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Stereoselective Synthesis of Tetrahydrofuran-3-ols by Photochemical δ-Hydrogen Abstraction of β-Allyloxy-Carbonyl Compounds

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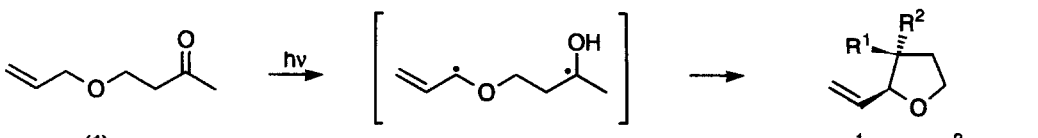
Abstract: On u.v. irradiation, the unsaturated ketones and aldehydes (**10**) and (**11**) underwent intramolecular δ-hydrogen abstraction, followed by ring closure of the 1,5-biradical to give 2-alkenyltetrahydrofuran-3-ols in reasonable yields. Photocyclisation occurred with retention of geometry about the alkenyl double bond; thus, u.v. irradiation of the geranyl ketone (**10a**) led to the tetrahydrofuranols (**12a**) and (**14a**), whereas photolysis of the neryl ketone (**11a**) gave the tetrahydrofuranol isomers (**13a**) and (**15a**).

Hydrogen abstraction by the oxygen atom of an nπ* photoexcited carbonyl group is a characteristic reaction. Thus, the Norrish type II photoreaction relies upon an efficient intramolecular 1,5-hydrogen abstraction by the excited carbonyl group, *via* a six-membered transition state.[1] In fact, compounds which lack these suitable γ-hydrogen atoms can still undergo a rapid and high-yielding intramolecular reaction involving hydrogen abstraction from more remote positions.[2,3] Besides having mechanistic interest, these photoreactions are capable of being put to synthetic use, as in Paquette's notable approach to dodecahedrane,[4] which successfully exploited δ-hydrogen abstraction. Moreover, the biradicals resulting from such longer-range hydrogen abstractions cannot easily fragment (as with the Norrish type II 1,4-biradical), and the radical centres generally combine to give formation of a new carbon-carbon bond, with concomitant ring synthesis. The u.v. irradiation of β-alkoxy-ketones[5] and β-allyloxy-carbonyl compounds such as **1**[6] therefore gives rise to high yields of the two stereoisomeric tetrahydrofuran-3-ols (*e.g.* **2** and **3**), with reaction occurring *via* 1,5-biradicals of the type shown in Scheme 1.

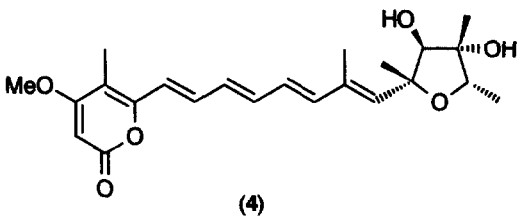


(**1**)

(**2**) R^1 = OH, R^2 = Me
(**3**) R^1 = Me, R^2 = OH

Scheme 1

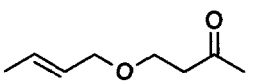
Tetrahydrofuran-3-ols are important units in a number of biologically-active compounds, such as citreoviridin (**4**),[7] asteltoxin[8] and muscarine.[9] Citreoviridin is the potent neurotoxin responsible for outbreaks of cardiac *beriberi* in East Asia, and is an exceptionally active inhibitor of oxidative phosphorylation. Any attempts to produce the tetrahydrofuran-3-ol ring of **4** by photochemical means must be by routes capable of controlling the geometry of the exocyclic double bonds, and we have therefore investigated the stereochemical implications at the double bond of the reaction shown in Scheme 1.



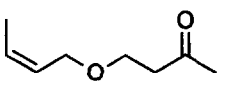
(**4**)

Results and Discussion

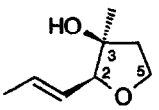
The β-butenyloxy-ketone (**5**) was prepared as a *trans/cis* mixture [**5a**:**5b** = 3:1] by Lewis-acid catalysed addition of but-2-en-1-ol to methyl vinyl ketone.[6] U.v. irradiation of the **5a**:**5b** mixture in benzene gave clean conversion to four products, detected by analytical glc. These four compounds, formed in the ratios 33:23:21:17, were subsequently isolated by preparative glc and assigned the structures of the tetrahydrofuran-3-ol isomers (**6**)-(**9**), respectively. The geometry of the propenyl side chain in each isomer was evident from ^{1}H nmr coupling constants across the double bond, and especially from ^{13}C nmr spectra (δ 13-14 for the methyl carbon of the *Z*-isomers, *vs.* δ 18 for that of the *E*-isomers).



