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PHOTOCHEMICAL TRANSFORMATIONS—II†

ORGANIC IODIDES—II:‡ CITRONELLYL IODIDE, 2,3-DIHYDRO-6(*Z*)-FARNESYL AND 2,3-DIHYDRO-6(*E*)-FARNESYL IODIDES§

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Abstract—Experimental parameters governing π-electrons participation during photolysis of citronellyl iodide have been investigated. Photoproducts resulting from irradiation of 2,3-dihydro-6(*Z*)- and 2,3-dihydro-6(*E*)-farnesyl iodides have been characterised.

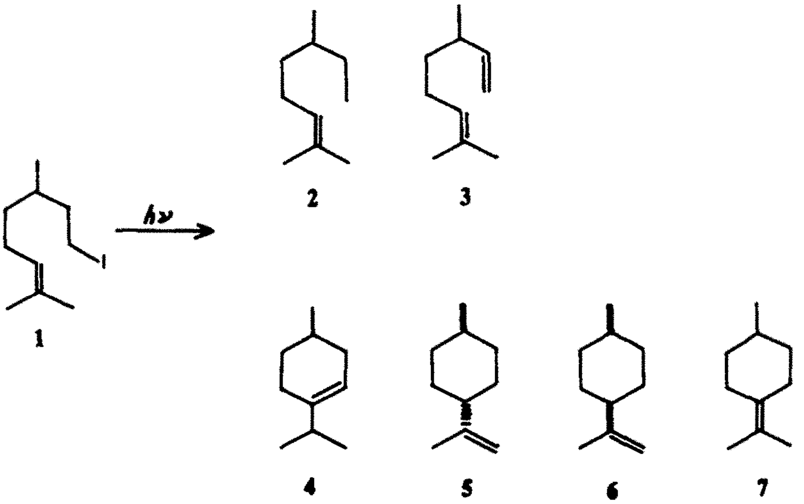
In our earlier communication,[1] it was reported that photo-irradiation of citronellyl iodide (1) led to both simple elimination (to furnish 2,6-dimethylocta-2,7-diene) and π-participation (to yield *trans-p*-menth-8-ene). The reaction was visualised as proceeding by way of initial homolytic photodissociation, followed by a rapid electron-transfer process in the solvent cage, to furnish a carbocation, which then undergoes its characteristic reactions. Before extending the cyclisation reaction to other systems of possible biomimetic interest, it was thought worthwhile to first delineate parameters for optimal cyclisation. This aspect has now been investigated using citronellyl iodide as the substrate, and the reaction has been extended to 2,3-dihydro-6(*Z*)-farnesyl and 2,3-dihydro-6(*E*) farnesyl iodides. The present communication summarises results of these investigations.

Citronellyl iodide. Table 1 summarises the results of a brief investigation on the effect of temperature, solvent, and intensity of radiation on the total yield of the cyclisation products (4 + 5 + 6 + 7) arising from photo-irradiation of citronellyl iode (1). A distinct temperature effect, noted in the earlier investigation,[1] is confirmed. Temperature effects in solution photochemical transformations are now well-recognised[2] and have been attributed[2a] to temperature dependence of primary and secondary chemical processes from the excited state.

In more polar solvents (tetrahydrofuran, triethylamine), the reaction is faster and higher amounts of cyclisation products are formed, as compared to the reaction in n-heptane (Table 1).

In the previous investigation,[1] wherein a 250 W lamp was used, instead of the 125 W lamp now employed, the yields of the cyclisation products (solvent, n-heptane; temp, 60°) were higher (~55%). Speculating, that this may be due to the difference in the intensity of the radiation, two experiments (solvent, n-heptane; temp, 50°) using 125 and 400 W lamps were carried out and the results (entries 2, 6, Table 1) clearly point to some sort of photon flux[3] effect, though any mechanistic explanation is not apparent.

It may be noted that in all the above experiments (except for the entry No. 5, Table 1), the yield of the total distilled product remains essentially constant. Thus, the small differences in the yield of the cyclisation



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† Part I: *Tetrahedron* 32, 1391 (1976).

‡ Part I of this series to be treated as "Organic Iodes (Part 1)".

§ MRC Communication No. 19.

