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PHOTOCHEMICAL TRANSFORMATIONS—III[a]

ORGANIC IODIDES (Part 3): GERANYL AND NERYL IODIDES AND 2(*E*), 6(*E*)- AND 2(*Z*), 6(*E*)-FARNESYL IODIDES[b,c]

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Abstract—Solution photolysis of geranyl and neryl iodides, and 2(*E*), 6(*E*)- and 2(*Z*), 6(*E*)-farnesyl iodides has been carried out. Products arising from simple elimination as well as π-participation are formed. Thus, both geranyl and neryl iodides furnished, besides some unidentified compounds, myrcene, *cis*-ocimene, limonene and terpinolene, though in different proportions. Likewise, the sesquiterpene analogues yielded different amounts of *trans*-β-farnesene, β-bisabolene, *trans*-α-bisabolene and *ar*-curcumene. Results have been discussed in terms of ionic intermediates.

In earlier publications,[1,2] it was disclosed that citronellyl iodide and related dihydrofarnesyl iodides, on photo-irradiation, besides undergoing simple elimination (and minor reduction), lead to cyclohexane derivatives arising from π-participation. The experimental parameters for optimal cyclization were also delineated.[2] We now wish to report extention of this reaction to geranyl, neryl, 2(*E*), 6(*E*)-farnesyl, and 2(*Z*), 6(*E*)-farnesyl iodides (**3**, **6**, **9**, **12** respectively), substrates of biomimetic interest.[3] An additional interest attaches to the substrates, genanyl iodide and 2(*E*), 6(*E*)-farnesyl iodide, in which *E* geometry of the Δ^2 presents a barrier to cyclization to a 6-membered ring.

Preparation of substrates. A literature survey revealed that the iodides required for the present study have not hitherto been reported in literature.[4] Moreover, preliminary experiments revealed, though not surprisingly, that these allylic iodides are labile to heat, light and usual adsorbants. Hence, a method had to be developed to obtain these iodides pure, directly from the reaction work-up (without any additional purification step), and to use them immediately for photo-irradiation.

After several unsuccessful attempts,[6] a method of preparation of pure geranyl iodide (**3**) was evolved by converting pure geraniol (**1**) into its chloride **2** (*in situ* displacement of mesylate with LiCl in DMF[8]) followed by brief treatment of the distilled geranyl chloride with excess NaI in dry acetone, at low temp and with exclusion of light, the reaction being monitored by PMR (disappearance of $C\underline{H}_2Cl$ at δ4.0 and appearance of $C\underline{H}_2I$ at δ3.87). The same method could successfully be employed for the preparation of other required iodides **6**, **9** and **12**.

The farnesols **7** and **10** required for the present work were synthesised by acetylene addition[10] to pure (*E*)-geranylacetone (**13**) to furnish (*E*)-dehydronerolidol (**14**), which was converted to 2(*E*), 6(*E*)-, and 2(*Z*), 6(*E*)-farnesals by the modified[2] method of Isler *et al.*,[11] followed by LAH reduction to the two farnesols (**7**, **10**) mixture. Pure **7** and **10** were obtained from this mixture by preparative GLC.

Photoirradiation of geranyl and neryl iodides. A 1% soln of geranyl iodide (**3**) containing a molar equivalent of Et_3N was irradiated (N_2; 25°) to photostationary state (TLC, GLC monitoring; 6 hr) to furnish a product consisting of at least six components (Table 1). The major photoproduct, GLC component 4 (RRT = 1) and three minor ones 5, 6 and 8 (RRT = 1.30, 1.54 and 2.00 respectively) were identified, respectively, as myrcene (**15**), limonene (**16**), *cis*-ocimene (**17**) and terpinolene (**19**) by mixed GLC with authentic samples. Component 7 (RRT = 1.71) was identified as *trans*-ocimene (**18**) by correlation with GLC of the $KHSO_4$-dehydration products of linalool, which are firmly identified in the literature.[12]

Photolysis of neryl iodide (**6**), under identical conditions, generated a hydrocarbon mixture, consisting of at least seven components, five of which were readily identified in the same manner and the results are summarised in Table 1. As expected, the favourable 2(*Z*) geometry in neryl iodide led to a larger proportion of cyclized products—limonene (**16**) and terpinolene (**19**).