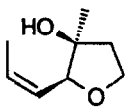
(**5a**)



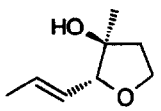
(**5b**)



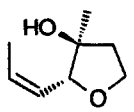
(**6**)



(**7**)



(**8**)



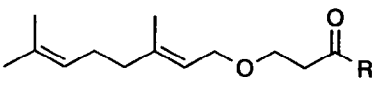
(**9**)

The geometry about the tetrahydrofuran ring was more difficult to assign at this stage. Comparison of the shifts of the tetrahydrofuran 2-H signal in the products (**6**)-(**9**) showed a downfield shift of ~0.2 ppm when 2-H was *cis* to the adjacent hydroxyl group, rather than when *cis* to the methyl group at C-3. In addition, only isomers (**8**) and (**9**) on acetylation showed a significant downfield shift (0.2 ppm) for the 2-H signal. It was noticeable that the two tetrahydrofuranol 5-H signals were separated in chemical shift by ~0.2 ppm in isomers (**6**) and (**7**), whereas the 5-H signals for isomers (**8**) and (**9**) overlapped.

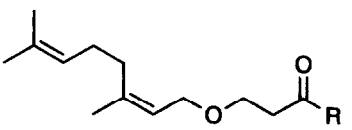
More revealing information came from separation by preparative glc of the ketone isomers **5a** and **5b**, and u.v. irradiation of each. Glc analysis showed that there was some interconversion of **5a** and **5b** during irradiation, as might be expected. However, an irradiation of **5a** showed that isomers (**6**) and (**8**) were the dominant products (>93% of the total tetrahydrofuranols) when there had been 6% isomerisation to **5b**. Likewise, irradiation of **5b** gave mainly the tetrahydrofuranols (**7**) and (**9**) (>94% of the total) when there had been only 5% isomerisation of the ketone to **5a**.

To investigate the possibility that other double bonds could be incorporated into the tetrahydrofuranol side-chains, the terpenoid adducts **10a** and **11a** were prepared from geraniol and nerol, respectively, by BF_3-catalysed reaction with methyl vinyl ketone. The geraniol-derived ketone (**10a**) underwent rapid reaction on irradiation in benzene solution: reaction was stopped at ~50% conversion, and the two main adducts which were detected by tlc were isolated by column chromatography, to yield the tetrahydrofuranols (**12a**) (51%) and (**14a**) (34%). Recovery of the unreacted ketone showed ~8% conversion to (**11a**) during this experiment.

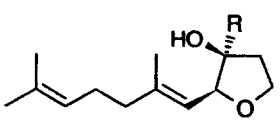
Likewise, u.v. irradiation of the nerol-derived ketone (**11a**) gave an efficient photocyclisation; irradiation was again stopped at ~50% conversion to products, and the tetrahydrofuranol isomers (**13a**) (44%) and (**15a**) (34%) were isolated by column chromatography.



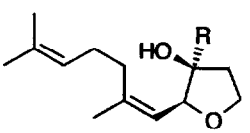
(**10**) **a**; R = Me
b; R = H



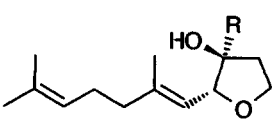
(**11**) **a**; R = Me
b; R = H



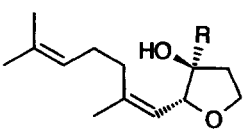
(**12**) **a**; R = Me
b; R = H



(**13**) **a**; R = Me
b; R = H



(**14**) **a**; R = Me
b; R = H



(**15**) **a**; R = Me
b; R = H

The configuration of the double bond adjacent to the ring for isomers (**12a**)-(**15a**) was established by analogy with tetrahydrofuranols (**6**)-(**9**), and from ^{13}C nmr. Thus, the presence of an *E*-substituted double bond at the 2-position of the ring in isomers (**12a**) and (**14a**) led to two allylic methyl signals in the δ 16-18 region and one methyl signal at δ 23-26. In contrast, the *Z* double bond at the 2-position in isomers (**13a**) and (**15a**) led to a single allylic methyl signal in the δ 16-18 region, with two such methyl signals in the δ 23-26 region. The increased shielding at C-3′ of the side-chain in the nerol-derived isomers reinforced these assignments; a shift of δ 32-33 was found for (**13a**) and (**15a**), in contrast to the value of δ ~40 in the geraniol-derived isomers (**12a**) and (**14a**).

The relative stereochemistry about the tetrahydrofuranol ring was most evident from analogy with the related compounds (**6**)-(**9**), using both criteria of 2-H proton chemical shift and the appearance of the 5-H protons as discrete signals in those isomers (**12a**) and (**13a**) bearing *cis* related alkenyl and hydroxyl groups.

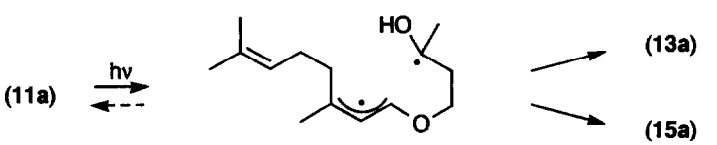
In comparison with the photochemistry of ketones, the photochemistry of aldehydes is increasingly dominated by decarbonylation reactions.[10] However, to achieve the desired secondary hydroxyl group at the 3-position of the tetrahydrofuran, the irradiation of β-allyloxy aldehydes needed to be examined. The relevant adducts **10b** and **11b** were prepared from geraniol or nerol and acrolein. An irradiation of the geraniol-derived aldehyde (**10b**) in benzene solution, carried out to ~45% conversion, showed partial isomerisation to aldehyde (**11b**) and the formation of the two tetrahydrofuranols (**12b**) and (**14b**) in 1:1 ratio, together formed in 51% yield. The isomer (**14b**) has the relative configuration of alkenyl and hydroxyl groups at C-2 and C-3 found in the citreoviridin (**4**) molecule.