Table 1. *Photo-irradiation of citronellyl iodide:[*] effect of temperature, solvent and photon flux*

No	Solvent	Temp.[+]	Lamp[‡] (watts)	Time[#] (hr)	Product Composition (%, GLC)[§] Relative Retention time							Product[¶] yield (%)	Total Cyclization products (%)
					RRT: 1.00	1.13	1.38	1.50	1.63	2.00	2.25		
					 2	 3	Unknown	 4	 5	 6	 7		
1	n-Heptane	25°	125	23	2.8	64	2	0	27	2	1.5	68.5	31
2	n-Heptane	50°	125	23	3	60	2	0	30	2.5	1.5	68.0	34
3	n-Heptane	70°	125	22	4	46	3	0	41	4	1.8	68.0	47
4	Tetrahydrofuran	25°	125	9	6.5	49.5	6	0	33	2	2	69.5	37
5	Triethylamine	25°	125	12	8.5	41.5	5	0	33.5	5.5	6	57	45
6	n-Heptane	50°	400	22	5	49	4.5	0	35.5	4	2	68.5	41.5
7	Tetrahydrofuran	50°	400	8	9	27	8	2	36	7	10	74	54

[*] 0.9 gm of the iodide in 90 ml of solvent containing Et_3N (0.85 ml) as HI scavenger (except for expt. No. 5); 2.4 g of the iodide in 240 ml of solvent containing 1% Et_3N was used for expt. Nos. 6 and 7.

[+] Jacket-water temperature.

[‡] Medium-pressure mercury vapour lamps.

[#] Time taken for disappearance of the substrate (t.l.c.)

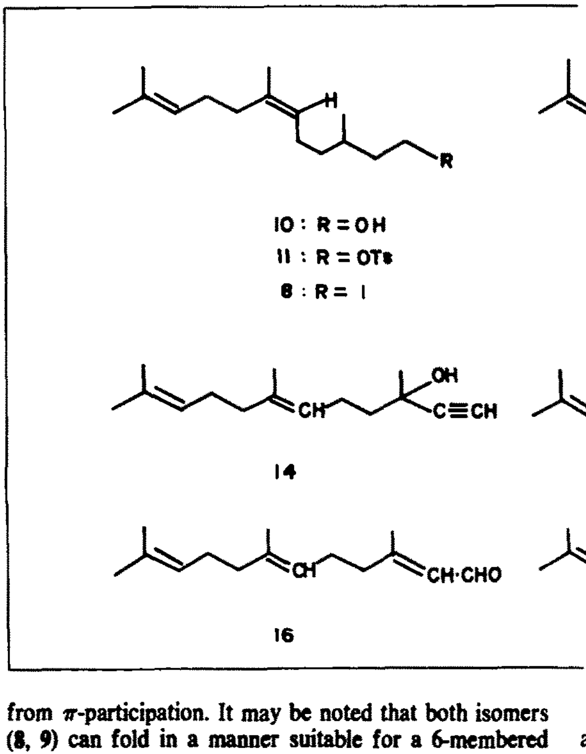
[§] Column: 360 cm x 0.6 cm Al column, packed with 10% carbowax on 60-80 mesh Chromosorb W; temp.: 100°; carrier gas: 60 ml H_2/min.

[¶] Total distilled product (% computed on the basis of elimination of HI) products are meaningful and are not due to any possible greater propensity of the diene (**3**) to polymerisation.

From the above considerations and from practical point of view, the following parameters were selected for work on other substrates: *solvent*, tetrahydrofuran; *temp*, 50°; *light source*, 400 W lamp. Under these conditions, citronellyl iodide gave maximum amount (54%) of cyclised products (entry 7, Table 1). Under these conditions, a small percentage of 3-methene (**4**) could also be detected.

A distinct difference between the present set of experiments and the previous results[1] is the consistent formation of 2,6-dimethyl-oct-2-ene (**2**) under all conditions investigated (Table 1). Since formation of **2** has obvious implications on the mechanism of this photoreaction (Discussion), we have specifically looked for this compound in the earlier investigation, but was always found to be absent.[5] The identity of **2** was confirmed by preparing an authentic sample by LAH reduction of citronellyl iodide and mixed glc on 3 different columns.

2,3-Dihydrofarnesyl iodide. As an obvious extension of this photochemical reaction, photolysis of both 6(*Z*), and 6(*E*) 2,3-dihydrofarnesyl iodides has been investigated, to see the extent of product development from π-participation. It may be noted that both isomers (**8**, **9**) can fold in a manner suitable for a 6-membered ring-closure (**8a**, **9a**); the possible participation of the other olefinic linkage (**8b**, **9b**) to generate a 10-membered cycle, is considered remote.[6]


