.1 mmol) and 3 Å molecular sieves (12 g) in dry dichloromethane (20 $cm^3$) maintained at 0 °C.[47] The resulting mixture was stirred for 1.25 h and then diluted with ether (100 $cm^3$), stirred for an additional 10 min and filtered through a short column of silica gel. The column was washed with additional ether (100 $cm^3$) and the combined filtrates were evaporated to leave the *aldehyde* **24c** (1.10 g, 61%) as a mobile yellow oil, $\nu_{max}/cm^{-1}$ 2930, 2860 and 1725; $\delta_H$(80 MHz) 9.76 (1 H, br, s, CHO), 7.37 (1 H, br s, furan 5-H), 6.36 (1 H, dd, *J* 3 and 2, furan 4-H), 6.28–6.12 (2 H, m, furan 3-H and 7-H), 5.50 (1 H, dt, *J* 12 and 7, 6-H), 2.68–2.12 (4 H, m, 2- and 5-$CH_2$) and 1.93–1.33 (4 H, m, 3- and 4-$CH_2$); *m/z* 178 ($M^+$, 50%), 162 (6), 134 (5), 121 (8), 113 (6),

107 (100), 94 (75), 91 (14), 81 (23), 79 (31), 77 (32), 65 (8) and 53 (9) (Found: $M^+$, 178.0990. $C_{11}H_{14}O_2$ requires *M*, 178.0994).

*Methyl* (2E,8Z)-9-(2-*Furyl*)*nona*-2,8-*dienoate* **25**.—Methyl (triphenylphosphoranylidene)acetate (1.94 g, 5.79 mmol) was added to a stirred solution of the foregoing aldehyde **24c** (0.86 g, 4.83 mmol) in dry dichloromethane (100 $cm^3$) cooled to 0 °C. The resulting solution was stirred without cooling for 16 h and then evaporated. The residue was separated by column chromatography using silica gel (Woelm dry column) eluted with 25% ether–light petroleum to give the (2E,8Z)-*dienoate* **25** (0.86 g, 76%) as a colourless oil, $R_f$ 0.57; $\nu_{max}/cm^{-1}$ 3010, 2930, 2850, 1705 and 1655; $\delta_H$ 7.43 (1 H, d, *J* 1, furan 5-H), 7.03 (1 H, dt, *J* 16 and 7, 3-H), 6.38 (1 H, dd, *J* 3 and 2, furan 4-H), 6.30–6.15 (2 H, m, furan 3-H and 9-H), 5.87 (1 H, dt, *J* 16 and 1, 2-H), 5.55 (1 H, dt, *J* 12 and 7, 8-H), 3.75 (3 H, s, OMe), 2.38–2.05 (4 H, m, 4- and 7-$CH_2$) and 1.70–1.38 (4 H, m, 5- and 6-$CH_2$); *m/z* 234 ($M^+$, 16%), 175 (18), 138 (32), 113 (43), 107 (78), 97 (35), 94 (73), 81 (100), 79 (49) and 67 (54) (Found: C, 71.9; H, 7.9%; $M^+$, 234.1246. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.8%; *M*, 234.1256).

*Methyl* (4RS,4aRS,8aRS)-4,4a,5,6,7,8,8a,9-*Octahydronaphtho*[2,3-b]*furan*-4-*carboxylate* **26**.—A solution of the (2*E*,8*Z*)-dienoate **25** (0.50 g, 2.14 mmol) in dry toluene (40 $cm^3$) was degassed by passage of a stream of nitrogen for 0.75 h, and then sealed in a Carius tube; this was then heated at 290 °C for 16 h. After cooling, the contents and washings were evaporated and the residue chromatographed using silica gel eluted with 25% ether–light petroleum to give the cis-*furanodecalin* **26** (0.47 g, 94%) as a fragrant, colourless oil, $R_f$ 0.48; $\nu_{max}/cm^{-1}$ 2930, 2860, 1730 and 1510; $\delta_H$(400 MHz) 7.26 (1 H, dd, *J* 1.9 and 0.7, 2-H), 6.26 (1 H, d, *J* 1.9, 3-H), 3.70 (3 H, s, OMe), 3.41 (1 H, br d, *J* 3.8, 4-H), 2.62 (1 H, dd, *J* 16.6 and 6.4, 9-$H_{eq}$), 2.55 (1 H, dd, *J* 16.6 and 7.3, 9-$H_{ax}$), 2.35–2.25 (2 H, m, 4a- and 8a-H) and 1.72–1.40 (8 H, m, 5-, 6-, 7- and 8-$CH_2$); $\delta_C$(20.15 MHz) 174.54 (C=O), 150.48 (C-9a), 140.96 (C-2), 112.74 (C-3a), 110.38 (C-3), 51.65 (OMe), 43.40 (C-4), 37.63 (C-4a), 32.75 (C-8a), 29.54 (C-9) and 28.02, 25.88, 24.44 and 22.78 (all $CH_2$); *m/z* 234 ($M^+$, 26%), 176 (18), 175 (100), 95 (11), 74 (12) and 59 (15) (Found: C, 71.6; H, 7.7%; $M^+$, 234.1262).

The sample contained *ca.* 5% of the corresponding *trans* isomer **35**, by comparison with the data for this compound given below.

*Methyl* (4E)-5-(2-*Furyl*)*pent*-4-*enoate* **32a**.—A solution of methyl phenylsulphonylacetate (7.53 g, 35.2 mmol) in dry THF (5 $cm^3$) was added dropwise during 5 min to a stirred suspension of sodium hydride (60% suspension in oil; 1.41 g, 35.2 mmol) in dry THF (80 $cm^3$) and the mixture was stirred at ambient temperature. After the vigorous effervescence had subsided, triphenylphosphine (2.0 g, 7.63 mmol) and tetrakis-(triphenylphosphine)palladium(0) (0.10 g, 0.09 mmol) were added to the resulting clear solution.[36] (*E*)-2-(3-Acetoxyprop-1-enyl)furan **30**[35] (4.00 g, 23.5 mmol) was then added dropwise to the solution which developed a deep red colouration and which was then maintained at gentle reflux overnight. The cooled reaction mixture was diluted with ether (100 $cm^3$) and the resulting solution washed with water (2 × 100 $cm^3$) and brine (200 $cm^3$) and then dried and evaporated. The presence of the desired sulphonyl ester **31** in the resulting red oil (10.22 g) was shown by the $^1H$ NMR data: $\delta_H$ 8.06–7.50 (5 H, m, Ph), 7.35 (1 H, br s, furan 5-H), 6.38 (1 H, dd, *J* 3 and 2, furan 4-H), 6.33–6.28 (2 H, m, furan 3-H and 5-H), 5.95 (1 H, dt, *J* 15 and 7, 4-H), 4.10 (1 H, t, *J* 7, 2-H), 3.66 (3 H, s, OMe) and 3.08–2.80 (2 H, m, 3-$CH_2$).