A similar reaction on the nerol-derived aldehyde (**11b**), taken to ~20% conversion, gave the tetrahydrofuranol isomers (**13b**) and (**15b**) in 2:1 ratio and a combined yield of 64%. Photochemical δ-hydrogen abstraction and cyclisation of the aldehydes thus gave yields which, although lower than those for the corresponding ketones, were preparatively acceptable.

In summary, there are three significant aspects to the photochemistry of the β-allyloxy ketones and aldehydes, (**5**), (**10**) and (**11**).

(i) Photochemical cyclisation *via* δ-hydrogen abstraction occurs in satisfactory to good yield. The major stereoisomer of tetrahydrofuran-3-ol that is formed is generally that having the hydroxyl and alkenyl groups *cis* related, though the stereochemical preference is not strong.

(ii) Double bond geometry in the alkenyl chain is completely maintained during photocyclisation. Scheme 2 , for example, shows the 1,5-biradical (**16**) derived from the ketone (**11a**). The present results require that rotation about the double bond in the allylic radical centre of the biradical (**16**) must therefore be sufficiently slow that it does not compete with ring closure or reverse hydrogen transfer. Such stereoretention might be expected on the basis of the known barrier to rotation in the allyl radical (15.7 kcal/mol).[11]



(**16**)

Scheme 2

(iii) On irradiation in benzene solution, the rate of *cis-trans* isomerisation of the starting allyloxy-carbonyl compounds is appreciably lower than the rate of cyclisation. Therefore, in preparative photoreactions carried out to *ca.* 50% conversion, between 85% and 95% of the cyclisation products formed have the double bond stereochemistry of the starting alkenyl unit. Photoisomerisation of alkenes by aliphatic carbonyl sensitisers can be efficient as an intermolecular reaction,[12] and may even occur in an intramolecular manner.[13] If such *cis-trans* isomerisation had predominated in the present examples of (**5**), (**10**) and (**11**), then the synthetic applications of the cyclisation would have been extremely limited.

Experimental

General.— Column chromatography was performed using SORBSIL™ C60-H silica gel (60-210μm). T.l.c. was carried out using pre-coated silica gel 60 F_{254} (Merck) plates, with additional detection by iodine vapour. G.l.c. was performed on Varian 2740 instruments with N_2 carrier gas and flame ionisation detection; for preparative work, a 100:1 splitter was used to allow simultaneous analysis and collection. N.m.r. spectra were recorded with Jeol FX 200 or JNM GSX 270 instruments. Petrol refers to light petroleum, b.p. 40-60°C, and ether refers to diethyl ether.

Preparation of Ketones (5a) and (5b)

To a solution of but-2-en-1-ol (*cis/trans* mixture, 7.2 g, 100 mmol) in ether (10 ml) containing boron trifluoride etherate (0.5 ml, 45% BF_3) at -78°C was added dropwise methyl vinyl ketone (7.0 g, 100 mmol). Upon completion of addition, the reaction mixture was kept at 0°C for 24 h. Addition of pyridine (1 ml), removal of solvent under reduced pressure and distillation gave the product (**5**) (12.5 g, 88%) as a mixture of isomers (**5a**:**5b** = 3:1), b.p. 116°C/35 mmHg, separated into pure samples of the two isomers by preparative g.l.c. (fluorosilicone oil QF-1, 180°C), in order of elution:

4-(2*E*-But-2-enyloxy)-butan-2-one (5a): ν_{max}(film) 1713, 970 cm^{-1}; δ_H (200 MHz, C_6D_6) 5.7-5.3 (2 H, m, H-2′ and H-3′), 3.8-3.7 (2 H, m, H-1′), 3.44 (2H, t, *J* 6 Hz, H-4), 2.32 (2 H, t, *J* 6 Hz, H-3), 1.80 (3 H, s, H-1) and 1.52 (3 H, m, $C\underline{H}_3$-C=); δ_C (67.9 MHz, $CDCl_3$) 207.58 (C-2), 129.68 and 127.35 (C-2′ and C-3′), 71.77 (C-1′), 64.82 (C-4), 43.74 (C-3), 30.38 (C-1) and 17.71 ($\underline{C}H_3$-C=). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.33; H, 10.01.