When photoirradiation of either **3** or **6** was carried out in THF (as 1% soln) at 50°, conditions more conducive to cyclization,[2] ratio of cyclic to elimination products improved from 0.05 to 0.11 for genanyl iodide (**3**) and from 0.56 to 0.87 for neryl iodide (**6**). The nature of components remained essentially unchanged.

No change was observed on keeping 1% hexane soln of either **3** or **6**, containing molar equivalents of Et_3N, in the dark at 30° for 20 hr and 7 hr respectively. However, in THF soln (10 hr; dark) and work-up by removal of solvent *in vacuo*, led to the isolation of stable solids, which were readily characterised on the basis of spectral and analytical data (Experimental) as the geranyl and neryl triethylammonium iodides **20** and **21** respectively.

Photoirradiation of 2(E), 6(E)- *and* 2(Z), 6(E)-*farnesyl iodides.* The above studies were next extended to the

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[a] Part II: *Tetrahedron* **36**, 1455 (1980).

[b] MRC Communication No. 42.

[c] Abstracted from the Ph.D. Thesis of K. M. Saplay, M.S. University, Baroda (1979).

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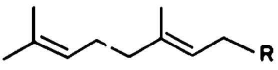
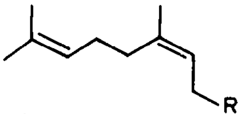


1: R = OH

2: R = Cl

3: R = I



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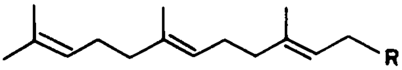
5: R = Cl

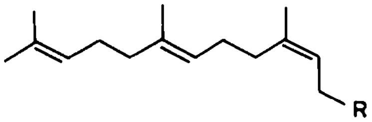
6: R = I



7: R = OH

8: R = Cl

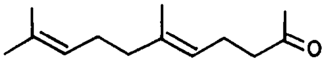
9: R = I



10: R = OH

11: R = Cl

12: R = I



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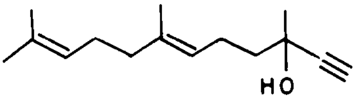

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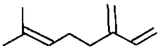
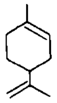
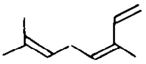
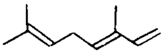
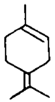
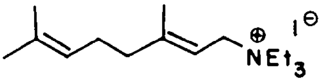
Table 1. Products from photolysis of geranyl and neryl iodides*

GLC Component^{+} Product from (isomer) 2(E)	 2(Z)	Relative retention time (RRT)	Product	Product composition (%, GLC) from (isomer) 2(E)	 2(Z)
1	-	0.16	Unidentified	12	-
-	2	0.30	Unidentified	-	1
3	3	0.50	Unidentified	5	2
4	4	1.00	 (15)	71	51
5	5	1.30	 (16)	4	27
6	6	1.54	 (17)	4	4
7	7	1.71	 (18)	4	7
-	8	2.00	 (19)	-	8

*1% soln in n-hexane; 125 watts medium pressure lamp; temp. of irradiation, 25°.

$^{+}$Column: 360 cm x 0.6 cm Al column, packed with 10% Carbowax 20M on 60-80 mesh Chromosorb W; temp. 100°; carrier gas: 60 ml H_2/min.