6% Sodium amalgam (60 g) was added in four equal batches during 0.25 h to a stirred, ice-cooled mixture of the crude ester **31** (10.22 g), anhydrous disodium orthophosphate (20 g) and dry methanol (350 $cm^3$).[37] The resulting mixture was stirred for a further 1.25 h with continued cooling and then allowed to warm to ambient temperature without stirring. The upper methanolic layer of the resulting two-phase mixture was separated by decantation, evaporated to *ca.* half its original volume and then partitioned between ether (200 $cm^3$) and water (100 $cm^3$). Water (150 $cm^3$) was added to the lower semi-solid layer and the resulting aqueous suspension extracted with ether (2 × 100 $cm^3$). The combined ether solutions were washed with water (150 $cm^3$) and brine (150 $cm^3$), dried and evaporated to leave a red oil (~4 g). This was chromatographed using alumina (Merck 90, Grade III) eluted with 20% ethyl acetate–light petroleum to give the *methyl ester* **32a** (2.71 g, 62%) as a pale yellow oil, $R_f$ 0.78; $\nu_{max}/cm^{-1}$ 1735; $\delta_H$(250 MHz) 7.31 (1 H, br s, furan 5-H). 6.34 (1 H, dd, *J* 3.3 and 1.8, furan 4-H), 6.26 (1 H, dd, *J* 15.8 and 1.0, 5-H), 6.15–6.07 (2 H, m, furan 3-H and 4-H), 3.69 (3 H, s, OMe) and 2.52–2.44 (4 H, m, 2- and 3-$CH_2$); $\delta_C$(62.8 MHz) 173.04 (C=O), 152.72 (furan C-2), 141.50 (furan C-5), 127.30 (C-5), 119.61 (C-4), 111.07 (furan C-4), 106.63 (furan C-3), 51.40 (OMe) and 34.70 and 33.34 (both $CH_2$); *m/z* 180 ($M^+$, 62%), 120 (64), 107 (100), 91 (23), 77 (32) and 55 (9) (Found: $M^+$, 180.0775. $C_{10}H_{12}O_3$ requires *M*, 180.0786).

*Methyl* (8E)-9-(2-*Furyl*)-3-*oxonon*-8-*enoate* **33a**.—To a stirred solution of the foregoing ester **32a** (2.71 g, 15 mmol) in dry ether (40 $cm^3$) maintained at 0 °C was added lithium aluminium hydride (0.57 g). The mixture was stirred at ambient temperature overnight and then cautiously treated with 0.5 mol $dm^{-3}$ aqueous sodium hydroxide (2 $cm^3$). The resulting precipitate was filtered off and washed with ether (40 $cm^3$). The combined filtrates were dried and evaporated to leave (4*E*)-5-(2-furyl)pent-4-en-1-ol **32b** (2.31 g, 98%) as an oil; $\nu_{max}/cm^{-1}$ 3530; $\delta_H$ 7.32 (1 H, br s, furan 5-H), 6.34 (1 H, dd, *J* 3 and 2, furan 4-H), 6.28–6.12 (3 H, m, furan 3-H, 4- and 5-H), 3.63 (2 H, t, *J* 7, C$H_2$OH), 2.64 (1 H, br s, OH), 2.38–2.12 (2 H, m, 3-$CH_2$) and 1.84–1.71 (2 H, m, 2-$CH_2$).

The foregoing crude alcohol **32b** (1.52 g, 10 mmol) in dry, ice-cold pyridine (60 $cm^3$) was treated with toluene-*p*-sulphonyl chloride (2.10 g, 11 mmol) and the resulting solution kept at this temperature for 16 h and then poured into water (150 $cm^3$). The aqueous mixture was extracted with ether (3 × 100 $cm^3$) and the combined extracts were washed with saturated aqueous copper(II) sulphate (3 × 150 $cm^3$) and brine (100 $cm^3$), dried and evaporated to leave the tosylate **32c** (3.05 g, ~100%) as a yellow oil; $\delta_H$ 7.75 (2 H, d, *J* 8, 2 × ArCH), 7.37 (2 H, d, *J* 8, 2 × ArCH), 7.35 (1 H, br s, furan 5-H), 6.37 (1 H, dd, *J* 3.3 and 1.8, furan 4-H), 6.28–6.04 (3 H, m, furan 3-H, 4- and 5-H), 4.07 (2 H, t, *J* 7, $CH_2OTs$), 2.40 (3 H, s, ArMe), 2.32–2.08 (2 H, m, 3-$CH_2$) and 1.98–1.58 (2 H, m, 2-$CH_2$). The product was used directly without further purification.

The tosylate **32c** (3.05 g, 9.97 mmol) was dissolved in dry acetone (150 $cm^3$) and the resulting solution treated with sodium iodide (8.0 g, 53.3 mmol). The stirred mixture was heated at gentle reflux with protection from light for 2 h and then cooled and partitioned between ether (250 $cm^3$) and saturated aqueous sodium thiosulphate (250 $cm^3$). The separated ethereal layer was washed with brine (200 $cm^3$) and then dried and evaporated to leave an orange oil (2.46 g) which was purified by column chromatography using alumina (Woelm dry column) eluted with light petroleum to give the *iodide* **32d** (1.38 g, 53%) as a colourless, sensitive oil, $R_f$ 0.66; $\nu_{max}/cm^{-1}$ 3030, 2930, 2850 and 1490; $\delta_H$ 7.30 (1 H, d, *J* 1, furan 5-H), 6.34 (1 H, dd, *J* 3 and 2, furan 4-H), 6.25–6.07 (3 H, m, furan 3-H, 4- and 5-H), 3.20 (2 H, t, *J* 7, $CH_2I$), 2.42–2.18 (2 H, m, 3-$CH_2$) and 2.16–1.86 (2 H, m, 2-$CH_2$); *m/z* 262 ($M^+$, 93%), 162 (10), 151 (6), 107 (100), 91 (7), 81 (12), 77 (25) and 41 (6) (Found: $M^+$, 261.9849.

$C_9H_{11}IO$ requires $M$, 261.9855). The sample was used promptly in the following step.

Following the procedure of Huckin and Weiler,[38] the dilithium salt of methyl acetoacetate (1.13 $cm^3$, 10.5 mmol) was generated using 2.1 equiv. of LDA in THF (40 $cm^3$). The resulting solution, maintained at −2 °C, was treated dropwise with a solution of the foregoing iodide **32d** (1.30 g, 5 mmol) in THF (8 $cm^3$). The mixture was then warmed to ambient temperature during 0.25 g and poured into water (240 $cm^3$). The aqueous mixture was extracted with ether (2 × 120 $cm^3$) and the combined extracts were washed with water (150 $cm^3$) and brine (150 $cm^3$), dried and evaporated. Chromatography of the residue using silica gel (Merck 9385) eluted with 30% ether–light petroleum gave the recovered iodide **32d** (0.34 g, 26%) followed by the *keto ester* **33a** (0.59 g, 47%) as a pale yellow oil, $\nu_{max}/cm^{-1}$ 3010, 2940, 2860, 1744 and 1712; $\delta_H$ 7.33 (1 H, d, $J$ 1, furan 5-H), 6.35 (1 H, dd, $J$ 3 and 2, furan 4-H), 6.25–6.11 (3 H, m, furan 3-H, 8- and 9-H), 3.69 (3 H, s, OMe), 3.41 (2 H, m, 2-$CH_2$), 2.52 (2 H, t, $J$ 7, 4-$CH_2$), 2.30–2.05 (2 H, m, 7-$CH_2$) and 1.82–1.23 (4 H, m, 5- and 6-$CH_2$); $m/z$ 250 ($M^+$, 7%), 232 (68), 177 (14), 134 (40), 120 (24), 107 (100), 94 (51), 91 (20), 81 (42), 77 (32), 59 (13) and 55 (13) (Found: $M^+$, 250.1178. $C_{14}H_{18}O_4$ requires $M$, 250.1205).