10 : R = OH
11 : R = OTs
8 : R = I

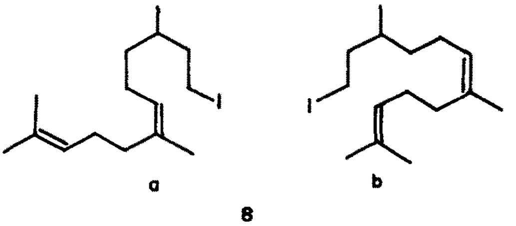
12 : R = OH
13 : R = OTs
9 : R = I

14

15

16

17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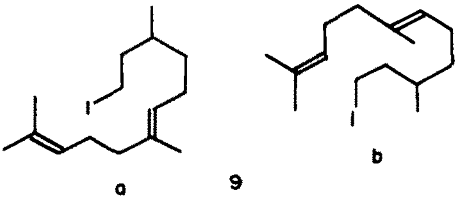
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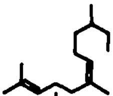
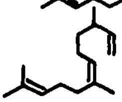
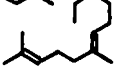
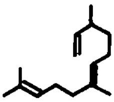
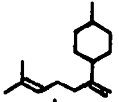
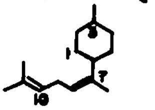
For the preparation of 2,3-dihydro-6(*Z*)-farnesol (**10**) and 2,3-dihydro-6(*E*)-farnesol[7] (**12**) required for the present work, the rearrangement of dehydronerolidol (**14**) to farnesal (**16**), described by Isler *et al.*,[8] was adopted after some modifications. In our hands, hydrolysis of the allenic acetate (**15**; mixed with some diacetate) arising from silver-catalysed rearrangement of **14**, was always incomplete with Na_2CO_3 and was best accomplished by an exchange reaction with NaOMe in methanol. Though, reduction of farnesal to 2,3-dihydrofarnesol (**17**) with sodium and amyl alcohol,[9] or with sodium and ammonia followed by exposure to LAH[7c] has been accomplished with varying degree of selectivity, we have, more conveniently and selectively, carried out this transformation with Raney-Ni alloy and alkali.[10]

The product **17**, thus obtained, was a mixture [11] of 6(*Z*) and 6(*E*) isomers in the ratio of ~1:2, and was readily separated by chromatography on $AgNO_3$–SiO_2 gel.

The dihydrofarnesol isomers (**10**, **12**), were next converted to the required iodides **8**, **9**, through the tosylates (**11**, **13**).

A 1% solution of 2,3-dihydro-6(*Z*)-farnesyl iodide (**8**) in tetrahydrofuran containing some triethylamine was irradiated (N_2) till a photostationary state was reached (4 hr). The product (yield, 80%) consisted of at least seven constituents, of which three accounted for ~84% of the material (Table 2). By preparative glc these major products, could be obtained pure and could be characterised as **19**, **20** and **21** (Table 2) on the basis of their spectral characteristics. None of these compounds ap-

Table 2. Products from photolysis of 2,3-dihydrofarnesyl iodides*

GLC Component^{+} Product from (isomer) 6(Z)	GLC Component^{+} Product from (isomer) 6(E)	Relative retention time (RRT)	Product		Product Composition (%, GLC)$^{+}$ from (isomer) 6(Z)	Product Composition (%, GLC)$^{+}$ from (isomer) 6(E)
1	-	0.37	Unidentified		5	-
2	-	0.47		18	5.5	-
3	-	0.54		19	22.5	-
-	1	0.54		22	-	6
-	2	0.60		23	-	35
4	3	0.77	Unidentified		3.5	2
5	4	0.85		20	40	37
6	5	1.00		21	21.5	18
7	6	1.14	Unidentified		2	2

*1% soln in tetrahydrofuran; 400 watts lamp; temp. of irradiation, 50°

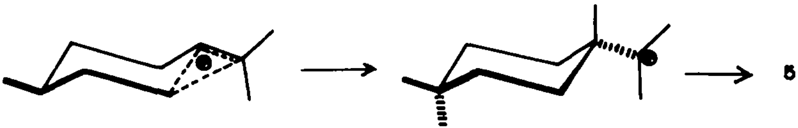
$^{+}$Column: 360 cm x 0.6 cm Al column, packed with 10% diethylene glycol polysuccinate on 60–80 mesh Chromosorb W; temp. 140°; carrier gas: 60 ml H_2/ min.

pear to have been described in the literature; however, the structures were obvious from their spectral data (IR, PMR, Mass) (Experimental). The glc component 2 (RRT = 0.47) was identified as 3,7,11-trimethyl-dodeca-6(*Z*), 10-diene (**18**) by mixed glc, on three different columns, with an authentic sample obtained from LAH reduction of the starting iodide (**8**). The remaining three components (glc components 1,4 and 7; Table 2) could not be obtained sufficiently pure for unequivocal identification.

