# THE PHOTOCHEMISTRY OF METHYL GERANATE, A MODEL CHROMOPHORE FOR INSECT JUVENILE HORMONE ANALOGS

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Abstract -- The irradiation of methyl geranate (3) in ether using 254 nm lamps produces methyl 5-methyl-2-isopropenyl-4-hexenoate (13), 1,6,6-trimethyl-endo-5-carbomethoxybicyclo-[2.1.1]hexane (11), methyl 2-isopropenyl-5-methylcyclopentanecarboxylate (12) and methyl (32)-3,7-dimethyl-3,6-octadienoate (14). Photolysis run in vater or in ether in the presence of base generates two additional dienes: methyl 3-methylene-7-methyl-6-octenoate (16) and methyl (3E)-3,7-dimethyl-3,6-octadienoate (17). The photolysis of methyl (2E, 6E)-3,7-dimethyl-2,6-nonadienoate (4a) in ether produces all Z/E isomers, 4a - 4d.

## INTRODUCTION:

In 1965 Bovers <u>et al</u> reported on the isolation and identification of juvabione, 1, from paper made from Canadian Balsam pine.<sup>1</sup> This compound was shown to have insect growth regulator properties without being closely similar in structure to parent insect juvenile hormones, 2. Since that time hundreds of analogs have been synthesized in order to evaluate the dependence of biological activity upon structure.<sup>2</sup> However, in all these studies, it is rare to find detailed studies on the environmental fate of the insect growth regulator or the nature of the decomposition products.





 $2 a : R_1 = R_2 = H$ b: R, = R, = CH,

Since it is reasonable to expect that insect growth regulators that are disseminated into the environment will be structurally similar to the parent insect juvenile hormones 2ab, we were prompted to initiate a study of the photochemistry of some insect juvenile hormone analogs beginning with model systems, 3 and 4a. For the initial stages of our work, it vas felt that the choice of methyl geranate, 3, would be advantageous. The reactive functional groups, substitution patterns and placement of the two double bonds are identical to those of insect juvenile hormone 2a, and, since methyl geranate is a symmetrically terminated molecule, the problem of E/Z isomerization at the C6-C7 double bond would be avoided in the early stages of mechanistic work.

Simple allphatic  $a,\beta$ -unsaturated esters have been studied and mechanistic schemes have been proposed for E/Z isomerization,<sup>3</sup> cyclization to cyclopropanes<sup>3b-d</sup> and photochemical deconjugation to  $\beta,\tau$ -unsaturated esters.<sup>3b-e,4,5</sup> Likevise, mechanistic studies of the photochemistry of citral, 5, the aldehyde analog of methyl geranate, have been carried out.<sup>6</sup> In addition to the expected E/Z isomerization reaction of 5, Cookson and Hudec also found two products of cyclization, 6 and 7, which were shown to arise from the triplet state. Buchi and Wuest took advantage of the stereoselectivity of this cyclization to 7 as the first step in the total synthesis of ( $\pm$ )-furopelargones, 8 and 9.<sup>7</sup> Agosta, <u>et</u> <u>al</u>. have studied the photochemistry of 5 at elevated temperatures and have reported that in



addition to the products already mentioned, two new products, arising from formy) group migration followed by cyclization, 10, were formed.<sup>6b-d</sup> The results with citral at elevated temperatures are in contrast to those obtained from the irradiation of 3 in refluxing chlorobenzene.<sup>6C</sup> Under these conditions methyl geranate only formed the two expected products of cyclization, 11 and 12, with significant loss of starting material by decomposition.



It is clear from the results reported for the triplet sensitized irradiation of methyl geranate, 3, that its reactivity parallels that of citral, 5, but is different enough to varrant further investigation. Furthermore, with the structural similarity between 3 and 2a the results of our photochemical studies of 3 are being applied to the study of 2a, the parent insect juvenile hormone. To date there has been no report in the literature on the singlet photochemistry of 3 and what the mechanistic pathways leading to the various photolysis products are. In the present paper, and the following one, we report our results in these areas.

# RESULTS AND DISCUSSION

Methyl geranate vas synthesized on a multi-gram scale by the method of Corey. Geraniol vas oxidized to citral with  $\tau$ -manganese dioxide<sup>9</sup> in hexane. The crude citral vas further oxidized with  $\tau$ -manganese dioxide in a solution of methanol, NaCN and acetic acid to provide starting ester 3 with less than 2% isomerization at the C-2-C-3 double bond after silica gel chromatography. Irradiation of a 0.1 H solution of methyl geranate, 3, with 254 nm light for 18.5 h led to the formation of seven product components, as determined by glc analysis of the photolysis mixture, together with recovered starting material, Scheme 1. The material balance was found to be 98%. Each component was collected by preparative glc and identified by spectroscopic and chemical means.



A GC-MS spectrum of each component was obtained which revealed that all the photolysis products (those present in >1.5%) were isomers of the starting material, methyl geranate, 3. The first compound to elute from the gas chromatograph was found to be methyl 5-methyl-2-isopropenyl-4-hexenoate, 13, (4.2% of the photolysis mixture). The spectroscopic properties (<sup>1</sup>H-nmr, <sup>13</sup>C-nmr, IR, MS, UV) of 13 are consistent with the proposed structure. The <sup>1</sup>H NMR (400 MHz) spectrum reveals absorptions for three vinylic protons (§ 4.86, 4.87 and 4.99 ppm) and the expected diastereotopic nature of the two protons attached to C-3 (two IH multiplets centered at § 2.24 and 2.48 ppm); finally, the methine proton on C-2 at § 3.01 ppm displays the expected triplet multiplicity. The <sup>13</sup>C NMR (100 MHz) spectrum reveals that the carbonyl carbon has shifted downfield from § 166.94 to 173.95 ppm (loss of conjugation) yet there are still four vinylic carbons, two of which (§ 113.64 and 142.39 ppm) have the chemical shift differences characteristic of an exo-methylene unit.