4-(2*Z*-But-2-enyloxy)-butan-2-one (5b): ν_{max}(film) 1715 cm^{-1}; δ_H (200 MHz, C_6D_6) 5.7-5.2 (2 H, m, H-2′ and H-3′), 3.83 (2 H, bd, *J* 5 Hz, H-1′), 3.44 (2H, t, *J* 6 Hz, H-4), 2.28 (2 H, t, *J* 6 Hz, H-3), 1.72 (3 H, s, H-1) and 1.44 (3 H, bd, *J* 5 Hz, $C\underline{H}_3$-C=); δ_C (67.9 MHz, $CDCl_3$) 207.58 (C-2), 128.08 and 126.63 (C-2′ and C-3′), 66.33 (C-1′), 65.04 (C-4), 43.74 (C-3), 30.38 (C-1) and 13.13 ($\underline{C}H_3$-C=). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.38; H, 10.06.

Preparation of Unsaturated Carbonyl Compounds (10) and (11)

(i) Ketone (10a): To a stirred solution of geraniol (7.0 g, 45.4 mmol) in ether (30 ml) at

0°C was added boron trifluoride etherate (0.5 ml, 45% BF_3), followed by the dropwise addition of a solution of methyl vinyl ketone (7.0 g, 100 mmol) in ether (30 ml). After the reaction had stood for 1 week at 4°C, pyridine (2 ml) was added and the precipitating material removed by filtration. Evaporation of the filtrate and chromatography of the residue on silica gel, eluting with 20% ether/80% petrol, afforded ketone (**10a**) as an oil (4.2 g, 40%).

(ii) Ketone (**11a**): Similarly, nerol (7.0 g, 45.4 mmol) and methyl vinyl ketone (7.0 g, 100 mmol) led, after work-up and chromatography, eluting with 25% ether/75% toluene, to the isolation of (**11a**) as an oil (3.55 g, 34%).

(iii) Aldehyde (**10b**): Using method (i), geraniol (10.0 g, 65 mmol) in ether (70 ml) was reacted with acrolein (14.5 g, 260 mmol) in the presence of boron trifluoride etherate (1 ml) at -10°C for 1 h, followed by storage for 1 week at 4°C. Work-up and chromatography, eluting with 10% ethyl acetate/90% toluene, gave (**10b**) as an oil (3.90 g, 29%).

(iv) Aldehyde (**11b**): Similarly, reaction of nerol (10.0 g, 65 mmol) in ether (70 ml) and acrolein (14.5 g, 260 mmol), followed by work-up and chromatography, eluting with 25% ethyl acetate/75% toluene, led to the isolation of (**11b**) as an oil (3.07 g, 23%).

4-(2*E*-3,7-dimethylocta-2,6-dienyloxy)-butan-2-one (10a): ν_{max}(film) 1718, 1376, 1359, 1106, 1077 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.33 (1 H, bt, *J* 7 Hz, H-2′), 5.09 (1 H, m, H-6′), 3.98 (2 H, d, *J* 7 Hz, H-1′), 3.68 (2 H, t, *J* 6.5 Hz, H-4), 2.69 (2 H, t, *J* 6.5 Hz, H-3), 2.18 (3 H, s, CH_3CO), 2.2-1.95 (4 H, m, H-4′ and H-5′), 1.68 (3 H, s, CH_3-C=), 1.66 (3 H, d, *J* 1 Hz, CH_3-C=) and 1.59 (3 H, s, CH_3-C=); δ_C (50 MHz, $CDCl_3$) 207.00 (C-2), 140.25 (C-3′), 131.52 (C-7′), 124.01 (C-6′), 120.77 (C-2′), 67.54 (C-4), 64.91 (C-1′), 43.89 (C-3), 39.62 (C-4′), 30.37 (C-1), 26.43 (C-5′), 25.67 (C-8′, *E*-methyl), 17.66 (C-8′, *Z*-methyl) and 16.44 (3′-CH_3). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.87; H, 10.76.

4-(2*Z*-3,7-dimethylocta-2,6-dienyloxy)-butan-2-one (11a): ν_{max}(film) 1718, 1377, 1361, 1104, 1075 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.32 (1 H, bt, *J* 7 Hz, H-2′), 5.08 (1 H, m, H-6′), 3.94 (2 H, d, *J* 7 Hz, H-1′), 3.65 (2 H, t, *J* 7 Hz, H-4), 2.67 (2 H, t, *J* 7 Hz, H-3), 2.16 (3 H, s, CH_3CO), 2.05 (4 H, m, H-4′ and H-5′), 1.74 (3 H, s, CH_3-C=), 1.68 (3 H, d, *J* 1 Hz, CH_3-C=) and 1.60 (3 H, s, CH_3-C=); δ_C (50 MHz, $CDCl_3$) 206.91 (C-2), 140.36 (C-3′), 131.78 (C-7′), 123.87 (C-6′), 121.76 (C-2′), 67.28 (C-3), 64.97 (C-1′), 43.83 (C-2), 32.24 (C-4′), 30.34 (C-1), 26.72 (C-5′), 25.67 (C-8′, *E*-methyl), 23.45 (3′-CH_3) and 17.61 (C-8′, *Z*-methyl). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.75; H, 11.06.