*Methyl* (8E)-9-(2-*Furyl*)-3-*hydroxynon*-8-*enoate* **33b**.—To a well-stirred solution of the foregoing keto ester **33a** (0.55 g, 2.2 mmol) in methanol (25 $cm^3$) at ambient temperature was added sodium borohydride (0.084 g, 2.2 mmol). The resulting mixture was stirred for 0.25 h and then poured into water (50 $cm^3$) and extracted with ether (2 × 30 $cm^3$). The combined extracts were washed with brine (30 $cm^3$), dried and evaporated to leave the *hydroxy ester* **33b** (0.37 g, 68%) as a colourless oil which was pure ($^1H$ NMR and TLC analysis) and showed $R_f$ 0.16 (50% ether–light petroleum); $\nu_{max}/cm^{-1}$ 3500–3200, 2940, 2860 and 1730; $\delta_H$ 7.29 (1 H, d, $J$ 1, furan 5-H), 6.31 (1 H, dd, $J$ 3 and 2, furan 4-H), 6.28–6.08 (3 H, m, furan 3-H, 8- and 9-H), 4.14–3.88 (1 H, m, 3-H), 3.68 (3 H, s, OMe), 3.15–3.00 (1 H, br, OH), 2.48–2.40 (2 H, m, 2-$CH_2$), 2.31–2.04 (2 H, m, 7-$CH_2$) and 1.62–1.27 (6 H, m, 4-, 5- and 6-$CH_2$); $m/z$ 252 ($M^+$, 4%), 234 (15), 160 (39), 136 (15), 120 (35), 107 (76), 94 (100), 81 (53), 79 (30), 77 (29) and 43 (18) (Found: $M^+$, 252.1343. $C_{14}H_{20}O_4$ requires $M$, 252.1362).

*Methyl* (2E,8E)-9-(2-*Furyl*)*nona*-2,8-*dienoate* **34**.—Methanesulphonyl chloride (0.13 $cm^3$, 1.68 mmol) was added to an ice-cooled stirred solution of the foregoing hydroxy ester **33b** (0.35 g, 1.39 mmol) in dry pyridine (25 $cm^3$). The resulting solution was stirred at 0 °C for 2 h, then at ambient temperature for a further 1 h and was finally poured into water (50 $cm^3$). The aqueous mixture was extracted with ether (3 × 35 $cm^3$) and the combined ethereal extracts were washed with aqueous copper(II) sulphate (3 × 30 $cm^3$) and brine (30 $cm^3$) and then dried and evaporated to leave the *mesylate* **33c** (0.39 g, 85%) as a pale yellow oil, $\nu_{max}/cm^{-1}$ 3030, 2940, 2865 and 1735; $\delta_H$ 7.37 (1 H, d, $J$ 1, furan 5-H), 6.40 (1 H, dd, $J$ 3 and 2, furan 4-H), 6.29–6.15 (3 H, m, furan 3-H, 8- and 9-H), 5.09 (1 H, pentet, $J$ ~ 7, 3-H), 3.72 (3 H, s, OMe), 3.02 (3 H, s, $OSO_2Me$), 2.80–2.68 (2 H, m, 2-$CH_2$), 2.33–2.03 (2 H, m, 7-$CH_2$), 1.91–1.66 (2 H, m, 4-$CH_2$) and 1.63–1.33 (4 H, m, 5- and 6-$CH_2$); $m/z$ 330 ($M^+$, 18%), 234 (6), 160 (59) 133 (10), 120 (51), 107 (100), 94 (98), 81 (37), 79 (26), 77 (31) and 53 (9) (Found: $M^+$, 330.1145. $C_{15}H_{22}O_6S$ requires $M$, 330.1137).

Without further purification, the foregoing mesylate **33c** (0.37 g, 1.12 mmol) was dissolved in dry benzene (30 $cm^3$) and the resulting solution treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.22 $cm^3$, 1.5 mmol); it was then heated under gentle reflux for 3 h. The cooled solution was diluted with ether (30 $cm^3$) and washed successively with 0.5 mol $dm^{-3}$ aqueous hydrochloric acid (40 $cm^3$), water (40 $cm^3$) and brine (40 $cm^3$) and then dried and evaporated. Chromatography of the residue using silica gel eluted with 20% ether–light petroleum gave the (2E,8E)-*dienoate* **34** (0.19 g, 73%) as a colourless oil, $\nu_{max}/cm^{-1}$ 3105, 3000, 2930, 2860, 1720 and 1655; $\delta_H$(400 MHz) 7.30 (1 H, d, $J$ 1.0, furan 5-H), 6.97 (1 H, dt, $J$ 15.6 and 6.9, 3-H), 6.33 (1 H, dd, $J$ 3.2 and 1.8, furan 4-H), 6.20–6.10 (3 H, m, furan 3-H, 8- and 9-H), 5.81 (1 H, dt, $J$ 15.6 and 1.4, 2-H), 3.71 (3 H, s, OMe), 2.32–2.01 (4 H, m, 4- and 7-$CH_2$) and 1.62–1.33 (4 H, m, 5- and 6-$CH_2$); $\delta_C$ 166.96 (C-1), 154.14 (furan C-2), 149.18 (C-3), 141.18 (furan C-5), 129.31 (C-9), 121.02 (C-2), 118.86 (C-8), 110.96 (furan C-4), 105.96 (furan C-3), 51.19 (OMe) and 32.38, 31.91, 28.60 and 27.43 (all $CH_2$); $m/z$ 234 ($M^+$, 2%), 138 (42), 122 (24), 107 (100), 95 (19), 81 (40), 79 (38), 67 (54), 55 (65) and 53 (35) (Found: C, 72.0; H, 8.1%; $M^+$, 234.1249. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.8%; $M$, 234.1256).

*Methyl* (4SR,4aRS,8aRS)- *and* (4SR,4aRS,8aSR)-4,4a,5,6,-7,8,8a,9-*Octahydronaphtho*[2,3,-b]*furan*-4-*carboxylate* **26** *and* **35**.—Thermolysis of the (*E*,*E*)-dienoate **34** (0.095 g, 0.41 mmol) in dry toluene (15 $cm^3$), as described above at 290 °C for 16 h gave an inseparable 45:55 mixture of the cis- and trans-*furanodecalins* **26** and **35** (0.086 g, 90%), $\nu_{max}/cm^{-1}$ 2930, 2860, 1738, 1730 and 1510; $m/z$ 234 ($M^+$, 20%), 176 (13), 175 (100), 107 (10), 95 (17), 91 (26), 81 (13), 77 (14), 74 (12) and 65 (11) (Found: $M^+$, 234.1256). The minor *cis* component **26** showed spectral data identical with those given above; the major *trans*-isomer **35** showed $\delta_H$(400 MHz) 7.22 (1 H, m, 2-H), 6.15 (1 H, d, $J$ 1.9, 3-H), 3.74 (3 H, s, OMe), 3.22 (1 H, ddd, $J$ 9.9, 3.0 and 1.6, 4-H), 2.65 (1 H, ddd, $J$ 16.3, 5.3 and 1.2, 9-$H_{eq}$), 2.28 (1 H, dddd, $J$ 16.3, 10.9, 3.0 and 0.9, 9-$H_{ax}$), 1.91–1.87 (2 H, m, 4a- and 8a-H), 1.86–1.70 (2 H, m), 1.62–1.50 (2 H, m), 1.36–1.18 (2 H, m) and 1.19–1.05 (2 H, m); $\delta_C$(20.15 MHz) 174.53 (C=O), 150.68 (C-9a), 140.71 (C-2), 114.57 (C-3a), 108.98 (C-3), 51.67 (OMe), 47.62 (C-4), 41.55 (C-4a), 38.20 (C-8a), 34.17 (C-9) and 32.02, 30.32, 26.08 and 25.26 (all $CH_2$).