Methyl 5-methyl-2-isopropenyl-4-hexenoate, 13, vas subjected to ozonolysis, folloved by oxidative vork-up vith Jones reagent and methylation of the resulting acid vith diazomethane, to yield 18. This compound has the expected <sup>1</sup>H NMR spectrum, displaying a doublet of doublets for the methylene protons and a downfield shift of the methine triplet, relative to the methine in 13. As a final check on our structural assignment, we repeated Katzenellenbogen and Crumrine's synthesis,<sup>10</sup> which employs the alkylation of the anion of methyl senecioate (19) with prenyl bromide, and found that the spectra of the synthetic and photochemical products matched exactly. The formation of 13 can be explained as the result of a photochemical [1,3]-sigmatropic shift of the terminal prenyl unit.



The second component to elute from the gas chromatograph was 1,6,6-trimethyl-endo-5-carbomethoxybicyclo[2.1.1]hexane, 11, (5.9% of the photolysis mixture). All spectroscopic data were found to be consistent with structure 11. The proton NHR spectrum exhibited singlets for three methyl groups all attached to quaternary carbons (\$ 0.75, 1.10 and 1.11 ppm) and provided no evidence of vinylic protons. The UV spectrum consisted only of end absorption, indicating a loss of conjugation. The endo stereochemistry was deduced by analogy to the analysis by Meinvald on the 5-endo and 5-exo acids of the bicyclo[2.1.1]hexanes,<sup>11</sup> supported by Agosta and Wolff's studies of the NHR properties of a large number of substituted bicyclo[2.1.1]hexanes, including 11.<sup>12</sup> Comparison of our spectroscopic data with that reported showed that they matched exactly. In all of our studies only the 5-endo isomer was detected with no hint of formation of the 5-exo isomer.

The third component to elute from the gas chromatograph was methyl 2-isopropenyl-5-methylcyclopentanecarboxylate, 12, (6.8% of the photolysis mixture). This compound displays tvo vinylic protons in the <sup>1</sup>H-NMR (§ 4.70 and 4.99 ppm) and in the <sup>13</sup>C-NMR there are two videly spaced signals, in the vinylic region, at § 109.37 and 146.93 ppm, which are highly indicative of an exo methylene group, <sup>13,14</sup> and an absorption for a carbonyl carbon, shifted downfield from 166.94 to 174.98 ppm, which indicates deconjugation. Deconjugation of the ester vas also supported by the UV spectrum, which showed only end absorption. Two dimensional <sup>1</sup>H-<sup>1</sup>H (<sup>1</sup>H-COSY45) and <sup>1</sup>H-<sup>13</sup>C(HETCOR) shift correlated spectra were run, which provided reinforcement for the assigned structure. In addition, the structure of 12 produced in the irradiation of 3 was shown to be identical, by comparison of spectroscopic data (IR, <sup>1</sup>H-NMR), to 12 obtained by Wolinsky and Eustace from the high temperature base catalyzed ring opening of lactone 20.<sup>15,16</sup>



The fifth component to elute from the gas chromatograph was readily identified as methyl (2Z)-3,7-dimethyl-2,6-octadienoate, 15 (47% of the photolysis mixture). Comparison of the glc retention times as well as spectroscopic properties (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR, UV and MS) of the photolysis product and an authentic sample of 15, prepared from neral, showed the two to be identical.

In the direct irradiation of 3 in ether, with scrupulous exclusion of base, only one photodeconjugation product could be isolated and identified: methyl (3Z)-3,7-dimethyl-3,6-octadienoate, 14. This product was formed in 5.7% yield and was the fourth component to elute from the gas chromatograph. If base was not scrupulously excluded from the photolysis or if the irradiation was carried out in the presence of a weak, non-nucleophilic base, 1,2-dimethylimidazole (1,2-DHI), two products were formed in addition to those already mentioned. They are both isomeric with starting material and are the other two possible deconjugation products: methyl 3-methylene-7-methyl-6-octenoate, 16, and methyl (3E)-3,7-dimethyl-3,6-octadienoate, 17. The details of the mechanism and kinetics of their formation are discussed in the accompanying paper.

Identification of 16 was straightforward. The UV and IR spectra both showed a loss of conjugation and analysis of the mass spectrum showed that this compound is indeed an isomer of starting material, exhibiting a parent peak at m/e 182. An analysis of the <sup>1</sup>H-NMR spectrum showed that there were three vinylic protons with a downfield shift of the C-2 methylene protons to 3.07 ppm since they are both allylic as well as alpha to the carbomethoxy group. The <sup>13</sup>C-NMR spectrum still shows four alkene carbons, two of which have the characteristic chemical shift differences of an exo-methylene group. Wolinsky and Bedoukian have synthesized 16 by deconjugation of geranyl chloride,<sup>17</sup> using the method of Ivakura.<sup>18</sup> Spectroscopic properties (IR, NMR, MS) in the literature all matched those of the product 16 from the photolysis.