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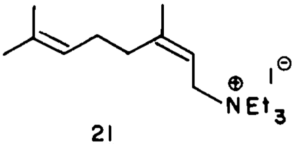

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sesquiterpene analogues: farnesyl iodides **9** and **12**. In the initial stages, photo-irradiations were carried out on the easily available mixture of **9** and **12** (5:4), under conditions "optimal[2]" for cyclization (THF, 50°). This product was separated by preparative GLC and the major component identified as *trans*-β-farnesene (**22**)[13], β-bisabolene (**23**)[14], *trans*-α-bisabolene (**24**)[14a,15] and *ar*-curcumene (**25**)[16] by spectral characteristics (IR, PMR and Mass). Pure **9** and **12**, as 1% heptane soln, were next irradiated and the products identified, making use of the compounds **22–25** isolated earlier in mixed GLC. Table 2 summarises the product composition, thus established.

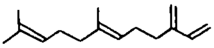
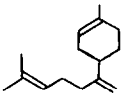
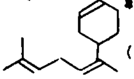
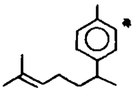
Dark reaction with pure **9** and **12** in heptane (in presence of triethylamine) did not show any change, whereas dark reaction in THF yielded the corresponding farnesyl triethylammonium iodides (*cf* **20**, **21**) as stable crystalline compounds.

DISCUSSION

Solvolysis of derivatives of geraniol, nerol and farnesols (and their allylic tertiary alcohol isomers: linalool and nerolidol) have been the subject of several investigations[15,17–34] in an effort to understand and simulate their biogenetically important[35] cyclizations to cyclic terpenes. Under a variety of reaction conditions and using different derivatives (alcohols,[24,30,32,33] halides,[27] *p*-nitrobenzoates,[28] phosphates,[15,25,32] pyrophosphates[25]) only isomerisation, elimination and cyclization to monocyclic 6-membered derivatives were observed. The ratio of elimination to cyclization is essentially dictated by the geometry of the 2,3-olefinic linkage, (*Z*)-isomers heryl, and 2(*Z*)-farnesyl leading largely to cyclic products, a fact easily understandable. These reactions have been rationalised in terms of ionic mechanisms and, anchimeric assistance,[15,25–37] from 6, 7 double bond, in case of (*Z*)-isomers, has been invoked to account for facile cyclization. The observed formation of some, albeit small, cyclization in case of geranyl and 2(*E*)-farnesyl derivatives, with unfavourable geometry of the 2,3 olefinic linkage has been explained by invoking intermediacy of linaloyl or nerolidyl derivative *via* an internal return mechanism; interconversion of allylic *E* and *Z* cations has been discounted[15,32] in view of considerable evidence for the configurational stability of allylic carbocations.[36]

The results obtained in the present investigations are strikingly similar to those obtained from solvolytic reactions, summarised above, and thus lend support to the ionic pathway as being the major source of product development from soln photolysis of alkyl iodides.[1,2,37] However, since an "internal return" mechanism for the cyclization of 2(*E*)-isomers during the photolysis re-

Table 2. Products from photolysis of (*E*,*E*)- and (*Z*,*E*)-farnesyl iodides*

GLC Component⁺ Product from (isomer)		Relative retention time (RRT)	Product	Product composition (%, GLC)	
(E,E)	(Z,E)			(E,E)	(Z,E)
1	1	0.80	Unidentified	1	19
2	2	0.90	Unidentified	1	5
3	3	1.00	 (22)	79.5	19
4	4	1.20	Unidentified	5	5
5	5	1.30	 (23)	12	38
6	6	1.60	 (24)	1.2	11
7	7	1.60	 (25)	0.3	3

*1% soln in n-heptane; 125 watts medium pressure lamp; temp. of irradiation, 25°.

⁺Column: 360 cm x 0.6 cm Al column, packed with 10% carbowax on 60-80 mesh Chromosorb W; temp. 150°; carrier gas: 60 ml H_2/min.

✱Since both compounds have the same RRT, under the conditions investigated, the relative proportions are based on PMR spectrum of the fraction, obtained by preparative GLC.

action cannot be considered as likely, an alternative rationalization is called for. In a previous study,[1] while comparing the products of solvolytic and photolytic transformation of longibornyl iodide, it was concluded that photolytic process generates the so-called "hot" carbonium ion.[38] Since "hot" carbonium ions are energy-rich and hence less discriminatory, the carbocations from the 2(*E*)-isomers, in the present case, may be expected to isomerise ($E \rightarrow Z$) to some extent, leading finally to some cyclization. In this connection, it may be noted that deamination[27] of geranylamine, a reaction which also generates[38] "hot" carbonium ions and where "internal return" is not possible, also gives some cyclization[39] to *p*-menthene system.