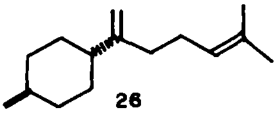
Likewise, photoirradiation of 2,3-dihydro-6(*E*)-farnesyl iodide (**9**) led to the generation of at least six compounds, and of these, four (accounting for ~96% of the product) were identified as **22**, **23**, **20** and **21** (Table 2), by following exactly the methodology described in some detail for the 6(*Z*) isomer. The elimination product (**23**) has been mentioned in the literature,[12] but no data were reported.

When either **8** or **9** in tetrahydrofuran containing some triethylamine was kept in the *dark* at ~30° for 28 hr, no change was detected.

At this stage, a brief reference to the stereochemistry of **20** and **21** would be in order. Both **20** and **21** can have *cis* or *trans* stereochemistry (with regard to the ring Me) and, in addition, **21**, can be (*Z*)-or (*E*)-configurated at Δ.[7] However, in view of the unequivocal assignment of *trans*-configuration (**5**) to the by far the major cyclisation product from the photoirradiation of citronellyl iodide (Table 1), it is obvious that the preferred conformation for this cyclisation reaction would be **24** leading to the



24 25



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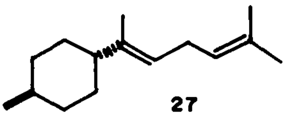

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observed stereochemistry in the product. In view of this, the major products (**20**, **21**) arising from the cyclisation of the related iodide **8** (and **9**) are also assigned the *trans*-configuration (**26**, **27**), the (*E*)-geometry for Δ^7 in **27** being preferred because of similar known results in a closely related system.[13] It is quite likely that the unidentified constituents (RRT: 0.77, 1.14) are stereoisomers of **26**, **27**.

It has now been recognised[14] for sometime that in acyclic isoprenoids there are useful, though small, differences in the chemical shifts of the vinylic Me in a (*E*), (*Z*) pair. During the course of the present investigation it was noted, in full confirmation of the above, that in the pairs **10**/**12**, **11**/**13**, **8**/**9**, **18**/**22**, and **19**/**23**, the signal due to the Me on C-7 was always at 1.67 ppm for the (*Z*)-isomer and at ~ 1.60 ppm for the (*E*)-isomer.

DISCUSSION

In our previous publication[1] we had suggested, in agreement with Kropp *et al.*,[15] that it was conceivable that products from solution photolysis of some iodides arise by way of initial homolytic photodissociation, followed rapidly by a fast electron-transfer reaction in the solvent cage to a "hot" carbocation. Since then, additional support for competing radical and ionic pathways during the photoirradiation of a number of alkyl iodides has been forthcoming.[16–18]

The results described in the present communication lend further support to the above. The formation of the "reduced" products **2**, **18**, **22** are typical of a radical pathway, as arising from the abstraction of an H atom by the radical from the solvent; the increase in the amount of **2** being formed as the solvent changes from n-heptane → tetrahydrofuran → triethylamine (Table 1) is consistent with the increasing ease of the ability of the solvent to part with an H atom.[19] The cyclisation is best interpreted in terms of a cationic species and the observed enhancement in the cyclisation with increasing polarity of the solvent (Table 1) is in accord with such a mechanism.

EXPERIMENTAL

All b.ps are uncorrected. All solvent extracts were finally washed with brine before drying (Na_2SO_4).

The following instruments were used for spectral/analytical data: Perkin–Elmer IR spectrophotometer, model 267; Perkin–Elmer, model R32 (90 MHz) NMR spectrometer; Varian Mat CH7 mass spectrometer (70 eV, direct inlet system); Hewlett–Packard 5712A (for analytical use; Al columns, 360 × 0.6 cm; support, 60–80 mesh Chromosorb W; stationary phase, 10% Carbowax, unless stated to the contrary; carrier gas, H_2) or 7624A (for preparative glc; Al columns, 360 × 0.9 cm; stationary phase, 20% Carbowax on 45–60 mesh Chromosorb W; carrier gas, 100 ml H_2/min) gas chromatographs. IR spectra were recorded on smears or in CCl_4 soln. All PMR spectra were recorded with 15–20% soln in CCl_4 with TMS as internal standard; signals are reported in ppm (δ); while citing PMR data, following abbreviations have been used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. While summarising mass spectral data, besides the molecular ion, ten most abundant ions (*m*/*e*) are reported with their relative intensities.