The remaining two dienes, 14 and 17 were found to be the result of in-chain deconjugation to the Z and E isomers. Identification of these compounds was readily accomplished. All the spectra, IR, NMR (both proton and carbon), MS and UV, are surprisingly similar and could be used to assign the basic carbon skeleton, but could not, on cursory examination, be used to differentiate the E from the Z isomer. As stated above, the mass spectra show that these compounds are isomers of the starting material 3. UV, IR and  $^{13}$ C NMR spectroscopic measurements all indicate loss of conjugation. The UV spectra show end absorption only, the IR exhibits a carbonyl peak shifted from 1720 to 1730 cm<sup>-1</sup>, and in the  $^{13}$ C NMR spectra, the carbonyl carbon is shifted downfield from 166 to 172 ppm. Analysis of the <sup>1</sup>H-NMR spectra reveals the expected features for the proposed structures: two 1H vinylic triplets as well as a triplet for the methylene protons on C-5 (broadened by allylic coupling), three methyl singlets and the C-2 methylene singlet at 3.08 ppm which is shifted downfield due to the fact that

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it is both allylic and alpha to the carbomethoxy group. <sup>1</sup>H-COSY45 spectra were run on the Z and E isomers, 14 and 17, respectively, which allowed for straightforward assignments of Erman<sup>19</sup> has synthesized both the E and Z isomers of these deconjugation hydrogen groups. products: 14 from cis-ocimene, 21a and 17 from trans-ocimene, 21b. The reported NMR spectral properties are in reasonable agreement with our data for 14 and 17, but due to the close similarity for the Z/E isomeric pair, a Z/E assignment is not possible on this basis alone. Analysis of HETCOR spectra of both isomers revealed that all the carbon lines stay essentially fixed in going from the E(17) to Z(14) except for the methylene carbon, C-2, which shifts upfield by 7.6 ppm, and the methyl attached to C-3, which shifts downfield by 7.6  $\tau$ -effect also manifests itself in simple di- and trisubstituted alkenes  $^{13}$  and This ppm. has been used to assign the <u>cis</u> or <u>trans</u> structure in prostacyclin analogs.<sup>20</sup> Erman also noted that the glc retention time of 14 is several minutes shorter than 17 on a Reoplex column; this is the same behavior exhibited in our glc studies using an OV-17 column. Since both are liquid phase activity (polarity) type III <sup>21</sup>, it is not expected that the retention time order would be reversed.

Before a detailed study of the mechanistic pathways involved in the irradiation of methyl geranate, 3, was undertaken, an irradiation of 3 in vater was run. The purpose of this irradiation was to assess the environmental significance of any subsequent irradiations done in ether. The results of irradiations in ether and water are summarized in Table 1. The point to note is that in water all the products that are formed in ether are produced in similar ratios with, however, an increased formation of deconjugation products.

With the identity of the products formed during the photolysis of methyl geranate established, the elucidation of the mechanistic pathways leading to the formation of each of those products was undertaken. The results of an irradiation time versus composition experiment for 3, with 254 nm lamps, are summarized in Figure 1. Composition versus time curves are plotted for 11, 12, 13, 14, 15 and 3. The notable feature of Figure 1 is the rapid photo-equilibration of 15 and 3, relative to the formation of 11, 12, 13 and 14. The ratio of 15/3 is 1.23 after photoequilibrium has been reached and this ratio does not change, even out to 48 h.

Relative Composition								
solvent	13	11	12	16	14	15	17	3
ether <sup>8</sup>	1.00	1.78	2.18	0	1.61	33.2	0	33.7
vater <sup>b</sup>	1.00	2.18	2.48	1.84	3.75	18.1	3.06	22.2

Table 1. Relative composition of Photolysis Products From Direct Irradiation of Methyl Geranate in Ether and Water

<sup>a</sup> 254 nm lamps. <sup>b</sup> Hanovia 450 vatt, medium pressure, mercury arc lamp

Earlier in the course of this project an experiment designed to develop a plot of irradiation time versus composition for methyl geranate photolysis was carried out without scrupulous exclusion of trace base sources. Under these conditions, photodeconjugation to 14, 16 and 17 becomes the predominant pathway.

In order to begin elucidation of the mechanism(s) for the formation of the methyl geranate photolysis products, 3 vas irradiated in the presence of acetophenone ( $E_T = 74.1 \text{ kcal/mol}$ ), propiophenone ( $E_T = 74.5 \text{ kcal/mol}$ ) and benzene ( $E_T = 84.3 \text{ kcal/mol}$ ) under conditions where the sensitizers absorbed greater than 95% of the incident light. In accordance with prior results on the triplet sensitized irradiation of methyl geranate, the only products formed are 11, 12 and 15.<sup>6C</sup> The photochemical E/Z isomerization of a, $\beta$ -unsaturated esters had previously been shown to be a triplet process by Barltrop, <u>et</u>. <u>al</u>.<sup>3f</sup> and Jorgenson.<sup>3b-d</sup> Scheme 2 presents a simple rationale to explain the origin of the products.





Figure 1. Plot of irradiation time versus composition for the photolysis of methyl geranate in ether at 254 nm.

16

8

Figure 2. Plot of irradiation time versus composition of double bond isomerization products for irradiation of ester 4a in ether at 254 nm.

14 + 17

8,'

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Use of acetophenone as the triplet sensitizer proved to be inconvenient, since acetophenone and 13 both had identical retention times. Therefore, propiophenone vas employed, since the retention time of propiophenone vas greater than that of 12 (the third component to elute from the gas chromatograph), which revealed that 13 vas not formed in detectable amounts in any of the irradiations. Thus, it is clear that 13 is not formed from a triplet intermediate. Scheme 2 shows the spin state responsible for the formation of each product formed in the irradiation of 3. The triplet intermediate,  $T_1$ , is assumed to have the same structure whether it is formed from either 3 or 15.