It may also be noted that photolysis of 2(*Z*), 6(*E*)-farnesyl iodide (**12**), like any solvolytic reaction, did not lead to any detectable amount of cyclization to 10-membered ring compounds, though this mode is quite frequent for enzymatic cyclization occurring in nature.[40]

EXPERIMENTAL

All m.ps and b.ps are uncorrected. All solvent extracts were finally washed with brine and dried over Na_2SO_4. Light pet. refers to fraction of b.p. 60–80°.

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) and 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 10–15% soln in CCl_4 with TMS as internal standard; signals are reported in ppm (δ); while citing PMR data the following abbreviations have been used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), b (broad).

Solvents used in photoirradiation were purified as under: n-Hexane, n-Heptane, by stirring with conc H_2SO_4–HNO_3 (1:1), washing, drying and passing through Al_2O_3/I;[41] tetrahydrofuran, by refluxing and distilling over LAH[42]; triethylamine, by refluxing over KOH pellets and distilling over Na[43].

Alcohols (**1**, **4**, **7**, **10**)

Geraniol (**1**) was separated from a commercial material by $CaCl_2$ adductation method[44] and was 95% pure (GLC), the balance being citronellol.

Nerol (**4**) was isolated by precise fractionation of a mixture of citronellol, nerol and geraniol (~3:3:4, obtained by Meerwein-Ponndorf[45] reduction of commercial citral) through a column of 80 theoretical plates, and was of ~93% GLC purity.

2(E), 6(E)-*Farnesol* (**7**), *and* 2(Z), 6(E)-*farnesol* (**10**). Commercial geranylacetone (36 g; *Z*-isomer:*E*-isomer/2:3) was carefully fractionated through an 80-plate spinning-band column at 9 mm to finally give 11.0 g of 100% (GLC) pure (*E*)-geranylacetone[46] (**13**) (b.p. 118–119°/9 mm). This material (17.8 g) in dry ether (18 ml) was next condensed[47] with acetylene in presence of t-AmOK[48] to get **14** in 94% yield. This product was next converted to a mixture of 2(*E*)-, and 2(*Z*)-farnesals (5:4) by a procedure, recently detailed by us.[2] The farnesal mixture (3.79 g, 0.017 mole), thus obtained, was added to a well-dispersed suspension of LAH (0.37 g, 0.0098 mole) in dry ether (15 ml) with stirring and cooling (~0°). After allowing the reaction to proceed at this temp for $2\frac{1}{2}$ hr, it was worked up in the usual manner (with ice-cold NaOH aq; ether) to furnish a product (3.5 g), which was distilled to get a central cut (2.7 g), b.p. 149–152° (bath)/1.3 mm, consisting of **7** and **10**. This product was next separated by preparative GLC (210°) to get **7** and **10**, each of ~93% GLC purity.

2(Z), 6(E)-*Farnesol* (**10**), b.p. 149–150° (bath)/1.3 mm. IR(CCl_4): 3380, 1660, 1225, 1145, 1100, 990, 828 cm^{-1}. PMR: Me–C = (1.60, 1.60, 1.68 and 1.74 ppm), $C\underline{H}_2OH$ (2H, *d*, 3.98 ppm, J = 7 Hz), C = C$\underline{H}$ (2H, ill-resolved *m*, 5.07 ppm; 1H, *t*, 5.38 ppm, J = 7 Hz) (lit. b.p.[47], PMR[49]).