The isomer ratio was determined from the integrals of the methyl ester and 3-H resonances.

*Methyl* (8Z)-9-(2-*Furyl*)*non*-8-*en*-2-*ynoate* **37**.—A mixture of zinc dust (0.793 g, 12.14 mmol), triphenylphosphine (3.18 g, 12.14 mmol), carbon tetrabromide (4.03 g, 12.14 mmol) and dry dichloromethane (50 $cm^3$) was stirred at ambient temperature for 18 h and then cooled to 0 °C and treated with a solution of the (*Z*)-aldehyde **24c** (1.80 g, 6.07 mmol) in dry dichloromethane (8 $cm^3$).[41] After 1 h at this temperature, the cooling bath was removed and stirring continued for a further hour before dilution of the mixture with dry pentane (200 $cm^3$). The supernatant layer was decanted and filtered and the combined solids redissolved in dichloromethane (70 $cm^3$). The resulting solution was diluted with pentane (150 $cm^3$) and filtered. Following a repetition of this dissolution–precipitation procedure, the combined filtrates were evaporated to leave the dibromo alkene **36** (1.80 g, 89%) as a yellow oil which was not further purified and which showed $\delta_H$ 7.36 (1 H, d, $J$ 1.8, furan 5-H), 6.47–6.11 (4 H, m, furan 3- and 4-H, 2- and 8-H), 5.50 (1 H, dt, $J$ 11.8 and 7.2, 7-H), 2.60–1.93 (4 H, m, 3- and 6-$CH_2$) and 1.88–1.27 (4 H, m, 4- and 5-$CH_2$).

To a mixture of freshly prepared dibromo alkene **36** (1.80 g, 5.39 mmol) and lithium bromide (5 g) in dry THF (30 $cm^3$) maintained at −78 °C was added butyllithium (1.6 mol $dm^{-3}$ solution in hexanes; 7.44 $cm^3$, 11.9 mmol). After 1 h at this temperature, the mixture was warmed to ambient temperature and stirred for 1 h before re-cooling to −60 °C. Methyl chloroformate (0.45 $cm^3$, 5.9 mmol) was added to the latter mixture in one portion and the cooling bath removed. When the mixture reached ambient temperature, it was poured into water (50 $cm^3$) and extracted with ether (3 × 50 $cm^3$). The combined extracts were washed with brine, dried and evaporated;

chromatography of the residue using silica gel eluted with 25% ethyl acetate–light petroleum gave the *acetylenic ester* **37** (0.58 g, 51%) as a colourless oil, $\nu_{max}/cm^{-1}$ 3020, 2940, 2860, 2240, 1710 and 1435; $\delta_H$ 7.37 (1 H, d, *J* 1, furan 5-H), 6.37 (1 H, dd, *J* 3 and 2, furan 4-H), 6.32–6.12 (2 H, m, furan 3-H and 9-H), 5.50 (1 H, dt, *J* 11.8 and 7, 8-H), 3.74 (3 H, s, OMe), 2.51–2.17 (4 H, m, 4- and 7-$CH_2$) and 1.71–1.42 (4 H, m, 5- and 6-$CH_2$); *m/z* 232 ($M^+$, 10%), 173 (69), 171 (27), 155 (16), 151 (18), 136 (27), 125 (26), 111 (27), 107 (100), 96 (37), 95 (50), 94 (45), 81 (52) and 79 (71) (Found: $M^+$, 232.1096, $C_{14}H_{16}O_3$ requires *M*, 232.1099).

*Methyl(2Z,8Z)-9-(2-Furyl)nona-2,8-dienoate* **38**.—A solution of the acetylenic ester **37** (1.32 g) in methanol (40 $cm^3$) containing 5% Pd–$BaSO_4$ (0.03 g) and quinoline (0.025 g) was shaken under an atmosphere of hydrogen for 2 h and then filtered and evaporated to leave the *2Z,8Z-dienoate* **38** (1.30 g, 98%) as a colourless oil; $\nu_{max}/cm^{-1}$ 1720 and 1655; $\delta_H$ 7.36 (1 H, d, *J* 1, furan 5-H), 6.36 (1 H, dd, *J* 3 and 2, furan 4-H), 6.30–5.83 (3 H, m, furan 3-H, 3-H and 9-H), 5.76 (1 H, br, d, *J* 11.5, 2-H), 5.52 (1 H, dt, *J* 11.7 and 7.2, 8-H), 3.70 (3 H, s, OMe), 2.70–2.30 (4 H, m, 4- and 7-$CH_2$) and 1.80–1.45 (4 H, m, 5- and 6-$CH_2$); *m/z* 234 ($M^+$, 8%), 175 (23), 138 (38), 113 (41), 107 (75), 97 (17), 94 (77), 81 (100), 79 (44) and 67 (67) (Found: C, 72.0; H, 8.0%; $M^+$, 234.1253. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.8%; *M*, 234.1256).

*Methyl* (2S,8E)-9-(2-*Furyl*)-3-*methylnona*-2,8-*dienoate* **41**.—Butyllithium (1.6 mol $dm^3$ solution in hexanes; 2.75 $cm^3$, 4.4 mmol) was added dropwise to a well-stirred suspension of 2-furylmethyl(triphenyl) phosphonium bromide **39**[42] (1.90 g, 4.5 mmol) in THF (60 $cm^3$) maintained at −78 °C. After 20 min, a solution of the aldehydo ester **40** (0.74 g, 4 mmol), prepared from the corresponding alcohol[43] by PCC oxidation exactly as described above (for **24c**), in THF (3 $cm^3$) was added dropwise. After 0.5 h, the mixture was warmed to −20 °C and then poured into water (120 $cm^3$) and ether (100 $cm^3$). The separated aqueous layer was further extracted with ether (2 × 50 $cm^3$) and the combined ether solutions were dried, filtered and evaporated. Chromatography of the residue using silica gel eluted with ether–light petroleum (1:5) separated the (2E,8E)-*dienoate* **41** (0.615 g, 62%), as a colourless oil, $\nu_{max}/cm^{-1}$ 3110, 3010, 2920, 2860, 1720 and 1650; $\delta_H$(250 MHz) 7.28 (1 H, d, *J* 1, furan 5-H), 6.32 (1 H, dd, *J* 3.2 and 1.8, furan 4-H), 6.20–6.10 (3 H, m, furan 3-H, 8- and 9-H), 5.71 (1 H, br s, 2-H), 3.73 (3 H, s, OMe), 2.35–2.05 (4 H, m, 4- and 7-$CH_2$), 2.13 (3 H, br s, 3-Me) and 1.68–1.21 (4 H, m, 5- and 6-$CH_2$); $\delta_C$ 167.08 (C-1), 164.23 (C-3) 153.18 (furan C-2), 141.12 (furan C-5), 129.37 (C-9), 118.91 (C-8), 114.52 (C-2), 111.20 (furan C-4), 105.99 (furan C-3), 50.85 (OMe), 33.70, 31.78, 28.65, 27.43 (all $CH_2$) and 19.41 (3-Me); *m/z* 248 ($M^+$, 29%), 189 (23), 174 (26), 125 (89) and 107 (100) (Found: $M^+$, 248.1416. $C_{15}H_{20}O_3$ requires *M*, 248.1413).