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In viewing the overall mechanistic manifold for the phototransformations of methyl geranate, it is pertinent to mention that intramolecular excipiexes, such as that formed from 22, are formed rapidly with 22 exhibiting a rate of triplet quenching which is 300 times faster than an analogous intermolecular process.<sup>22</sup> An examination of the relative locations of the functional groups in methyl geranate, 3, shows that it is perfectly set up to form an intramolecular excipiex in the triplet excited state.

To test this hypothesis a 0.1 M solution of 4a vas irradiated for 8 h with samples removed at intervals and analyzed for the relative composition resulting from E/Z isomerization about the two double bonds (4a, 4b, 4c, and 4d). The results of this are presented in Figure 2 and it can be seen that the C-6 double bond does undergo isomerization, but with a lover relative quantum yield than the corresponding C-2 double bond. The point to note in the above experiment is that with the 254 nm light source used the isolated double bond does not absorb any light (absorption is effectively zero at vavelengths greater than 215 nm) and isomerization of this double bond must proceed by a mechanism other than direct energy absorption. A likely intermediate, therefore, in the isomerization about the C-6 alkene unit in 4 is the exciplex formed from the triplet. If this is the case a similar intermediate might be a key intermediate in the photochemistry of methyl geranate, presumably being formed from T<sub>1</sub> (Scheme 2) and generating cyclic products 11 and 12 as well as E/Z isomerization product 15. Intramolecular radical addition of triplet enoate to the remote double bond is an alternative. These mechanistic possibilities are presently being investigated.



## EXPERIMENTAL SECTION

Nuclear magnetic resonance spectra (NMR) were recorded on either a Brüker General. AM-400 (<sup>1</sup>H at 400.14 MHz, <sup>13</sup>C at 100.62 MHz) or Varian FT-80 (<sup>1</sup>H at 79.54 MHz, <sup>13</sup>C at 20.00 MHz) in CDCl3. Infrared spectra (IR) were obtained with a Perkin-Elmer Model 1258 or a Mattson Sirius 100 spectrometer. Ultraviolet spectra vere obtained using a Cary 210 spectro-GLC analyses were carried out using a Varian 3700 gas chromatograph equipped with a meter. flame ionization detector and Hevlett-Packard 3312B integrator using one of the following columns: (A), 10% OV-17, 20 ft; (B), 7% OV-17, 20 ft; (C), 3% OV-17, 20 ft. All columns were packed in 0.125 inch copper tubing using Chromesorb-W, AW, DMCS, 60/80 mesh. Preparative GLC vas carried out on a Hevlett-Packard, F and H scientific 700 gas chromatograph equipped with a thermal conductivity detector using one of the following columns: (D), 10% OV-17, 20 ft; (E), 15% OV-17, 20 ft. Both columns were packed in 0.25 inch copper tubing with Chromesorb-W, AW, Mass spectra were obtained on a Finnigan 4023 mass spectrometer equipped DMCS, 60/80 mesh. vith a Finnigan 9610 gas chromatograph. Exact mass determinations were performed on a Kratos MS-50 mass spectrometer.

All solvents were used as received from the manufacturer except as noted. Diethyl ether and tetrahydrofuran were both distilled from sodium/benzophenone ketyl immediately prior to use. Cyclohexane, 1,2-dimethoxyethane (DME) and methylene chloride were fractionally distilled from calcium hydride onto 3 Å molecular sieves. Tert-Butanol was fractionally distilled from barium oxide onto 3 Å molecular sieves. Hethanol was predried over sodium sulfate folloved by careful fractional distillation onto 3 Å molecular sieves.

All photolysis samples were placed in Ace Glass Co. 170x15 mm quartz, resealable sample tubes and degassed with three freeze/thaw cycles on a vacuum line. All articles of glassware used in making up samples for photolyses (quartz tubes, volumetric flasks, etc.) were rinsed with 10% aqueous HCl, distilled water and acetone prior to being oven dried. The light source for all photolyses was a Rayonet Type RS, preparative photochemical reactor (Southern New England Ultraviolet Co.) equipped with eight 253.7 nm lamps and a merry-go-round device.

Tvo-dimensional MMR Experiments. All tvo-dimensional spectra of 12, 14 and 17 vere recorded at 297 K with a Brüker AM-400 spectrometer equipped with an Aspect 3000 computer operating in Fourier transform mode with quadrature detection. Standard Brüker pulse programs vere used unless otherwise noted.

Two-dimensional  ${}^{1}\text{H}$  -  ${}^{1}\text{H}$  shift correlated (COSY-45) were aquired with the following parameters. For all samples a sinebell resolution enhancement was performed prior to Fourier transformation and other parameters are listed below for each sample: for 12 there were 1024 data points in the f2 and f1 domains, sweep width of 1923 Hz, 256 experiments (8 scans each) with an incremental delay of 0.4 ms; for 14 there were 1024 datapoints in the f2 and f1 domains, sweep width of scans each) with an incremental delay of 0.4 ms; for 14 there were 1024 datapoints in the f2 and f1 domains, sweep width of 2809 Hz, 256 experiments (8 scans each) with an incremental delay of 0.356 ms; for 17 there were 1024 data points in the f2 and f1 domains, sweep width of 2427 Hz, 256 experiments (8 scans each) with an incremental delay of 0.412 ms.