2(E), 6(E)-*Farnesol* (**7**), b.p. 151–152 (bath)/1.3 mm. IR (CCl_4): 3400, 1665, 990, 829 cm^{-1}. PMR: $\underline{Me}$–C = (1.59, 1.59, 1.66 and 1.66 ppm), $C\underline{H}_2OH$ (2H, *d*, 4.02 ppm, J = 7 Hz), C = C$\underline{H}$ (2H, ill-resolved *m*, 5.05 ppm; 1H, *t*, 5.35 ppm, J = 7 Hz) (lit. b.p.,[47] PMR[49]).

Chlorides (**2**, **5**, **8**, **11**)

Of several methods,[50–52] now available, for preparation of allylic chlorides from allylic alcohols, without rearrangement, method of Collington and Meyers[52] proved convenient and effective. All four chlorides were prepared by this method on a 0.02 mole (or smaller) scale, and were pure.

Farnesyl chloride (**2**), yield, 86%; b.p. 59–60°/2.4 mm, n_D^{21} 1.4785. IR (liq.) 1670, 1257, 840 cm^{-1}. PMR: $\underline{Me}$–C = (1.60, 1.68 and 1.73 ppm), $C\underline{H}_2Cl$ (2H, *d*, 4.0 ppm, J = 7.5 Hz), C = C$\underline{H}$ (1H, ill-resolved *m*, 5.04 ppm; 1H, *t*, 5.41 ppm, J = 7.5 Hz). (lit. IR[52], PMR[52]).

Neryl chloride (**5**), yield, 82%; b.p. 70–71°/3 mm, n_D^{21} 1.4783. IR (liq.) 1670, 1250, 835 cm^{-1}. PMR: $\underline{Me}$–C = (1.61, 1.68 and 1.78 ppm), $C\underline{H}_2Cl$ (2H, *d*, 4.0 ppm, J = 7.5 Hz), C = C$\underline{H}$ (1H, ill-resolved *m*, 5.08 ppm; 1H, *t*, 5.42 ppm, J = 7.5 Hz).

2(E), 6(E)-*Farnesyl chloride* (**8**), yield, 81%. IR (CCl_4) 1665, 1260 cm^{-1}. PMR: $\underline{Me}$–C = (1.59, 1.59, 1.67 and 1.73 ppm), $C\underline{H}_2Cl$ (2H, *d*, 4.0 ppm, J = 7.5 Hz), C = C$\underline{H}$ (2H, ill-resolved *m*, 5.05 ppm; 1H, *t*, 5.41 ppm, J = 7.5 Hz) (lit.: IR,[52] PMR[52]).

2(Z), 6(E)-*Farnesyl chloride* (**11**), yield, 82%. IR (CCl_4) 1665, 1260 cm^{-1}. PMR: $\underline{Me}$–C = (1.59, 1.59, 1.67 and 1.78 ppm), $C\underline{H}_2Cl$ (2H, *d*, 3.98 ppm, J = 7.5 Hz), C = C$\underline{H}$ (2H, ill-resolved *m*, 5.05 ppm; 1H, *t*, 5.40 ppm, J = 7.5 Hz).

Iodides (**3**, **6**, **9**, **12**)

Geranyl iodide (**3**). The following procedure is typical and all other iodides were prepared in exactly the same manner. These iodides are best characterised as quaternary ammonium salts.

To a soln of dry NaI (6.0 g, 0.04 mole; NaI is conveniently dried by azeotropic distillation with xylene) in dry acetone (25 ml), cooled to 0–2° and protected from light, geranyl chloride (1.50 g, 0.0087 mole) was added and after stirring at that temp for 1 hr, was diluted with ice water (50 ml), saturated with NaCl and product taken up in purified hexane/heptane (10 ml × 4). The combined organic extract was washed with 5% $Na_2S_2O_3$ aq (5 ml × 2), brine and dried. An aliquote was freed of solvent at room temp (30°), under vacuum, taken up in CCl_4 and its PMR spectrum recorded. The main lot was diluted with pure hexane/heptane to get 1% conc of the iodide, and the soln immediately subjected to photolysis (*vide infra*). PMR: $\underline{Me}$–C = (1.60, 1.67 and 1.67 ppm), $C\underline{H}_2I$ (2H, *d*, 3.87 ppm, J = 8 Hz), C = C$\underline{H}$ (1H, ill-resolved *m*, 5.05 ppm; 1H, *t*, 5.53 ppm, J = 8 Hz).