Solvents used in photoirradiation were purified as under;

n-*Heptane*: by stirring with conc H_2SO_4–HNO_3 (1 : 1), washing, drying and passing through Al_2O_3–I.[20] *Tetrahydrofuran*: by refluxing and distilling over LAH.[21] *Triethylamine*: by refluxing with KOH pellets and distilling over Na.[22]

General procedure for photoirradiation. Photoirradiation was carried out with Applied Photophysics medium-pressure[23] mercury lamps 100 LQ (125 W) or 400 LQ (400 W), suspended in a double-walled, water-cooled, clear-fused quartz well, without filter. The substrate was used at 1% concentration in appropriate solvent, containing molar equivalent of triethylamine. A minute, steady flow of oxygen-free N_2 was passed through the soln. The reaction was monitored by tlc (10% benzene in pet. ether). When the photostationary state was reached (4–23 hr), the mixture was worked up by washing with water, followed by 5% $Na_2S_2O_3$ aq. The solvent was carefully stripped off through an efficient Vigreaux column. The product so obtained was passed throgh a short column of SiO_2–gel/IIB[24] and eluted with pet. ether. The hydrocarbon mixture obtained by removing the pet. ether was distilled *in vacuo* and the individual compounds identified by mixed glc with authentic samples on at least three stationary phases (10% carbowax; 10% SE-30; 10% diethyleneglycol polysuccinate) or by isolation by preparative glc and analysis of spectral data. In photolysis experiments in THF or Et_3N soln, the solvent was first stripped through a column, the residue passed through a column of SiO_2–gel, eluted with pet. ether and the pet. ether soln subjected to the above aqueous work up.

2.6-*Dimethyl-oct-2-ene* (**2**). Citronellyl iodide (0.7 g, 0.0026 mole) in dry THF (3 ml) was added to a suspension of LAH (0.08 g) in dry THF (3 ml) and the mixture refluxed for 5 hr, when the reduction was complete (tlc, 10% benzene in pet. ether). The excess of LAH was destroyed with ice-cold 5% NaOH, the soln filtered, residue washed with ether (20 ml) and the filtrate extracted with Et_2O (20 ml × 3). The combined Et_2O extract was washed with water till neutral. Careful solvent removal followed by distillation afforded **2** (0.3 g, 97% pure; glc) as a colourless liquid; b.p. 109.5–110° (bath)/94 mm, n_D^{25} 1.4335 (Lit.[25] b.p. 59°/12 mm; n_D^{20} 1.4330). IR (film): 1650, 830 cm^{-1}. PMR: $CH_3{\cdot}CH$, $CH_3{\cdot}CH_2$ (6 H, m, overlapping d & t at 0.9 ppm), $(CH_3)_2C{=}C$ (3 H singlets at 1.59 and 1.67 ppm), $CH{=}C(CH_3)_2$ (1 H, ill-resolved t, 5.05 ppm). MS: *m*/*e* 140 (M^+, 26%), 69 (100%), 41 (82%), 70 (67%), 55 (65%), 56 (53%), 43 (38%), 57 (23%), 83 (19%), 111 (10%).

Farnesal(*s*) (**16**). Dehydronerolidol(s) (10 g, 0.045 mole) was acetylated with Ac_2O (8.03 g, 0.079 mole) and H_3PO_4 (0.115 g) and the acetate (without isolation) rearranged by treatment with glacial AcOH (19.9 g) and Ag_2CO_3 (0.05 g) under Isler's[8] conditions, to afford the crude **15** containing diacetate as a pale yellow oil (12.98 g). This acetate (12.98 g) was added to a soln of NaOMe (0.924 gm Na dissolved in 308 ml MeOH) and the mixture kept at room temp (~ 30°) for 1 hr. The mixture was poured into water (200 ml), saturated with NaCl and extracted with Et_2O (75 ml × 3). The Et_2O extract was washed (till neutral) with water. Solvent removal furnished crude farnesal (8.5 g, 85% yield based on **14**). A small quantity (1.3 g) on distillation (169–71°, bath/14 mm) gave farnesal(s) (1.03 g, 90% pure; glc) as a colourless oil.

Dihydrofarnesol(*s*) (**17**). Farnesal(s) (**16**) (7.15 g) and Ni–Al alloy (36.7 g) were added simultaneously in portions (0.5 g and 2 g respectively) to a well-stirred soln of 2 N NaOH (461 ml) and MeOH (229 ml) at 0–2°, during 6 hr. The rest of Ni–Al alloy was added in portions at 0–2° during 2 hr and stirring was continued (1 hr) at 10°. The mixture was filtered, residue washed with Et_2O (40 ml), the aqueous filtrate saturated with NaCl and extracted with Et_2O (75 ml × 3). The combined Et_2O extract was washed with water (till neutral). Solvent removal gave crude dihydrofarnesol(s) (6.76 g) which was freed from impurities by passing through a column of SiO_2-gel (IIB, 53 × 3 cm) and eluting with pet. ether containing increasing proportions of benzene. Elution with pure benzene afforded 91.5% (glc) pure dihydrofarnesol(s) **17** (4.17 g) as a colourless liquid.