Two-dimensional heteronuclear  ${}^{1}$ H -  ${}^{13}$ C shift correlated (HETCOR) experiments were acquired with the following parameters. For 12 there were 256 and 2000 data points in f1 and f2, respectively, sweep widths were 2300 Hz and 14286 Hz in f1 and f2, respectively, 128 experiments (32 scans each) with an incremental delay of 0.217 ms. Gaussian-Lorentz resolution enhancement (Gaussian factor of 0.8) with resolution enchancement in f2 of -13 Hz and -8 Hz in f1 prior to Fourier transform was employed. For 14 there were 512 and 2000 data points in f1 and f2 respectively, sweep widths were 1400 Hz and 12500 Hz in f1 and f2 respectively, 256 experiments (144 scans each) with an incremental delay of 0.179 ms. Gaussian-Lorentz resolution enhancement (Gaussian factor of 0.8) with resolution enhancement of -5 Hz and -12 Hz in f1 and f2 respectively, prior to Fourier transform. For 17 there were 512 and 2000 data points in f1 and f2 respectively, sweep widths were 1250 and 13158 Hz in f1 and f2 respectively, 256 experiments (144 scans each) with an incremental delay of 0.200 ms. Gaussian-Lorentz resolution enhancement (Gaussian factor of 0.8) with resolution enhancement of -5 Hz and -12 Hz in f1 and f2 respectively, prior to Fourier transform. For 17 there were 512 and 2000 data points in f1 and f2 respectively, sweep widths were 1250 and 13158 Hz in f1 and f2 respectively, 256 experiments (144 scans each) with an incremental delay of 0.200 ms. Gaussian-Lorentz resolution enhancemment (Gaussian factor of 0.8) with resolution enhancement in f2 of -6 Hz and -4 Hz in f1 prior to Fourier transform was used.

Preparation of Activated Manganese Dioxide. A 5% solution of aqueous potassium permanganate (79 g in 1.5 L) at 60 °C was added in three portions over 5 minutes to a stirred 5% solution of aqueous manganese sulfate (113 g in 1.5 L) also at 60 °C. The resulting brown suspension was stirred for an additional hour at 60 °C. The fine brown precipitate was collected on a fritted glass filter and washed with 4 L of distilled water to ensure removal of excess salts of potassium and manganese. The precipitate was oven dried at 60 °C to yield 120 g of a brown amorphous powder which was ground to a fine powder in a mortar and pestle prior to use.

Methyl (2E)-3,7-dimethyl-2,6-octadienoate (3)(methyl geranate).8 Dry methanol (300 mL) was placed into a 1 L round-bottomed flask and cooled to 0 °C. To this flask was slowly added, with vigorous stirring, 25 g of activated manganese dioxide. To this suspension was added citral, 5, (5.00 g, 32.9 mmol), sodium cyanide (6.00 g, 122 mmol) and 1 mL of glacial acetic acid. The mixture was stirred at room temperature for 24 h at which time 7 mL of saturated sodium bicarbonate was added to neutralize any excess hydrogen cyanide. The manganese dioxide was removed by filtration and washed with 600 mL of ether. The combined organic portions were concentrated in vacuo to an orange slurry. The crude product was extracted from 300 mL of vater with ether (3 x 200 mL) and the combined extracts were washed with vater and brine. After drying over MgSO4, the solvent was removed in vacuo to give 4.2 g of crude 3 as an orange oil. The crude product vas purified via silica gel chromatography (85:15 hexane:ethyl acetate) to yield 3.0 g (50%) of methyl geranate, 3, as a pale yellow oil: <sup>1</sup>H NMR (80 MHz) & 1.60 (3H, s), 1.69 (3H, s), 2.16 (7H, s), 3.69 (3H, s), 5.07 (1H, br s) and 5.67 (1H, s); <sup>13</sup>C NHR (20 NHz) & 17.67, 18.71, 25.70, 26.36, 41.13, 50.54, 115.59, 123.39, 132.37, 159.76 and 166.94; IR (f11m) 2970 (s, br), 1720 (s), 1650 (m), 1430 (m), 1220 (s), 1140 (s) and 1050 (v)  $cm^{-1}$ ; HS m/e 182 (H<sup>+</sup>), 123, 114 and 69 (100); UV (methanol)

 $\epsilon_{254} = 1900.$ 

Ozonolysis of methyl 5-methyl-2-isopropenyl-4-hexenoate (13).

Ozone was bubbled through a solution of 17 mg of 13 in 5 mL of methylene chloride in a 10 mL flask which contained a magnetic stir bar. The addition was carried out at -78 °C until a blue color persisted. The solution was stirred an additional 15 min at -78 °C at which time nitrogen was bubbled through the system to remove excess ozone. Solvent was removed in vacuo and the residue was dissolved in 5 mL of acetone. After cooling the flask to 0 °C, excess Jones reagent (KCrO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, acetone) was added and the solution was stirred for 15 min at 0 °C. The mixture was filtered through celite, the solid washed with hot acetone, and the acetone was removed in vacuo. The crude product was dissolved in 5 mL of ether and cooled to 0 °C. Excess diazomethane was added to the solution and the solution was stirred at 0 °C for 15 min. Solvent was removed in vacuo and the crude product was purified by preparative glc (column D) to yield 2 mg of ketodiester (18): <sup>1</sup>H NMR (80 MHz) S 2.36 (3H, s), 2.90 (1H, d J = 7.5 Hz), 3.67 (3H, s), 3.77 (3H, s) and 4.01 (1H, t J = 7.5 Hz); high resolution MS m/e calcd for  $C_{BH_{12}O_5}$  188.068, found 188.068  $\pm$  0.010.