3-(2*E*-3,7-dimethylocta-2,6-dienyloxy)-propanal (10b): ν_{max}(film) 1729, 1445, 1377, 1103 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 9.80 (1 H, t, *J* 2 Hz, H-1), 5.33 (1 H, bt, *J* 7 Hz, H-2′), 5.08 (1 H, m, H-6′), 4.00 (2 H, d, *J* 7 Hz, H-1′), 3.75 (2 H, t, *J* 6 Hz, H-3), 2.67 (2 H, dt, *J* 2 and 6 Hz, H-2), 2.06 (4 H, m, H-4′ and H-5′), 1.67 (6 H, bs, 2 x CH_3-C=) and 1.60 (3 H, s, CH_3-C=); δ_C (50 MHz, $CDCl_3$) 201.07 (C-1), 140.54 (C-3′), 131.60 (C-7′), 123.98 (C-6′), 120.60 (C-2′), 67.57 (C-3), 63.54 (C-1′), 44.00 (C-2), 39.62 (C-4′), 26.43 (C-5′), 25.67 (C-8′, *E*-methyl), 17.67 (C-8′, *Z*-methyl) and 16.44 (3′-CH_3). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55. Found: C, 74.29; H, 10.70.

3-(2*Z*-3,7-dimethylocta-2,6-dienyloxy)-propanal (11b): ν_{max}(film) 1728, 1099, 734 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 9.78 (1 H, t, *J* 2 Hz, H-1), 5.33 (1 H, bdt, *J* 1.5 and 7 Hz, H-2′), 5.09 (1 H, m, H-6′), 3.97 (2 H, dd, *J* 1 and 7 Hz, H-1′), 3.75 (2 H, t, *J* 6 Hz, H-3), 2.66 (2 H, dt, *J* 2 and 6 Hz, H-2), 2.07 (4 H, m, H-4′ and H-5′), 1.75 (3 H, d, *J* 1.5 Hz, CH_3-C=), 1.68 (3 H, s, CH_3-C=) and 1.61 (3 H, s, CH_3-C=); δ_C (50 MHz, $CDCl_3$) 200.95 (C-1), 140.68 (C-3′), 131.87 (C-7′), 123.87 (C-6′), 121.65 (C-2′), 67.36 (C-3), 63.65 (C-1′), 44.03 (C-2), 32.29 (C-4′), 26.75 (C-5′), 25.70 (C-8′, *E*-methyl), 23.48 (3′-CH_3) and 17.64 (C-8′, *Z*-methyl). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55. Found: C, 74.57; H, 10.66.

Photoreaction of Ketone (5)

(a) A solution of ketone (5) (**5a**:**5b**, *trans*/*cis* = 3:1) (2.0 g) in benzene (80 ml) was irradiated using water-cooled quartz apparatus and a centrally-positioned 450 W medium-pressure mercury arc for 5 h. Analytical g.l.c. (Carbowax 20M, 150°C) showed the presence of four products, (6)-(9), in 33%, 23%, 21% and 17% yields, respectively. The products were separated by evaporation of solvent and preparative g.l.c. (Carbowax, 185°C) of the residue to give, in order of elution:

***t*-3-Methyl-*c*-2-(*trans*-prop-1-enyl)-tetrahydrofuran-*r*-3-ol (6):** ν_{max}(film) 3410, 970 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.82 (1 H, dq, *J* 15.5 and 6 Hz, =C<u>H</u>-CH_3), 5.53 (1 H, dd, *J* 15.5 and 7 Hz, =C<u>H</u>-CH), 4.03 (1 H, q, *J* 8 Hz, 5-H), 3.85 (2 H, m, 5-H and 2-H), 2.63 (1 H, bs, OH), 2.2-1.9 (2 H, m, 2 x 4-H), 1.76 (3 H, d, *J* 6 Hz, C<u>H</u>$_3$-CH=) and 1.28 (3 H, s, 3-CH_3); δ_C (50 MHz, $CDCl_3$) 131.2 (=<u>C</u>H-CH), 125.7 (=<u>C</u>H-CH_3), 87.1 (C-2), 78.1 (C-3), 65.6 (C-5), 40.8 (C-4), 23.3 (3-CH_3) and 18.1 (<u>C</u>H_3-C=). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.32; H, 9.86.

***t*-3-Methyl-*c*-2-(*cis*-prop-1-enyl)-tetrahydrofuran-*r*-3-ol (7):** ν_{max}(film) 3412, 1114, 1057 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.85 (1 H, ddq, *J* 11.5, 1 and 7 Hz, =C<u>H</u>-CH_3), 5.50 (1 H, ddq, *J* 11.5, 9 and 1.5 Hz, =C<u>H</u>-CH), 4.27 (1 H, dd, *J* 9 and 1 Hz, 2-H), 4.07 (1 H, q, *J* 8 Hz, 5-H), 3.86 (1 H, dt, *J* 5.5 and 8 Hz, 5-H), 2.51 (1 H, bs, OH), 2.05 (2 H, m, 2 x 4-H), 1.72 (3 H, dd, *J* 7 and 1.5 Hz, C<u>H</u>$_3$-CH=) and 1.29 (3 H, s, 3-CH_3); δ_C (50 MHz, $CDCl_3$) 130.6 (=<u>C</u>H-CH), 125.5 (=<u>C</u>H-CH_3), 81.7 (C-2), 79.3 (C-3), 65.9 (C-5), 41.0 (C-4), 23.3 (3-CH_3) and 14.0 (<u>C</u>H_3-C=). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.25; H, 9.78.