*Methyl*(4SR,4aRS,8aSR)-*and*(4SR,4aRS,8aRS)-4a-*Methyl*-4,4a,5,6,7,8,8a,9-*octahydronaphtho*[2,3-b]*furan*-4-*carboxylate* **42** *and* **43**.—Thermolysis of the (*E,E*)-dienoate **41** (0.310 g, 1.25 mmol) in dry toluene (35 $cm^3$), as described above at 280 °C for 16 h, followed by evaporation of the cooled solution left a dark oil. Careful integration of the methyl ester resonances in the $^1H$ NMR spectrum of this material, guided by the data exhibited by the purified compounds, indicated an isomer ratio of *ca.* 55:45. Chromatography of the residue using silica gel eluted with 10% ether in light petroleum gave the trans-*furanodecalin* **43** (0.111 g, 36%) as a colourless oil, $\nu_{max}/cm^{-1}$ 2920, 2860, 1730 and 1510; $\delta_H$(400 MHz) 7.26 (1 H, m, 2-H), 6.19 (1 H, d, *J* 1.9, 3-H), 3.72 (3 H, s, OMe), 3.37 (1 H, dd, *J* 2.7 and 1.4, 4-H), 2.66 (1 H, ddd, *J* 16.2, 5.1 and 1.0, 9-$H_{eq}$), 2.28 (1 H, ddd, *J* 16.2, 10.8 and 2.7, 9-$H_{ax}$), 1.86–1.80 (1 H, m, 8a-H), 1.75–1.10 (8 H, m) and 1.01 (3 H, br s, 4a-Me); $\delta_C$(20.15 MHz) 174.76 (C=O), 151.03 (C-9a), 140.98 (C-2), 114.68 (C-3a), 109.21 (C-3), 51.71 (OMe), 48.63 (C-4), 48.22 (C-4a), 39.52 (C-8a), 34.23 (C-9), 32.87, 30.41, 26.12 and 25.60 (all $CH_2$) and 23.39 (4a-Me), *m/z* 248 ($M^+$, 29%), 190 (19), 189 (100), 95 (23) and 81 (32) (Found: $M^+$, 248.1419), followed by the cis-*furanodecalin* **43** (0.083 g, 27%) as a colourless oil, $\nu_{max}/cm^{-1}$ 2920, 2860, 1725 and 1510; $\delta_H$(400 MHz) 7.22 (1 H, dd, *J* 1.9 and 0.7, 2-H), 6.22 (1 H, d, *J* 1.9, 3-H), 3.71 (3 H, s, OMe), 3.46 (1 H, br s, 4-H), 2.64 (1 H, dd, *J* 16.4 and 6.6, 9-$H_{eq}$), 2.59 (1 H, dd, *J* 16.4 and 7.6, 9-$H_{ax}$), 2.44–2.27 (1 H, m, 8a-H), 1.70–1.42 (8 H, m, 5-, 6-, 7- and 8-$CH_2$) and 0.98 (3 H, br s, 4a-Me); $\delta_C$(20.15 MHz) 174.67 (C=O), 150.35 (C-9a), 141.09 (C-2), 112.63 (C-3a), 110.67 (C-3), 51.77 (OMe), 44.39 (C-4), 44.20 (C-4a), 31.69 (C-8a), 29.76 (C-9), 27.69, 25.65, 24.60 and 22.78 (all $CH_2$) and 21.58 (4a-Me); *m/z* 248 ($M^+$, 22%), 190 (27), 189 (100), 94 (14) and 81 (45) (Found: $M^+$, 248.1419).

The total isolated yield was 63%, in a *trans/cis* ratio of 57:43.

*Methyl* (8E)-9-(2-*Furyl*)-4-*methyl*-3-*oxonon*-8-*enoate* **45**.—Following the established procedure,[38] the dilithio dianon **44** of methyl 3-oxopentanoate (10.6 mmol) was prepared in THF (40 $cm^3$) using LDA and treated dropwise at 0 °C with a solution of the foregoing (*E*)-iodide **32d** (1.38 g, 5.3 mmol) in THF (10 $cm^3$). The cooling bath was removed and the red solution stirred for 2 h before being poured into water (200 $cm^3$). The resulting mixture was extracted with ether (2 × 150 $cm^3$) and the combined extracts were washed with water (150 $cm^3$) and brine (150 $cm^3$), dried and evaporated to leave a red oil. Chromatography of this using silica gel eluted with 20% ether in light petroleum gave the *keto ester* **45** (0.64 g, 46%) as a colourless oil, $R_f$ 0.20; $\nu_{max}/cm^{-1}$ 2990, 2940, 2860, 1742, 1710 and 1625; $\delta_H$(250 MHz) 7.29 (1 H, d, *J* 1.5, furan 5-H), 6.33 (1 H, dd, *J* 3.2 and 1.9, furan 4-H), 6.19–6.09 (3 H, m, furan 3-H, 8- and 9-H), 3.71 (3 H, s, OMe), 3.48 (2 H, m, 2-$CH_2$), 2.63 (1 H, app t, *J* 7.0, 4-H), 2.33–2.01 (2 H, m, 7-$CH_2$), 1.67–1.26 (4 H, m, 5- and 6-$CH_2$) and 1.11 (3 H, d, *J* 6.9, 4-Me); $\delta_C$ 206.04 (C-3), 167.17 (C-1), 153.16 (furan C-2), 141.31 (furan C-5), 129.14 (C-9), 119.13 (C-8), 111.09 (furan C-4), 106.19 (furan C-3), 52.19 (OMe), 47.42 (C-2), 46.49 (C-4), 32.67, 32.03 and 26.68 (all $CH_2$) and 15.96 (4-Me); *m/z* 264 ($M^+$, 6%), 246 (95), 212 (11), 191 (19), 150 (21), 134 (48), 120 (51), 107 (100), 101 (45), 94 (64), 91 (27), 81 (54), 77 (34) and 59 (29) (Found: $M^+$, 264.1346. $C_{15}H_{20}O_4$ requires *M*, 264.1362).