(2E)-3,7-Dimethyl-1-triphenylmethoxy-2,6-octadiene (23). A 250 mL single-necked, roundbottomed flask fitted with a magnetic stir bar was charged with geraniol (10.0 g, 64.9 mmol, Aldrich), trityl chloride (18.1 g, 64.9 mmol) and 100 mL dry pyridine. The solution was varmed to 50 °C and stirred for 24 h. The crude product was diluted with 300 mL of diethyl ether and washed repeatedly with 10% aqueous HCl to remove the pyridine. The ether solution was then vashed with saturated NaHCO<sub>3</sub> and brine. Solvent was removed in vacuo, after drying with MgSO4, to yield 24.4 g (95%) of 23 as a very viscous, yellow oil which was used without further purification:  $^{1}$ H NMR (400 MHz) § 1.46 (3H, s), 1.61 (3H, s), 1.69 (3H, s), 2.04 (2H, m), 2.08 (2H, m) 3.59 (2H, d, J = 6.5 Hz), 5.11 (1H, br t J = 5.5 Hz), 5.44 (1H, br t J = 6.5 Hz) and 7.20-7.48 (15H, m); <sup>13</sup>C NHR (100 HHz) & 16.52, 17.71, 25.70, 26.41, 39.57, 61.28, 86.58, 121.31, 124.07, 126.80, 127.72, 128.69, 131.54, 138.48 and 144.39; IR (film) 3060 (v), 3025 (v), 2925 (s), 1600 (v), 1490 (m), 1450 (s), 1060 (s) and 715 (s)  $cm^{-1}$ ; MS (m/e) no detectable M<sup>+</sup> peak (388), 243 (100), 165, 105 and 69.

(2E)-6,7-Epoxy-3,7-dimethyl-1-triphenylmethoxy-2-octene (24). A 1 L, three-necked, round-bottomed flask fitted with a mechanical stirrer and a 500 mL addition funnel, was charged vith trityl ether, 23, (24.4 g, 61.6 mmol) and 500 ml of methylene chloride and was cooled to -20 °C (dry ice/ carbon tetrachloride). The addition funnel was charged with technical (85%) 3-chloroperoxybenzoic acid (13.0 g, 60.0 mmol, Aldrich) dissolved in 300 mL of methylene chloride. The contents of the addition funnel were added dropwise over a period of 30 min. The solution was stirred an additional 3 h at -20 °C. At this time, 500 mL of a 10%  ${\sf Na}_2{\sf SO}_3$ vas added to destroy any remaining peroxides. The aqueous layer was separated and extracted once with methylene chloride. The combined organic layers were washed twice with brine and dried over  $MgSO_4$  prior to removal of solvent in vacuo to yield 25.4 g (100%) of 24 as a very viscous, yellov oil: <sup>1</sup>H NMR (400 MHz) & 1.27 (3H, s), 1.31 (3H, s), 1.48 (3H, s), 1.63 (2H, m), 2.16 (2H, m), 2.72 (1H, t J = 6.3 Hz), 3.61 (2H, d J = 6.3 Hz), 5.47 (1H, br t J = 6.3 Hz)Hz) and 7.20 - 7.47 (15H, m); <sup>13</sup>C NHR (100 MHz) & 16.51, 18.74, 24.86, 27.16, 36.15, 58.35, 61.14, 64.03, 86.61, 121.94, 126.83, 127.72, 128.65, 137.53 and 144.29; IR (film) 3060 (m), 3030 (m), 2960 (s), 2930 (s), 1600 (v), 1495 (s), 1455 (s), 1050 (s) and 715 (s)  $cm^{-1}$ ; MS (m/e) 412 (M<sup>+</sup>), 261, 260, 228, 215, 181, 169, 153, 106, 85 (100) and 59 (100).

(2E)-3,7-Dimethyl-1-triphenylmethoxy-2,7-octadien-6-ol (25). A dry, 1 L three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser, pressure equalizing addition funnel and nitrogen inlet was charged with disopropyl amine (34.8 mL, 247 mmol) and 300 mL of dry ether. This solution was cooled to 0 °C and purged with dry nitrogen. To the addition funnel was added, using a cannula for transfer, n-butyllithium (98.8 mL, 247 mmol, 2.5 M). The butyllithium solution was added dropwise over 5 min to the flask and the resulting solution was stirred an additional 5 min at 0 °C. Epoxide 24 (25.4 g, 61.6 mmol) dissolved in 100 mL of ether was placed into the addition funnel and added dropwise over a 5 min period to the LDA solution. After stirring at 0 °C for 5 min the solution was heated at reflux for 2 h. The reaction was cooled to 0 °C and quenched with saturated NH<sub>4</sub>Cl. The aqueous phase was separated and extracted twice with ether. The combined ether portions were washed with saturated NaHCO<sub>3</sub>, until the ether layer was neutral to lithus, followed by brine. The solvent was removed, after drying with HgSO<sub>4</sub>, in vacuo to yield a viscous yellow oil. The crude product was purified by silica gel chromatography. Hexane:ether (90:10) was used to elute off all products with a higher R<sub>f</sub> than the desired alcohol, which remained at the baseline, followed by elution with hexane:ethyl acetate (75:25). After removal of solvent in vacuo 24.2 g (95.3%) of the allylic alcohol 25 was isolated as a colorless, viscous oil. <sup>1</sup>H NHR (400 MHz) & 1.48 (3H, s), 1.60 (1H, br s), 1.67 (2H, m), 1.74 (3H, s), 2.06 (2H, m), 3.60 (2H, d J = 6.4 Hz), 4.06 (1H, t J = 6.4 Hz), 4.85 (1H, d J = 1.4 Hz), 4.95 (1H, d J = 1.7 Hz), 5.48 (1H, t J = 6.3 Hz) and 7.20-7.50 (15H, m); <sup>13</sup>C NMR & 16.54, 17.60, 32.89, 35.50, 61.20, 75.56, 86.62, 111.11, 121.70, 126.83, 127.72, 128.68, 138.22, 144.35 and 147.41; IR (film) 3600-3200 (s, br), 3060 (m), 3030 (m), 2940 (s), 2860 (s, sh), 1600, (w), 1490 (m), 1450 (s), 900 (s) and 770 (m) cm<sup>-1</sup>.