The pure 6(*Z*)- and 6(*E*)-isomers (**10** and **12**) were isolated by column chromatography of **17** (6.3 g, from 2 expts.) on 15% $AgNO_3$–SiO_2 gel (~ IIB; 2.5 × 125 cm).

Fr. 1	Benzene	150 ml × 16	0.2 g	Less polar impurities
Fr. 2	Benzene + 5–10% EtOAc	150 ml × 8	0.2 g	~80% pure **10** (glc)
Fr. 3	Benzene + 10% EtOAc	150 ml × 12	1.8 g	pure **10** (glc)

Fr. 4	Benzene + 10% EtOAc	150 ml × 11	1.1 g	Mixture of **10** and **12**
Fr. 5	Benzene + 10 EtOAc	150 ml × 11	2.0 g	Slightly impure **12** (purified by rechromatography on 15% $AgNO_3$–SiO_2 gel)
Fr. 6	Benzene + 10% EtOAc	150 ml × 3	0.6 g	Pure **12** (glc)

2,3-*Dihydro*-6(Z)-*farnesol* (**10**) was obtained by distillation of Fr. 3 as a colourless oil: b.p. 124°/1.5 mm, n_D^{25} 1.4724 IR (film): 3300, 1055, 830 cm^{-1}. PMR: CH_3·CH (3 H, d, 0.89 ppm, J = 6 Hz), three CH_3·C=C (9 H; 3 H, s, 1.6 and 6 H, s; 1.67 ppm), CH_2·OH (2 H, t, 3.6 ppm, J = 7 Hz), two HC=C (2 H, ill resolved t, 5.05 ppm).

2,3 *Dihydro* 6(E)-*farnesol* (**12**) was obtained by distillation of Fr. 6 as a colourless oil: b.p. 124–124.5°/1.5 mm, n_D^{25} 1.4728. IR (film): 3300, 1058, 830 cm^{-1}. PMR: CH_3·CH (3H, d, 0.89 ppm, J = 6 Hz), three CH_3·C=C (9 H; 6 H, s, 1.6 and 3 H, s, 1.67 ppm), CH_2·OH (2 H, t, 3.6 ppm, J = 7 Hz), two HC=C (2 H, ill resolved t, 5.05 ppm).

Dihydrofarnesyl tosylates

2,3-*Dihydro*-6(Z)-*farnesyl tosylate* (**11**). To a cooled soln (0–2°) of 2,3-dihydro 6(*Z*)-farnesol (0.9 g, 0.004 mole) in dry pyridine (4 ml) was added *p*-toluenesulphonyl chloride (1.2 g, 0.006 mole) in portions under intermittent shaking of the mixture which was then kept at ~5° for 18 hr. The mixture was poured into crushed ice, extracted with Et_2O (25 ml × 3) and the combined Et_2O extract washed with 10% HCl (5 ml × 3), followed by water. The solvent was flashed off at room temp (~30°) under reduced pressure to furnish **11** (tlc single spot), as a colourless, viscous liquid. (1.354 g). IR (CCl_4): C=C 1600 cm^{-1}, C–SO_2–O–C 1350, 1178 cm^{-1}. PMR: CH_3·CH (3 H, d, 0.84 ppm, J = 6 Hz), three CH_3·C=C (9 H; 3 H, s, 1.59 and 6H, s, 1.67 ppm), CH_3·Ar (3 H, s, 2.44 ppm), CH_2·OSO_2 (2 H, t, 4.01 ppm, J = 6 Hz), two HC=C (2 H, m, 4.9–5.2 ppm), H·Ar (4 H; 2 H, d, 7.28, J = 8 Hz; 2 H, d, 7.74 ppm, J = 8 Hz). (Found: C, 70.06; H, 8.68. $C_{22}H_{34}O_3S$ requires: C, 69.84; H, 8.99%).

2,3-*Dihydro*-6(E)-*farnesyl tosylate* (**13**). By the same procedure as above, 2,3-dihydro-6(*E*)-farnesol (0.9 g) furnished the corresponding **13** as a colourless, viscous liquid (1.4 g). IR (CCl_4): C=C 1600 cm^{-1}, C–SO_2–O–C 1350, 1175 cm^{-1}. PMR: CH_3·CH (3 H, d, 0.84 ppm, J = 6 Hz), three CH_3·C=C (9 H; 6 H, s, 1.59 and 3 H, s, 1.68 ppm), CH_3·Ar (3 H, s, 2.45 ppm), CH_2·OSO_2 (2 H, t, 4.1 ppm, J = 6 Hz), two HC=C (2 H, m, bet 4.9–5.2 ppm), H·Ar (4 H; 2 H, d, 7.35, J = 8 Hz; 2 H, d, 7.82 ppm, J = 8 Hz). (Found: C, 69.55; H, 8.72. $C_{22}H_{34}O_3S$ requires: C, 69.84; H, 8.99%).