*Methyl* (2E,8E)-3,4-*Dimethyl*-9-(2-*furyl*)*nona*-2,8-*dienoate* **46b** *and Methyl* (2E,8E)-9-(2-*Furyl*)-4-*methylnona*-2,8-*dienoate* **46c**.—According to the general procedure of Sum and Weiler,[43] addition of the foregoing keto ester **45** (0.60 g, 2.27 mmol) in ether (5 $cm^3$) to a vigorously stirred suspension of washed sodium hydride (2.7 mmol) in ether (10 $cm^3$), maintained at 0 °C, gave the corresponding sodium enolate in 20 min at this temperature. The mixture was then treated with diethyl chlorophosphate (0.36 $cm^3$, 2.5 mmol) and stirred without cooling for 2 h. Work-up gave the crude enol phosphate **46a** (0.90 g, 99%) as a pale brown oil, homogeneous by TLC, which was not further purified and which appeared to be a single geometric isomer showing $\delta_H$ 7.29 (1 H, br s, furan 5-H), 6.31 (1 H, dd, *J* 3 and 2, furan 4-H), 6.19–6.09 (3 H, m, furan 3-H, 8-H and 9-H), 5.39 (1 H, s, 2-H), 4.24 (4 H, q, *J* 7, 2 × $OCH_2CH_3$), 3.68 (3 H, s, OMe), 2.92–2.37 (1 H, m, 4-H), 2.34–2.02 (2 H, m, 7-$CH_2$), 1.84–*ca.* 1.20 (4 H, m, 5- and 6-$CH_2$), 1.34 (6 H, t, *J* 7, 2 × $OCH_2CH_3$) and 1.15 (3 H, d, *J* 7, 4-$CH_3$).

A solution of freshly prepared enol phosphate **46a** (0.90 g, 2.25 mmol) in ether was added dropwise to a stirred solution of lithium dimethylcuprate (4.5 mmol) in ether (20 $cm^3$) maintained at −78 °C. The resulting mixture was stirred at this temperature for 2 h, then at −47 °C for 1 h before being poured into

saturated aqueous ammonium chloride (50 $cm^3$). The aqueous layer was separated and extracted with ether (2 × 25 $cm^3$) and the combined organic solutions were washed successively with 20% aqueous ammonia–brine (1:1, 3 × 15 $cm^3$) and brine (2 × 25 $cm^3$) then dried and evaporated. The residue was separated using HPLC [7.8 mm × 30 cm 5 μm Porasil column eluted with 5% ether–light petroleum at a flow rate of 3 $cm^3$ $min^{-1}$] to give the 3,4-*dimethyl-dienoate* **46b** (0.13 g, 22%), eluted first as a colourless oil with $R_t$ 10.3 min; $\nu_{max}/cm^{-1}$ 2938, 2860, 1715, 1642 and 1157; $\delta_H$(250 MHz) 7.29 (1 H, d, *J* 1.5, furan 5-H), 6.33 (1 H, dd, *J* 3.3 and 1.8, furan 4-H), 6.19–6.10 (3 H, m, furan 3-H, 8- and 9-H), 5.68 (1 H, br s, 2-H), 3.68 (3 H, s, OMe), 2.38–1.95 (3 H, m, 4-CH and 7-$CH_2$), 2.09 (3 H, d, *J* 1.2, 3-Me), 1.60–1.18 (4 H, m, 5- and 6-$CH_2$) and 1.05 (3 H, d, *J* 6.8, 4-$CH_3$); $\delta_C$ 167.36 (C-1), 164.40 (C-3), 153.20 (furan C-2), 141.27 (furan C-5), 129.60 (C-9), 118.94 (C-8), 114.88 (C-2), 111.09 (furan C-4), 106.06 (furan C-3), 50.74 (OMe), 43.94 (C-4), 34.25, 32.78 and 27.20 (all $CH_2$), 19.22 (3-Me) and 15.43 (4-Me); *m/z* 262 ($M^+$, 39%) 203 (15), 188 (26), 139 (98), 133 (28), 120 (74), 107 (100), 94 (73), 91 (27), 81 (43), 79 (34) and 77 (35) (Found: C, 72.8; H, 9.1%; $M^+$, 262.1565. $C_{16}H_{22}O_3$ requires C, 73.3; H, 8.5%; *M*, 262.1569) and the 4-*methyl-dienoate* **46c** (0.11 g, 19%), eluted second as a colourless oil with $R_t$ 12.0 min; $\nu_{max}/cm^{-1}$ 2935, 2860, 1727 and 1660; $\delta_H$(250 MHz) 7.29 (1 H, d, *J* 1.5, furan 5-H), 6.97 (1 H, dd, *J* 15.7 and 7.8, 3-H), 6.33 (1 H, dd, *J* 3.2 and 1.8, furan 4-H), 6.19–6.09 (3 H, m, furan 3-H, 8- and 9-H), 5.77 (1 H, dd, *J* 15.7 and 1.0, 2-H), 3.72 (3 H, s, OMe), 2.47–2.03 (3 H, m, 4-CH and 7-$CH_2$), 1.56–1.27 (4 H, m, 5- and 6-$CH_2$) and 1.05 (3 H, d, *J* 6.7, 4-$CH_3$); *m/z* 248 ($M^+$, 20%), 189 (19), 166 (16), 133 (19), 120 (44), 107 (100), 94 (76), 91 (26), 81 (55), 79 (49) and 77 (48) (Found: C, 72.7; H, 8.3%; $M^+$, 248.1418. $C_{15}H_{20}O_3$ requires C, 72.5; H, 8.1%; *M*, 248.1413).

*Thermolysis of Methyl* (2E,8E)-9-(2-*Furyl*)-4-*methylnona*-2,8-*dienoate* **46c**: *Methyl* (4SR,4aRS,5SR,8aSR)- *and* (4SR,4aRS,5SR,8aRS)-5-*Methyl*-4,4a,5,6,7,8,8a,9-*octahydronaphtho*-[2,3-b]*furan*-4-*carboxylate* **47a** *and* **48a**.—A solution of the (2*E*,8*E*)-dienoate **46c** (0.035 g) in benzene (6 $cm^3$) was heated at 285 °C for 14 h as described above. The crude product was chromatographed over silica gel eluted with 10% ether–light petroleum as eluent to give a mixture of four furanodecalins (0.024 g, 68%) as a colourless oil in a ratio of 20:14:4:3. The latter was estimated by the integrals of resolved methyl ester, 3-H and 5-methyl resonances in the $^1H$ NMR spectrum. Further separation of a sample using HPLC [7.8 mm × 30 cm 5 μm Porasil column eluted with 3.5% ether–light petroleum at a flow rate of 3 $cm^3$ $min^{-1}$] furnished the major component, which was identified as the (4SR,4aRS,5SR,8aSR)-(trans) *isomer* **47a** as a colourless oil which showed $R_t$ 8.0 min; $\nu_{max}/cm^{-1}$ 1735; $\delta_H$(400 MHz) 7.21 (1 H, d, *J* 1.9 and 0.7, 2-H), 6.18 (1 H, d, *J* 1.9, 3-H), 3.72 (3 H, s, OMe), 3.31 (1 H, ddd, *J* 9.0, 2.8 and 1.3, 4-H), 2.62 (1 H, dd, *J* 16.3 and 4.8, 9-$H_{eq}$), 2.32 (1 H, ddd, *J* 16.3, 11.0 and 2.8, 9-$H_{ax}$), 1.87 (1 H, m, 8a-H), 1.77–1.64 (3 H, m, 4a-H, 5-H and 8-$H_{ax}$), 1.55 (1 H, m, 8-$H_{eq}$), 1.39–1.12 (4 H, m, 6- and 7-$CH_2$) and 0.89 (3 H, d, *J* 6.6, 5-$CH_3$); $\delta_C$(100 MHz; from DEPT sequence; no quaternaries) 140.89 (C-2), 109.01 (C-3), 52.20 (OMe), 46.50 (C-4), 46.33 (C-4a), 39.70 (C-5), 38.90 (C-8a), 36.30 (C-9), 34.58, 30.30 and 26.06 (all $CH_2$) and 20.10 (5-Me); *m/z* 248 ($M^+$, 21%), 190 (15), 189 (100), 131 (10), 108 (12), 95 (66) and 91 (12) (Found: $M^+$, 248.1414. $C_{15}H_{20}O_3$ requires *M*, 248.1413). Eluted second was the (4SR,4aRS,5SR,8aRS)-(cis) *isomer* **48a**, also a colourless oil, which showed $R_t$ 8.9 min; $\nu_{max}/cm^{-1}$ 1735; $\delta_H$(400 MHz) 7.27 (1 H, d, *J* 1.9, 2-H), 6.28 (1 H, d, *J* 1.9, 3-H), 3.70 (3 H, s, OMe), 3.55 (1 H, br d, *J* 9.9, 4-H), 2.62 (1 H, dd, *J* 16.5 and 9.9, 9-$H_{ax}$), 2.50 (1 H, dd, *J* 16.6 and 6.2, 9-$H_{eq}$), 2.40 (1 H, m, 8a-H), 1.91 (1 H, br d, *J ca.* 9.9, 4a-H), 1.74–1.40 (7 H, m, 5-H, 6-, 7- and 8-$CH_2$) and 0.93 (3 H, d, *J* 6.5, 5-Me); *m/z* 248 ($M^+$, 26%), 190 (14), 189 (100), 131 (11), 108 (12), 95 (53), 91 (18) and 81 (12) (Found: $M^+$, 248.1402). This second fraction also contained the two minor components **47b** and **48b** (probably epimeric with the major isomers at the 5-methyl site), which were identified by resonances at $\delta_H$ 6.17 and 6.18 (both d, *J* 1.9, 3-H), 3.73 and 3.72 (s, OMe) and 0.99 and 0.84 (d, *J* 7.1, 5-Me).