Geranyl chloride (70 mg) was treated with NaI in acetone, exactly as above. After 1 hr, tetrahydrofuran (THF) (purified, 8 ml) and Et_3N (80 mg) were added and the mixture kept at room temp (~30°), in the dark, for 4 hr. THF was removed at room temp under vacuum, the residue treated with dry ether and the solid (90 mg) collected by filtration. The product was recrystallised from acetone-light pet. to furnish crystals of *triethyl geranyl ammonium iodide* (**20**), m.p. 123–125°. PMR ($CDCl_3$): $\underline{Me}\text{–}CH\text{–}\overset{/\,\oplus}{N}$ (9H, *t*, 1.41 ppm, J = 7 Hz), $\underline{Me}$–C = (1.61, 1.68 and 1.84 ppm), $Me\text{–}C\underline{H}_2\text{–}\overset{\oplus}{N}$ (6H, q, 3.47 ppm. J = 7 Hz), $=CH_2\text{–}C\underline{H}_2\text{–}\overset{\oplus}{N}$ (2H, *d*, 4.03 ppm, J = 8 Hz), C=C$\underline{H}$ (1H, ill-resolved *m*, 5.02 ppm; 1H, *t*, 5.24 ppm, J = 8 Hz). (Found: C, 52.22; H, 8.29; N, 3.69. $C_{16}H_{32}NI$ requires: C, 52.60; H, 8.76; N, 3.84%.)

Neryl iodide (**6**). PMR: $\underline{Me}$–C = (1.63, 1.70 and 1.74 ppm), $C\underline{H}_2I$ (2H, *d*, 3.88 ppm, J = 8 Hz), C = C$\underline{H}$ (1H, ill-resolved *m*, 5.11 ppm: 1H, *t*, 5.53, J = 8 Hz).

Triethyl neryl ammonium iodide (**21**), m.p. 86–88° (acetone-light pet.). PMR ($\mathrm{CDCl_3}$): $\underline{\mathrm{Me}}\mathrm{{-}CH_2{-}}\overset{\oplus}{\mathrm{N}}$ (9H, *t*, 1.41 ppm, J = 7 Hz), $\underline{\mathrm{Me}}\mathrm{{-}C{=}}$ (1.62, 1.70 and 1.92 ppm), $\underline{\mathrm{Me}}\mathrm{{-}CH_2{-}}\overset{\oplus}{\mathrm{N}}$ (6H, *q*, 3.50 ppm, J = 7 Hz), $\mathrm{{=}CH{-}C\underline{H}_2{-}}\overset{\oplus}{\mathrm{N}}$ (2H, *d*, 3.92 ppm, J = 8 Hz), $\mathrm{C{=}C\underline{H}}$ (1H, ill-resolved *m*, 5.08 ppm; 1H, *t*, 5.34 ppm, J = 8 Hz). (Found: C, 52.82; H, 8.99. $\mathrm{C_{16}H_{32}NI}$ requires: C, 52.60; H, 8.76%.)

2(E), 6(E)-*Farnesyl iodide* (**9**). PMR: $\underline{\mathrm{Me}}\mathrm{{-}C{=}}$ (1.59, 1.59, 1.67 and 1.67 ppm), $\mathrm{C\underline{H}_2I}$ (2H, *d*, 3.85 ppm, J = 8 Hz), $\mathrm{C{=}C\underline{H}}$ (2H, ill-resolved *m*, 5.02 ppm; 1 H, *t*, 5.50 ppm, J = 8 Hz).