Dihydrofarnesyl iodides

2,3-*Dihydro*-6(Z)-*farnesyl iodide* (**8**). A mixture of 2,3-dihydro-6(*Z*)-farnesyl tosylate (1.328 g, 0.0035 mole) and dry NaI (2.1 g, 0.014 mole) in dry acetone (15 ml) was stirred at room temp (~30°) under tlc monitoring (pet. ether) for 14 hr, when the reaction was complete. The bulk of the solvent was stripped off and the residue treated with water (25 ml), the product taken up in Et_2O (30 ml × 3). The combined Et_2O extract was washed with 10% $Na_2S_2O_3$aq (10 ml) and water. The solvent was distilled off and the residue distilled to furnish **8** as a pale yellow oil (1.03 g): b.p. 133.5–134°/1.2 mm, n_D^{25} 1.5060, $\lambda_{max}^{heptane}$ 259 nm (ε, 510). PMR: CH_3·CH (3 H, d, 0.9 ppm, J = 6 Hz), three CH_3·C=C (9 H; 3 H, s, 1.6 and 6 H, s, 1.67 ppm), CH_2·I (2 H, m, bet 3.04–3.30 ppm), two HC=C (2 H, ill resolved, t, 5.07 ppm). (Found: C, 54.19; H, 7.83. $C_{15}H_{27}I$ requires C, 53.93; H, 8.08%).

2,3-*Dihydro*-6(E)-*farnesyl iodide* (**9**). By following the above procedure 2,3-dihydro-6(*E*)-farnesyl tosylate (1.32 g) afforded **9** as a pale yellow oil (1.02 g): b.p. 134°/1.2 mm, n_D^{25} 1.5060, $\lambda_{max}^{heptane}$ 259 nm (ε, 575). PMR: CH_3·CH (3 H, d, 0.91 ppm, J = 6 Hz), three CH_3·C=C (9 H; 6 H, s, 1.6 and 3 H, s, 1.67 ppm), CH_2·I (2 H, m, bet 3.04–3.34 ppm), two HC=C (2 H, ill-resolved, t, 5.08 ppm), (Found: C, 53.81; H, 8.21. $C_{15}H_{27}I$ requires C, 53.93; H, 8.08%).

3,7,11-*Trimethyldodeca*-6(Z),10-*diene* (**18**). Compound **8** (0.55 g, 0.00165 mole) in dry THF (3 ml) was reduced with LAH (0.06 g) in 3 ml dry THF (by the same procedure as was used for the reduction of citronellyl iodide to **2**) to afford **18** as a colourless oil, (0.3 g): b.p. 116–8°(bath)/2.5 mm, n_D^{25} 1.4529. IR(film): 1665, 830 cm^{-1}. PMR:CH_3·CH, CH_3·CH_2 (6 H, m, overlapping of d and t at 0.9 ppm), three CH_3·C=C (9 H; 3 H, s, 1.6 and 6 H, s, 1.67 ppm), two HC=C (2 H, ill resolved t, 5.05 ppm). MS: *m/e* 208 (M$^+$, 14%), 69 (100%), 41 (49%), 83 (35%), 123 (35%), 55 (33%), 95 (22%), 109 (15%), 165 (9%). (Found: C, 86.42; H, 13.58. $C_{15}H_{28}$ requires: C, 86.54; H, 13.46%).

3,7,11-*Trimethyldodeca*-6(E),10-*diene* (**22**). Using the same procedure as for **18**, compound **9** (0.55 g) gave **22** as a colourless oil (0.31 g): b.p. 117–118° (bath)/2.5 mm, n_D^{25} 1.453. IR (film): 1665, 830 cm^{-1}. PMR: (CH_3·CH, CH_3·CH_2 (6 H, m, overlapping of d and t at 0.9 ppm), three CH_3·C=C (9 H; 6 H, s, 1.6 and 3 H, s, 1.67 ppm), two HC=C (2 H, ill resolved t, 5.04 ppm). MS: *m/e* 208 (M$^+$, 34%), 69 (100%), 123 (78%), 83 (67%), 41 (61%), 55 (48%), 95 (28%), 109 (20%), 165 (13%). (Found: C, 86.52; H, 13.5. $C_{15}H_{28}$ requires: C 86.54; H, 13.46%).