***t*-3-Methyl-*t*-2-(*trans*-prop-1-enyl)-tetrahydrofuran-*r*-3-ol (8):** ν_{max}(film) 3402, 1117, 1030, 970 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.73 (1 H, dq, *J* 16 and 6.5 Hz, =C<u>H</u>-CH_3), 5.35 (1 H, ddq, *J* 16, 7 and 1.5 Hz, =C<u>H</u>-CH), 4.04 (1 H, d, J 7 Hz, 2-H), 4.0-3.9 (2 H, m, 2 x 5-H), 2.74 (1 H, bs, OH), 2.1-1.8 (2 H, m, 2 x 4-H), 1.73 (3 H, d, J 6.5 Hz, C<u>H</u>$_3$-CH=) and 1.25 (3 H, s, 3-CH_3); δ_C (50 MHz, $CDCl_3$) 129.5 (=<u>C</u>H-CH), 128.7 (=<u>C</u>H-CH_3), 88.8 (C-2), 79.7 (C-3), 65.9 (C-5), 40.0 (C-4), 23.1 (3-CH_3) and 18.0 (<u>C</u>H_3-C=). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.47; H, 9.95.

***t*-3-Methyl-*t*-2-(*cis*-prop-1-enyl)-tetrahydrofuran-*r*-3-ol (9):** ν_{max}(film) 3401, 1149, 787 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.73 (1 H, ddq, *J* 11, 1.5 and 7 Hz, =C<u>H</u>-CH_3), 5.28 (1 H, ddq, *J* 11, 9 and 1.5 Hz, =C<u>H</u>-CH), 4.52 (1 H, d, *J* 9 Hz, 2-H), 3.98 (2 H, m, 2 x 5-H), 2.08 (1 H, bs, OH), 1.98 (2 H, m, 2 x 4-H), 1.73 (3 H, dd, *J* 7 and 1.5 Hz, C<u>H</u>$_3$-CH=) and 1.27 (3 H, s, 3-CH_3); δ_C (50 MHz, $CDCl_3$) 128.9

(=CH-CH), 127.9 (=CH-CH_3), 83.3 (C-2), 80.3 (C-3), 65.9 (C-5), 40.6 (C-4), 22.8 (3-CH_3) and 13.5 (CH_3-C=). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.20; H, 10.02.

(b) A solution of (**5a**) (100 µl) in benzene (1 ml) was irradiated in a quartz tube, and the contents analysed periodically by g.l.c. The isomers (**6**) and (**8**) formed >93% of the total tetrahydrofuranols when the remaining **5a**:**5b** ratio was 94:6.

(c) A similar irradiation of (**5b**) in benzene showed that isomers (**7**) and (**9**) formed >94% of the total tetrahydrofuranols when the remaining **5a**:**5b** ratio was 5:95.

Photoreaction of Ketones (10a) and (11a)

(a) A solution of ketone (**10a**) (0.58 g) in benzene (200 ml) was irradiated (450 W Hg arc, quartz apparatus) for 1 h. Evaporation and column chromatography (ether/toluene 1:3 v/v) of the residue gave recovered ketone (**10a**) (304 mg, containing 8% **11a** by ^{1}H n.m.r.), followed in order of elution by (**12a**) (140 mg, 51%), (**13a**) (27 mg, 10%) and (**14a**) (94 mg, 34%).

(b) A similar irradiation of ketone (**11a**) (0.76 g) in benzene (210 ml) was carried out for 1.5 h. Evaporation and column chromatography (ether/toluene 1:3 v/v) of the residue gave recovered ketone (**11a**) (350 mg), followed in order of elution by (**15a**)(139 mg, 34%) and (**13a**)(180 mg, 44%).

***c*-2-(1*E*-2,6-dimethylhepta-1,5-dienyl)-*t*-3-methyltetrahydrofuran-*r*-3-ol (12a)**: ν_{max}(film) 3435, 1376, 1037 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.23 (1 H, d, *J* 8.5 Hz, H-1′), 5.09 (1 H, m, H-5′), 4.20 (1 H, d, *J* 8.5 Hz, H-2), 4.05 (1 H, q, *J* 8 Hz, H-5), 3.85 (1 H, dt, *J* 5 and 8 Hz, H-5), 2.2-1.9 (6 H, m, H-3′, H-4′ and H-4), 1.72 (3 H, d, *J* 1.5 Hz, CH_3-C=), 1.68 (3 H, s, CH_3-C=), 1.60 (3 H, s, CH_3-C=), 1.27 (3 H, s, 3-CH_3) and 1.25 (1 H, s, OH); δ_C (50 MHz, $CDCl_3$) 142.67 (C-2′), 131.75 (C-6′), 124.03 (C-5′), 119.59 (C-1′), 82.84 (C-2), 78.99 (C-3), 65.64 (C-5), 40.84 (C-4), 40.02 (C-3′), 26.40 (C-4′), 25.68 (C-7′, *E*-methyl), 23.49 (3-CH_3), 17.69 (C-7′, *Z*-methyl) and 17.15 (2′-CH_3). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.98; H, 10.90.