Triethyl 2(E), 6(E)-*farnesyl ammonium iodide*, m.p. 121–122 (acetone-light pet.). PMR ($\mathrm{CDCl_3}$): $\underline{\mathrm{Me}}\mathrm{{-}CH_2{-}}\overset{\oplus}{\mathrm{N}}$ (9H, *t*, 1.41 ppm, J = 7 Hz), $\underline{\mathrm{Me}}\mathrm{{-}C{=}}$ (1.60, 1.60, 1.68 and 1.86 ppm), $\mathrm{Me{-}C\underline{H}_2{-}}\overset{\oplus}{\mathrm{N}}$ (6H, *q*, 3.45 ppm, J = 7 Hz), $\mathrm{{=}CH{-}C\underline{H}_2{-}}\overset{\oplus}{\mathrm{N}}$ (2H, *d*, 4.0 ppm, J = 8 Hz), $\mathrm{C{=}C\underline{H}}$ (2H, ill-resolved *m*, 5.02 ppm; 1H, *t*, 5.25 ppm, J = 8 Hz). (Found: C, 57.72; H, 8.80. $\mathrm{C_{21}H_{40}NI}$ requires: C, 58.20; H, 9.20%.)

2(Z), 6(E)-*Farnesyl iodide* (**12**). PMR: $\underline{\mathrm{Me}}\mathrm{{-}C{=}}$ (1.60, 1.60, 1.67 and 1.67 ppm), $\mathrm{C\underline{H}_2I}$ (2H, *d*, 3.87 ppm, J = 8 Hz), $\mathrm{C{=}C\underline{H}}$ (2H, ill-resolved *m*, 5.05, 1H, *t*, 5.50 ppm, J = 8 Hz).

Triethyl 2(Z), 6(E)-*farnesyl ammonium iodide*, m.p. 111–113° (acetone-light pet.). PMR ($\mathrm{CDCl_3}$): $\underline{\mathrm{Me}}\mathrm{{-}CH_2{-}}\overset{\oplus}{\mathrm{N}}$ (9H, *t*, 1.41 ppm, J = 7 Hz), $\underline{\mathrm{Me}}\mathrm{{-}C{=}}$ (1.61, 1.61, 1.69 and 1.90 ppm), $\mathrm{Me{-}C\underline{H}_2{-}}\overset{\oplus}{\mathrm{N}}$ (6H, *q*, 3.48 ppm, J = 7 Hz), $\mathrm{{=}CH{-}C\underline{H}_2{-}}\overset{\oplus}{\mathrm{N}}$ (2H, *d*, 3.90 ppm, J = 8 Hz), $\mathrm{C{=}C\underline{H}}$ (2H, ill-resolved *m*, 5.10 ppm; 1H, *t*, 5.32 ppm, J = 8 Hz). (Found: C, 57.77; H, 9.31. $\mathrm{C_{21}H_{40}NI}$ requires: C, 58.20; H, 9.20%.)

General procedure for photoirradiation

Photoirradiation was carried out with Applied Photophysics medium-pressure 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 approx. 1% conc in appropriate solvent, containing molar equivalent of $\mathrm{Et_3N}$. A minute, steady flow of oxygen-free $\mathrm{N_2}$ was passed through the soln. The reaction was monitored by tlc (10% benzene in light petroleum). When the photostationary state was reached, the reaction mixture was worked up by washing with water, followed by 5% $\mathrm{Na_2S_2O_3}$ aq. The solvent was carefully stripped off through an efficient Vigreaux column. The product so obtained was passed through a short column of $\mathrm{SiO_2}$-gel/IIB[53] and eluted with light pet. The eluate was freed of the solvent and the residue distilled *in vacuo* and the individual components of the hydrocarbon mixture, thus obtained, were identified by mixed GLC with authentic samples on three stationary phases (10% Carbowax; 10% SE-30; 10% diethylene-glycol polysuccinate) or by isolation by preparative GLC and comparison of the spectral data. When photolysis was carried out in THF soln, the solvent was first stripped off through a column, of $\mathrm{SiO_2}$-gel/IIB, eluted with light pet. and the eluate subjected to the above aqueous work-up.