*Methyl* (6Z)-7-(3-*Furyl*)*hept*-6-*enoate* **55a**.—Following the foregoing procedure for the preparation of the (*Z*)-2-furyl isomer **25** from furan-2-carbaldehyde, condensation between furan-3-carbaldehyde and the phosphorane **23** derived from (5-carboxypentyl)triphenylphosphonium bromide on a 34 mmol scale gave a crude alkenoic acid which showed $\delta_H$ 7.45–7.30 (2 H, m, furan 2- and 5-H), 6.42 (1 H, br s, furan 4-H), 6.14 (1 H, br d, *J* 11.4, 7-H), 5.52 (1 H, dt, *J* 11.4 and 6.9, 6-H), 2.42–2.02 (4 H, m, 2- and 5-$CH_2$) and 1.88–1.22 (4 H, m, 3- and 4-$CH_2$). Subsequent esterification using diazomethane and chromatography using alumina (Merck 90, grade III) eluted with 20% ethyl acetate–light petroleum gave the (Z)-*alkenoate* **55a** (3.44 g, 46%) as a pale yellow oil; $\nu_{max}/cm^{-1}$ 3010, 2940, 2860 and 1738; $\delta_H$(250 MHz) 7.39 (1 H, br s, furan 2-H), 7.34, m, furan 5-H), 6.42 (1 H, app. t, *J* 1.0, furan 4-H), 6.12 (1 H, dt, *J* 11.5 and 1.0, 7-H), 5.50 (1 H, dt, *J* 11.5 and 7.0, 6-H), 3.63 (3 H, OMe), 2.46-2.13 (4 H, m, 2- and 5-$CH_2$) and 1.88–1.33 (4 H, m, 3- and 4-$CH_2$); $\delta_C$(62.8 MHz) 173.95 (C-1), 142.73 (furan C-5), 140.88 (furan C-2), 131.30 (C-7), 122.60 (furan C-3), 119.21 (C-6), 110.98 (furan C-4), 51.40 (OMe) and 33.93, 29.05, 28.85 and 24.71 (all $CH_2$); *m/z* 208 ($M^+$ 26%). 193 (5), 177 (4), 151 (8), 137 (20), 121 (23), 107 (41), 97 (58), 83 (53), 79 (48), 71 (74), 69 (73), 57 (100) and 55 (87) (Found: $M^+$, 208.1089. $C_{12}H_{16}O_3$ requires *M*, 208.1099).

(6Z)-7-(3-*Furyl*)*hept*-6-*en*-1-*ol* **55b**.—Using the procedure described above (for **24b**), reduction of the foregoing ester **55a** (3.14 g) using lithium aluminium hydride gave the (Z)-*alcohol* **55b** (2.49 g, 92%) as a colourless oil, $R_f$ 0.14 ($CH_2Cl_2$); $\nu_{max}/cm^{-1}$ 3600–3050, 3010, 2995, 2840 and 1500; $\delta_H$(80 MHz) 7.38 (2 H, m, furan 2- and 5-H), 6.43 (1 H, br s, furan 4-H), 6.15 (1 H, br d, *J* 11.7, 7-H), 5.55 (1 H, dt, *J* 11.7 and 6.8, 6-H), 3.63 (2 H, t, *J* 7.0, 1-$CH_2$), 2.48–2.08 (2 H, m, 5-$CH_2$) and 1.85–1.17 (6 H, m, 2-, 3- and 4-$CH_2$); *m/z* 180 ($M^+$, 82%), 162 (7), 147 (6), 134 (9), 133 (15), 121 (36), 120 (18), 108 (31), 107 (99), 95 (49), 94 (100), 91 (44), 82 (85), 81 (34), 79 (83), 77 (68), 65 (13), 53 (16) and 51 (16) (Found: $M^+$, 180.1155. $C_{11}H_{16}O_2$ requires *M*, 180.1150).

*Methyl* (2E,8Z)-9-(3-*Furyl*)*nona*-2,8-*dienoate* **56**.—Using the method given above for the preparation of the aldehyde **24c**, oxidation of the foregoing alcohol **55b** using pyridinium chlorochromate (10 mmol scale) gave the (Z)-*aldehyde* **55c** (1.32 g, 77%) which showed $R_f$ 0.55 ($CH_2Cl_2$); $\nu_{max}/cm^{-1}$ 3050, 2990, 2900, 1755 and 1525; $\delta_H$(80 MHz) 9.70 (1 H, br s, CHO), 7.40 (2 H, m, furan 2- and 5-H), 6.43 (1 H, br s, furan 4-H), 6.14 (1 H, br d, *J ca.* 12, 7-H), 5.60–5.37 (1 H, m, 6-H), 2.81–2.00 (4 H, m, 2- and 5-$CH_2$) and 1.98–1.25 (4 H, m, 3- and 4-$CH_2$); *m/z* 178 ($M^+$, 54%), 150 (17), 134 (11), 121 (27), 119 (11), 108 (22), 107 (100), 105 (15), 95 (29), 94 (44), 91 (30), 84 (28), 82 (57), 81 (30), 79 (77), 77 (64), 67 (11) and 53 (14) (Found: $M^+$, 178.0989. $C_{11}H_{14}O_2$ requires *M*, 178.0994). Subsequent condensation of the aldehyde **55c** (1.20 g; 6.74 mmol) with methyl (triphenylphosphoranylidene)acetate, as described above, followed by chromatography using silica gel eluted with 20% ether–light petroleum gave the (2E,8Z)-*dienoate* **56** (1.36 g, 86%) as a colourless oil; $\nu_{max}/cm^{-1}$ 3010, 2920, 1722, 1655 and 1500; $\delta_H$(400 MHz) 7.41 (1 H, br s, furan 2-H), 7.38 (1 H, app t, *J ca.* 1.0, furan 5-H), 6.96 (1 H, dt, *J* 15.7 and 7.0, 3-H), 6.44 (1 H, app t, *J ca.* 0.8, furan 4-H), 6.14 (1 H, br d, *J* 11.4, 9-H), 5.82 (1 H, dt, *J* 15.7 and 1.4, 2-H), 5.53 (1 H, dt, *J* 11.4 and 7.0, 8-H),