***c*-2-(1*Z*-2,6-dimethylhepta-1,5-dienyl)-*t*-3-methyltetrahydrofuran-*r*-3-ol (13a)**: ν_{max}(film) 3425, 1377 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.27 (1 H, d, *J* 9 Hz, H-1′), 5.08 (1 H, m, H-5′), 4.16 (1 H, d, *J* 9 Hz, H-2), 4.03 (1 H, q, *J* 8 Hz, H-5), 3.84 (1 H, dt, *J* 5 and 8 Hz, H-5), 2.2-1.9 (6 H, m, H-3′, H-4′ and H-4), 1.80 (3 H, d, *J* 1.5 Hz, CH_3-C=), 1.68 (3 H, s, CH_3-C=), 1.60 (3 H, s, CH_3-C=), 1.28 (3 H, s, 3-CH_3) and 1.25 (1 H, s, OH); δ_C (50 MHz, $CDCl_3$) 143.78 (C-2′), 131.93 (C-6′), 123.90 (C-5′), 119.69 (C-1′), 82.28 (C-2), 78.66 (C-3), 65.41 (C-5), 41.11 (C-4), 32.85 (C-3′), 27.01 (C-4′), 25.67 (C-7′, *E*-methyl), 23.83 (2′-CH_3), 23.36 (3-CH_3) and 17.67 (C-7′, *Z*-methyl). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.60; H, 10.89.

***t*-2-(1*E*-2,6-dimethylhepta-1,5-dienyl)-*t*-3-methyltetrahydrofuran-*r*-3-ol (14a)**: ν_{max}(film) 3421, 1288, 1137 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.05 (2 H, m, H-1′ and H-5′), 4.42 (1 H, d, *J* 9.5 Hz, H-2), 3.96 (2 H, dd, *J* 6 and 8.5 Hz, H-5), 2.2-1.9 (7 H, m, H-3′, H-4′, H-4 and OH), 1.72 (3 H, d, *J* 1.5 Hz, CH_3-C=), 1.67 (3 H, s, CH_3-C=), 1.60 (3 H, s, CH_3-C=) and 1.26 (3 H, s, 3-CH_3); δ_C (50 MHz, $CDCl_3$) 140.42 (C-2′), 131.55 (C-6′), 124.07 (C-5′), 122.09 (C-1′), 84.39 (C-2), 80.00 (C-3), 65.53 (C-5), 40.53 (C-4), 39.95 (C-3′), 26.37 (C-4′), 25.67 (C-7′, *E*-methyl), 22.86 (3-CH_3), 17.67 (C-7′, *Z*-methyl) and 16.79 (2′-CH_3). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.01; H, 10.84.

***t*-2-(1*Z*-2,6-dimethylhepta-1,5-dienyl)-*t*-3-methyltetrahydrofuran-*r*-3-ol (15a):** ν_{max}(film) 3428, 1378 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.06 (2 H, m, H-1′ and H-5′), 4.38 (1 H, d, *J* 9 Hz, H-2), 3.94 (2 H, dd, *J* 6 and 8 Hz, H-5), 2.2-1.9 (6 H, m, H-3′, H-4′ and H-4), 1.76 (3 H, d, *J* 1.5 Hz, CH_3-C=), 1.68 (3 H, s, CH_3-C=), 1.60 (3 H, s, CH_3-C=) and 1.25 (3 H, s, 3-CH_3); δ_C (50 MHz, $CDCl_3$) 141.01 (C-2′), 132.01 (C-6′), 124.01 (C-5′), 122.64 (C-1′), 83.92 (C-2), 79.63 (C-3), 65.47 (C-5), 40.59 (C-4), 32.41 (C-3′), 26.92 (C-4′), 25.70 (C-7′, *E*-methyl), 23.71 (2′-CH_3), 23.13 (3-CH_3) and 17.69 (C-7′, *Z*-methyl). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.85; H, 10.94.

Photoreaction of Aldehydes (10b) and (11b)

(a) A solution of aldehyde (**10b**) (4.50 g) in benzene (400 ml) was irradiated (450 W Hg arc, quartz apparatus) for 1 h. Evaporation and column chromatography (ether/toluene 1:3 v/v) of the residue gave recovered aldehyde (**10b**) (2.50 g, containing 20% **11b** by ^1H n.m.r.), followed in order of elution by (**12b**) (0.50 g, 25%) and (**14b**) (0.51 g, 26%).

(b) A similar irradiation of aldehyde (**11b**) (1.00 g) in benzene (200 ml) was carried out for 0.5 h. Evaporation and column chromatography (ether/toluene 1:3 v/v) of the residue gave recovered aldehyde (**11b**) (0.79 g, containing 6% **10b** by ^1H n.m.r.), followed in order of elution by (**15b**) (45 mg, 21%) and (**13b**) (90 mg, 43%).