Photoirradiation of geranyl iodide

(i) *In n-hexane*. Iodide from 1.5 g of geranyl chloride; lamp, 100 LQ; time of irradiation, 6 hr; temp. 25°; length of $\mathrm{SiO_2}$-gel column, 31 cm × 1.5 cm (vol. of eluant, 200 ml); yield of product, b.p. 145–148° (bath)/100 mm, 556 mg.

(ii) *In tetrahydrofuran*. Iodide from 2.95 g of geranyl chloride; lamp, 400 LQ; time of irradiation, 3.5 hr; temp. 50°; length of $\mathrm{SiO_2}$-gel column, 50 cm × 2.5 cm (vol. of eluant, 40 ml); yield of product, b.p. 140–148° (bath)/100 mm, 975 mg.

Photoirradiation of neryl iodide

Reaction conditions exactly as above; yields similar.

Photoirradiation of farnesyl iodide

(i) *Mixture of* 2(E)- *and* 2(Z)-*isomers*. Substrate isomer ratio, 5:4, iodide from 2.5 g of chloride; solvent, THF; lamp, 400 LQ; time of irradiation, 3 hr; temp. 50°; length of $\mathrm{SiO_2}$-gel column, 50 cm × 2.5 cm (vol. of eluant, 400 ml); yield of product, b.p. 120–140° (bath)/2 mm, 1.15 g. This material was subjected to preparative GLC separation (temp 170°; $\mathrm{H_2}$ flow, 60 ml/min; 60 μl/injection) and the following compounds isolated (in order of increasing retention times):

trans-β-Farnesene (**22**), b.p. 113–115° (bath)/2 mm. $\mathrm{M^+}$, *m/z* 204, IR ($\mathrm{CCl_4}$) 1600, 990, 895 $\mathrm{cm^{-1}}$. PMR: $\underline{\mathrm{Me}}\mathrm{{-}C{=}}$ (1.59, 1.59 and 1.66 ppm), $\mathrm{C{=}C\underline{H}}$ (7H, 4.94–6.3 ppm) (lit. IR.[13] PMR[13]).

β-Bisabolene (**23**), b.p. 114–116° (bath)/2 mm. $\mathrm{M^+}$, *m/z* 204, IR ($\mathrm{CCl_4}$) 1635, 890 $\mathrm{cm^{-1}}$. PMR: $\underline{\mathrm{Me}}\mathrm{{-}C{=}}$ (9H, *bs* 1.60–1.67 ppm), $\mathrm{C{=}CH_2}$ (2H, *bs*, 5.32 ppm), $\mathrm{{-}\underset{|}{C}{=}C\underline{H}}$ (2H, ill-resolved multiplets 5.05 and 5.32 ppm) (lit. IR[14a,b], PMR[14c]).

trans-α-*Bisabolene* (**24**), PMR: $\underline{\mathrm{Me}}\mathrm{{-}C{=}}$ (*bs*, ~1.63), $\mathrm{{=}CH{-}C\underline{H}_2{\cdot}\ CH{=}}$ (*t*, 2.62 ppm, J = 7 Hz), $\mathrm{C{=}C\underline{H}}$ (ill-resolved multiplets at 5.00 and 5.30 ppm) (lit.[15]).

ar-Curcumene (**25**), PMR: $\underline{\mathrm{Me}}\mathrm{{-}CH}$ (*d*, 1.20 ppm, J = 7 Hz), $\underline{\mathrm{Me}}\mathrm{{-}C{=}}$ (*bs*, 1.50, 1.63 ppm), $\underline{\mathrm{Me}}\mathrm{{-}Ar}$ (*s*, 2.27 ppm), $\mathrm{C{=}C\underline{H}}$ (*m*, 5.00 ppm), $\mathrm{Ar{-}\underline{H}}$ (s, 6.95 ppm), (lit.[16]).

(ii) *Pure isomers*. Iodide from 0.48 g of each chloride; solvent n-heptane; lamp, 100 LQ; time of irradiation, 5 hr; temp, 25°; yield 200 mg of distilled product.

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