Photoirradiation of 2,3-*dihydro*-6(Z)-*farnesyl iodide* (**8**)

A soln of compound **8** (2.2 g) in purified THF (220 ml), containing triethylamine (2.2 ml) was irradiated (N_2) using a 400 W lamp as described under "General Procedure" and the total product worked up and distilled to afford a colourless liquid (1.09 g; b.p. 140–175(bath)/5.8 mm) and a residue (0.14 g). The major compounds having RRT 0.54, 0.85 and 1.0 were isolated by preparative glc (temp 170°) and identified as **19**, **20** and **21** respectively.

3,7,11-*Trimethyldodeca*-1,6(Z),10-*triene* (**19**) was a colourless oil, b.p. 120–2°(bath)/2.5 mm, n_D^{25} 1.4598. IR (film): 1630, 905, 825 cm^{-1}. PMR: CH_3·CH (3 H, d, 0.98 ppm, J = 7 Hz), three CH_3·C=C (9 H; 3 H, s, 1.59, 6 H, s, 1.67 ppm), CH_2=C, two HC=C (4 H, m, 4.8–5.2 ppm), CH_3·CH=CH_2 (1 H, octet 5.65 ppm). MS: *m/e* 206 (M$^+$, 8%), 69 (100%), 81 (61%), 95 (46%), 41 (43%), 55 (32%), 109 (22%), 123 (18%), 163 (13%). (Found: C, 87.3; H, 12.7. $C_{15}H_{26}$ requires: C, 87.38; H, 12.62%).

Dihydro-β-*bisabolene* (**20**) was a colourless oil, b.p. 125–7°(bath)/2.5 mm, n_D^{25} 1.4720. IR (CCl_4): 1640, 888, 830 cm^{-1}. PMR: CH_3·CH (3 H, d, 0.88 ppm, J = 6 Hz), two CH_3·C=C (6 H; singlets at 1.6 and 1.67 ppm), CH_2=C (2 H, d, 4.67 ppm, J = 3 Hz) HC=C (1 H, ill resolved t, 5.07 ppm). MS: *m/e* 206 (M$^+$, 56%), 81 (100%), 69 (94%), 109 (90%), 95 (63%), 163 (47%), 67 (40%), 82 (39%), 137 (29%). (Found: C, 87.22; H, 12.78. $C_{15}H_{26}$ requires: C, 87.38; H, 12.62%).

Dihydro-α-*bisabolene* (**21**) was a colourless oil, b.p. 135–7°(bath)/2.5 mm, n_D^{25} 1.4771. IR (CCl_4): 1660 cm^{-1} PMR: CH_3·CH (3 H, d, 0.9 ppm, J = 6 Hz), three CH_3·C=C (9 H; singlets at 1.62 and 1.69 ppm), =C–CH_2–C= (2 H, t, 2.63 ppm, J = 7 Hz), two H–C=C (2 H, t, 5.05 ppm, J = 7 Hz). This assignment was further confirmed by decoupling experiments. MS: *m/e* 206 (M$^+$, 36%), 109 (100%), 82 (54%), 95 (31%), 81 (31%), 69 (21%), 67 (18%), 55 (17%), 163 (14%). (Found: C, 87.3; H, 12.69. $C_{15}H_{26}$ requires: C, 87.38; H, 12.62%).

Photoirradiation of 2,3-*dihydro*-6(E)-*farnesyl iodide* (**9**)

A soln of **9**(2.8 g) in purified THF (280 ml) containing triethylamine (2.8 ml) was irradiated as described for **8**, the product worked up and distilled to afford a colourless liquid (1.4 g; b.p. 130–168(bath)/5 mm) and a residue (0.18 g). The major compounds having RRT 0.6, 0.85 and 1.0 were isolated by preparative glc and identified as **23**, **20** and **21** respectively on the basis of their spectral characteristics.

3,7,11-*Trimethyldodeca*-1,6(E),10-*triene* (**23**) was a colourless oil, b.p. 120–3°(bath)/2.5 mm, n_D^{25} 1.4635. IR (film): 1630, 907, 820 cm^{-1}. PMR: CH_3·CH (3 H, d, 0.98 ppm, J = 7 Hz), three CH_3·C=C (9 H; 6 H, s, 1.59 and 3 H, s, 1.67 ppm), CH_2=C, two HC=C (4 H, m, 4.8–5.2 ppm), CH_3–CH=CH_2 (1 H, octet, 5.67 ppm). MS: *m/e* 206 (M$^+$, 14%), 69 (100%), 41 (98%), 81 (98%), 95 (76%), 55 (64%), 123 (35%), 163 (30%), 109 (29%). (Found: C, 87.08, H, 12.29. $C_{15}H_{26}$ requires: C, 87.38; H, 12.62%).

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