***c*-2-(1*E*-2,6-dimethylhepta-1,5-dienyl)-tetrahydrofuran-*r*-3-ol (12b):** ν_{max}(film) 3415 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.29 (1 H, dd, *J* 1 and 7 Hz, H-1′), 5.08 (1 H, m, H-5′), 4.43 (1 H, dd, *J* 3.5 and 7 Hz, H-2), 4.25 (1 H, m, H-3), 4.08 (1 H, q, *J* 8 Hz, H-5), 3.80 (1 H, dt, *J* 5 and 8 Hz, H-5), 2.2-1.8 (7 H, m, H-3′, H-4′, H-4 and OH), 1.69 (6 H, s, 2 x CH_3-C=) and 1.60 (3 H, s, CH_3-C=); δ_C (50 MHz, $CDCl_3$) 141.53 (C-2′), 132.19 (C-6′), 123.87 (C-5′), 120.04 (C-1′), 80.47 (C-2), 72.94 (C-3), 65.99 (C-5), 39.71 (C-3′), 35.16 (C-4), 26.28 (C-4′), 25.67 (C-7′, *E*-methyl), 17.69 (C-7′, *Z*-methyl) and 17.11 (2′-CH_3). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55. Found: C, 74.47; H, 10.74.

***c*-2-(1*Z*-2,6-dimethylhepta-1,5-dienyl)-tetrahydrofuran-*r*-3-ol (13b):** ν_{max}(film) 3421, 1044 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.32 (1 H, dd, *J* 1.5 and 8.2 Hz, H-1′), 5.09 (1 H, m, H-5′), 4.40 (1 H, dd, *J* 3.7 and 8.2 Hz, H-2), 4.21 (1 H, m, H-3), 4.06 (1 H, q, *J* 8 Hz, H-5), 3.78 (1 H, dt, *J* 4.7 and 8.5 Hz, H-5), 2.25-1.9 (6 H, m, H-3′, H-4′ and H-4), 1.81 (3 H, d, *J* 1.5 Hz, CH_3-C=), 1.70 (3 H, s, CH_3-C=) and 1.62 (3 H, s, CH_3-C=); δ_C (50 MHz, $CDCl_3$) 142.17 (C-2′), 132.28 (C-6′), 123.69 (C-5′), 120.48 (C-1′), 79.89 (C-2), 73.55 (C-3), 65.90 (C-5), 35.39 (C-4), 32.94 (C-3′), 26.63 (C-4′), 25.67 (C-7′, *E*-methyl), 23.62 (2′-CH_3) and 17.69 (C-7′, *Z*-methyl). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55. Found: C, 74.43; H, 10.74.

***t*-2-(1*E*-2,6-dimethylhepta-1,5-dienyl)-tetrahydrofuran-*r*-3-ol (14b):** ν_{max}(film) 3402, 1103, 1047 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.08 (2 H, m, H-1′ and H-5′), 4.42 (1 H, dd, *J* 3.5 and 8.5 Hz, H-2), 4.06 (1 H, m, H-3), 3.96 (2 H, m, H-5), 2.45 (1 H, bs, OH), 2.2-1.9 (6 H, m, H-3′, H-4′ and H-4), 1.74 (3 H, d, *J* 1.5 Hz, CH_3-C=), 1.68 (3 H, s, CH_3-C=) and 1.60 (3 H, s, CH_3-C=); δ_C (50 MHz, $CDCl_3$) 140.83 (C-2′), 131.66 (C-6′), 123.92 (C-5′), 123.05 (C-1′), 82.87 (C-2), 77.32 (C-3), 66.11 (C-5), 39.65 (C-3′), 34.89 (C-4), 26.43 (C-4′), 25.67 (C-7′, *E*-methyl), 17.70 (C-7′, *Z*-methyl) and 16.88 (2′-

CH_3). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55. Found: C, 74.38; H, 10.69.

***t*-2-(1*Z*-2,6-dimethylhepta-1,5-dienyl)-tetrahydrofuran-*r*-3-ol (15b)**: ν_{max}(film) 3412, 1377 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.12 (2 H, m, H-1′ and H-5′), 4.38 (1 H, dd, *J* 3.7 and 8.9 Hz, H-2), 4.03 (1 H, m, H-3), 3.97 (2 H, m, H-5), 2.25-1.8 (6 H, m, H-3′, H-4′ and H-4), 1.76 (3 H, d, *J* 1.5 Hz, CH_3-C=), 1.69 (3 H, s, CH_3-C=) and 1.61 (3 H, s, CH_3-C=); δ_C (50 MHz, $CDCl_3$) 141.14 (C-2′), 132.16 (C-6′), 123.91 (C-5′), 123.84 (C-1′), 82.47 (C-2), 77.22 (C-3), 66.11 (C-5), 34.83 (C-4), 32.45 (C-3′), 26.83 (C-4′), 25.67 (C-7′, *E*-methyl), 23.53 (2′-CH_3) and 17.69 (C-7′, *Z*-methyl). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55. Found: C, 74.19; H, 10.66.

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