(2E)-6-Acetoxy-3,7-dimethyl-1-triphenylmethoxy-2,7-octadiene (28). To a 500 mL singlenecked, round-bottomed flask was added a magnetic stir bar, 200 mL of dry pyridine, allylic alcohol, 25, (24.2 g, 58.7 mmol), 100 mL of acetic anhydride and 4-N,N-dimethylaminopyridine (DMAP) (0.10 g, 0.82 mmol (cat.)). The resulting solution was stirred for 18 h at room temperature at which time it was cooled to 0 °C and 100 mL of methanol was added to destroy the unreacted acetic anhydride. The crude reaction mixture was diluted with 500 mL ether and vashed repeatedly with 10% aqueous HCI to remove the pyridine. The combined aqueous portions vere extracted tvice with other then the combined organic portions were washed tvice with saturated NaHCO<sub>3</sub> followed by brine. After drying the organic layer with MgSO<sub>4</sub> solvent vas removed in vacuo to yield 23.5 g (88.2%) of 26 as a viscous, orange oil: <sup>1</sup>H NMR (400 MHz) δ 1.46 (3H, s), 1.70 - 1.79 (5H, m (includes 3H, s ), 1.99 (2H, q J = 6.6 Hz), 2.06 (3H, s), 3.60 (2H, d J = 6.3 Hz), 4.90 (1H, s, br), 4.95 (1H, s), 5.14 (1H, t J = 6.6 Hz), 5.43 (1H, t J = 5.8 Hz) and 7.20 - 7.47 (15H, m); <sup>13</sup>C NHR (100 HHz) § 16.56, 18.08, 21.20, 30.64, 35.14, 61.17, 77.04, 86.62, 112.88, 121.81, 126.83, 127.72, 128.67, 137.46, 142.99, 144.32 and 170.27; IR (f11m) 3055 (m), 3020 (m), 2930 (s), 1740 (s), 1650 (v), 1595 (v), 1490 (m), 1450 (s), 1370 (m), 1240 (s), 1050 (s) and 710 (s) cm<sup>-1</sup>; HS (m/e); 454 (H<sup>+</sup>), 395, 259, 228, 211, 195, 183, 167, 151, 105 (100), 93, 77, 67 and 55. High resolution MS m/e calculated for C31H3403 454.2408, found 454.2491.

(2E,6E)-3,7-Dimethyl-1-triphenylmethoxy-2,6-nonadiene (27). A dry 1 L, three-necked, round-bottomed flask fitted with a magnetic stir bar, nitrogen inlet and 250 mL addition funnel containing methyl lithium (207 mL, 311 mmol, 1.50 H, Alpha Ventron) vas charged vith CuI (29.6 g, 155 mmol) and 300 mL of dry ether. The system was purged with dry nitrogen and kept under an inert atmosphere throughout the reaction. After cooling the flask to -20 °C the methyl lithium solution was added dropwise, with vigorous stirring, until the initially formed yellow turbidity clarified to a faint brown solution. The lithium dimethylcuprate was stirred an additional 5 min. The addition funnel was rinsed with 25 mL of dry ether and charged with 26 (23.5 g, 51.7 mmol) in 100 mL of dry ether. The acetate solution was added dropwise over a 10 min period during which time the reaction vent from clear to yellov with a yellov/white preci-The reaction was stirred for 1 h at -20 °C and then guenched by the addition of 300 mL pitate. of saturated aqueous NH\_C1. After filtration of the crude reaction mixture through celite, the aqueous layer was drawn off and extracted twice with ether. The combined organic portions vere vashed repeatedly with 10% ammonia in brine until the blue copper color disappeared. The organic portion was then washed with brine twice, and solvent was removed in vacuo after drying over MgSO4 to yield 21.2 g (100%) of crude 27 as a viscous yellow oil which was not purified prior to use in the subsequent reaction:  $^{1}$ H NMR (400 MHz) & 0.99 (3H, t J = 7.5 Hz), 1.47 (3H, s), 1.61 (3H, s), 1.96 -2.13 (6H, m), 3.59 (2H, d J =6.5 Hz), 5.11 (1H, br t J = 6.5 Hz), 5.45 (1H, br t J = 6.5 Hz), and 7.20 - 7.48 (15H, m);  $^{13}$ C NHR (100 HHz) & 12.79,

15.94, 16.54, 26.25, 32.32, 39.61, 61.28, 86.58, 121.34, 122.47, 126.80, 127.71, 128.69, 137.06, 138.49 and 144.40; IR (film) 3060 (m), 3030 (m), 2960 (s), 2930 (s), 1665 (v), 1600 (v), 1500 (m), 1460 (s), 1390 (v), 1230 (v), 1060 (s) and 715 (s)  $cm^{-1}$ .