3.71 (3 H, s, OMe), 2.30–2.15 (4 H, m, 4- and 7-$CH_2$) and 1.53–1.44 (4 H, m, 5- and 6-$CH_2$); $\delta_C$(100 MHz) 167.07 (C-1), 149.32 (C-3), 142.71 (furan C-5), 140.82 (furan C-2), 131.40 (C-9), 122.54 (furan C-3), 121.09 (C-2), 119.08 (C-8), 110.93 (furan C-4), 51.34 (OMe) and 32.03, 28.98, 28.85 and 27.69 (all $CH_2$); *m/z* 234 ($M^+$, 18%), 175 (100), 121 (35), 107 (86), 94 (52), 91 (33), 82 (48), 81 (54), 79 (56), 77 (61) and 53 (19) (Found: $M^+$, 234.1255. $C_{14}H_{18}O_3$ requires *M*, 234.1256).

*Methyl* (4aSR,8aSR,9RS)-4,4a,5,6,7,8,8a,9-*Octahydronaptho*[2,3-b]*furan*-9-*carboxylate* **57**.—Thermolysis of the foregoing (2*E*,8*Z*)-3-furyl-dienoate **56** (0.413 g) in toluene (35 $cm^3$) at 290 °C for 18 h followed by evaporation left a residue (0.413 g), a pale yellow oil, which appeared pure by $^1H$ NMR analysis. A portion of the product (0.15 g) was passed through a short column of silica gel eluted with 20% ether–light petroleum to provide the cis-*furanodecalin* **57** (0.145 g; 97%) as a colourless oil showing $\nu_{max}/cm^{-1}$ 2935, 2860, 1735 and 1505; $\delta_H$(400 MHz) 7.30 (1 H, d, *J* 1.8, 2-H), 6.21 (1 H, d, *J* 1.8, 3-H), 3.72 (3 H, s, OMe), 3.53 (1 H, br d, *J* 3.7, 9-H), 2.47 (2 H, app. d, *J* 7.1, 4-$CH_2$), 2.32 (1 H, m, 8a-H), 2.20–2.14 (1 H, m, 4a-H) and 1.70–1.43 (8 H, m, 5-, 6-, 7- and 8-$CH_2$); $\delta_C$(100 MHz) 173.25 (C=O), 145.37 (C-9a), 141.91 (C-2), 117.38 (C-3a), 110.43 (C-3), 52.19 (OMe), 44.59 (C-9), 39.41 (C-8a), 32.16 (C-4a), 29.39 (C-4), 28.07, 24.63, 24.11 and 22.42 (all $CH_2$); *m/z* 234 ($M^+$, 15%), 176 (15), 175 (100), 95 (13), 91 (21), 81 (15), 79 (10), 77 (10) and 67 (10) (Found: C, 71.6; H, 7.7%; $M^+$ 234.1265. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.8%).

The sample contained *ca.* 5% of the corresponding *trans*-fused isomer **60** (see below).

*Methyl* (2E,8E)-9-(3-*Furyl*)*nona*-2,8-*denoate* **59**.—Wittig condensation between 3-furylmethyl(triphenyl)phosphonium bromide[45] (1.27 g, 3 mmol) and (*E*)-methyl 7-formylhept-2-enoate,[46] as described above for the preparation of the dienoate **41** from the corresponding 2-furylphosphonium salt **39**, followed by careful chromatography using silica gel eluted with 15% ether–light petroleum gave the (2E,8E)-*dienoate* **59** (0.274 g, 39%) as a colourless oil; $\nu_{max}/cm^{-1}$ 3010, 2910, 1720, 1650 and 1500; $\delta_H$(400 MHz) 7.42 (1 H, br s, furan 2-H), 7.33 (1 H, t, *J* 1.0, furan 5-H), 6.99 (1 H, dt, *J* 15.6 and 6.9, 3-H), 6.49 (1 H, app t, *J ca.* 1.0, furan 4-H), 6.22 (1 H, br d, *J* 17.0, 9-H), 6.07 (1 H, m, 8-H), 5.85 (1 H, dt, *J* 15.6 and 1.4, 2-H), 3.73 (3 H, s, OMe), 2.35–2.10 (4 H, m, 4- and 7-$CH_2$) and 1.65–1.35 (4 H, m, 5- and 6-$CH_2$); $\delta_C$(100 MHz) 167.10 (C-1), 149.42 (C-3), 143.31 (furan C-5), 139.43 (furan C-2), 130.01 (C-9), 124.45 (furan C-3), 121.19 (C-2), 119.76 (C-8), 107.54 (furan C-4), 51.39 (OMe) and 32.60, 31.56, 28.10 and 27.54 (all $CH_2$); *m/z* 234 ($M^+$, 22%), 175 (100), 121 (39), 107 (92), 94 (46), 91 (35), 82 (49), 81 (43), 79 (71), 77 (65) and 53 (23) (Found: $M^+$ 234.1258).

*Methyl* (4aSR,8aSR,9RS)- *and* (4aRS,8aSR,9RS)-4,4a,5,6,-7,8,8a,9-*Octahydronaphtho*[2,3-b]*furan*-9-*carboxylate* **57** *and* **60**.—Thermolysis of the foregoing (2*E*,8*E*)-dienoate **59** (0.15 g) in heptane (20 $cm^3$) at 280 °C for 16 h followed by column chromatography using silica gel eluted with 10% ether–light petroleum gave a 40:60 mixture of the cis- and trans-*furanodecalins* **57** and **60** (0.125 g, 83%) as a colourless oil. The mixture was not further separated; the isomer ratio was determined by the integrals of the methyl ester protons ($\delta_H$ *cis* 3.72; $\delta_H$ *trans* 3.78) and the resonances due to 9-H ($\delta_H$ *cis* 3.53; $\delta_H$ *trans* 3.37). The IR and mass spectral data for the mixture were essentially identical with those exhibited by the *cis*-isomer **57**. The *trans*-isomer **60** showed $\delta_C$ (100 MHz) 173.15 (C=O), 143.33 (C-9a), 141.40 (C-2). 118.18 (C-3a), 110.07 (C-3), 52.19 (OMe), 48.54 (C-9), 42.78 (C-8a), 38.34 (C-4a), 33.79 (C-4), 29.58, 28.81, 25.99 and 25.86 (all $CH_2$).

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