(2E,SE)-3,7-Dimethyl-2,6-nonadien-1-ol (28). A 250 mL round-bottom flask containing 27 (21.2 g, 51.7 mmol) and 175 mL of 6% HCl in methanol was stirred at room temperature for 2 h. The reaction was quenched by the addition of  $K_2CO_3$ . The reaction mixture was transferred to a separatory funnel and diluted with 300 mL of ether. The organic portion was vashed twice with saturated NaHCO<sub>3</sub> followed by brine. The solvent was removed in vacuo, after drying over MgSO<sub>4</sub>. The crude alcohol was purified by silica gel chromatography (75:25 hexane: ether) to yield 5.2 g (48%) of 28 as a colorless oil: <sup>1</sup>H NMR (400 MHz) & 0.98 (3H, t J = 7.5 Hz), 1.60 (3H, s), 1.67 (3H, s), 2.01 - 2.14 (6H, m), 4.14 (2H, d J = 6.9 Hz), 5.10 (1H, br t J = 6 Hz) and 5.40 (1H, br t J = 6 Hz); <sup>13</sup>C NMR (100 MHz) & 12.69, 15.78, 16.16, 26.17, 29.61, 32.24, 39.50, 59.18, 122.25, 123.34, 137.14 and 139.44; IR (film) 3320 (br,s), 1670 (v), 1455 (m), 1390 (m) and 1010 (s) cm<sup>-1</sup>; HS m/e 168 (H<sup>+</sup>), 150, 137, 121, 111, 93, 83, 67, 55 (100), 43 and 41; high resolution HS m/e calcd for  $C_{11}H_{20}O$ 168.1514, found 168.1515.

(2E,6E)-3,7-Dimethyl-2,6-nonadienal (29). To a 1 L round-bottomed flask containing a stirred suspension of 25 g activated manganese dioxide in 300 mL of hexane at 0 °C vas added 28 (5.20 g, 31.0 mmol). The brown suspension was stirred at 0 °C for 30 min. After removal of the manganese dioxide by filtration, it was washed with 300 mL of ether and all solvents were removed in vacuo to yield 4.1 g (80%) of the aldehyde 29. Aldehyde 29 was shown to be >98% pure by glc (column B) and was used without further purification: <sup>1</sup>H NMR (400 MHz) & 0.97 (3H, t J = 7.5 Hz), 1.26 (3H, s), 1.61 (3H, s), 1.98 (2H, q J = 7.5 Hz), 2.24 (4H, m), 5.07 (1H, br t J = 6.8 Hz), 5.88 (1H, d J = 8.1 Hz) and 10.0 (2H, d J = 8.1 Hz); <sup>13</sup>C NMR (100 MHz) & 12.67, 15.91, 17.56, 25.57, 32.24, 40.62, 120.97, 127.40, 138.43, 163.86 and 191.28; 1R (film) 2960 (s, sh), 2930 (s), 2860 (s, sh), 1675 (s), 1635 (m, sh), 1450 (s), 1380 (m), 1200 (s), 1125 (s) and 850 (m) cm<sup>-1</sup>; MS m/e 166 (M<sup>+</sup>), 151, 137, 83, 55 (100) and 41; high resolution MS m/e calcd for  $C_{11}H_{18}0$  166.1358, found 166.1358.

Methyl (2E,6E)-3,7-dimethyl-2,6-nonadienoate (4a). Dry methanol (300 mL) vas placed into a 1 L round-bottomed flask and cooled to 0 °C. To this flask was slowly added, with vigorous stirring, 27 g of activated manganese dioxide. To this suspension was added 30 (4.10 g, 24.7 mmol), sodium cyanide (5.00 g, 102 mmol) and 1 mL of glacial acetic acid. The mixture vas stirred at room temperature for 24 h at which time 7 mL of saturated sodium bicarbonate vas added to neutralize any excess hydrogen cyanide. The manganese dioxide was removed by filtration and vashed with 600 mL of ether. The combined organic portions were concentrated in vacuo to an orange slurry. The crude product was extracted from 300 mL of water with ether (3 x 200 mL), and the combined extracts were washed with water and brine. After drying over  $MgSO_4$ , the solvent was removed in vacuo to yield, after silica gel chromatography (85:15, hexane ethyl acetate), 1.6 g (33%) of the pure ester as a pale yellow oil. Glc analysis of the product showed it to be a mixture of the desired (2E,6E) isomer, 4a, (>95%)(with minor (columin B) contamination by the (2E,6Z) and (2Z,6E) isomers, combined <5%): <sup>1</sup>H NMR (400 MHz) & 0.98 (3H, t J= 7.4 Hz), 1.60 (3H, s), 1.97 (2H, q J = 7.4 Hz), 2.17 (7H, s), 3.69 (3H, s), 5.07 (1H, s, br), and 5.67 (1H, s); <sup>13</sup>C NMR (100 MHz) & 12.72, 15.89, 18.82, 25.89, 32.29, 40.95, 50.75, 115.16, 121.38, 138.05, 160.17 and 167.26; IR (f11m) 2960 (s), 1720 (s), 1650 (s), 1440 (s), 1230 (s), 1150 (s) and 870 (m) cm<sup>-1</sup>; HS m/e 196 (H<sup>+</sup>), 165, 137, 114, 83, 67, 55 (100) UV (methanol)  $\lambda_{max}$  (n-->x<sup>\*</sup>) 300 nm  $\epsilon_{300}$  = 63,  $\epsilon_{254}$  = 1340; high resoluand 41; tion MS m/e calcd for  $C_{12}H_{20}O_2$  196.1463, found 196.1456.

Photolysis of methyl geranate in ether. A solution of methyl geranate (0.182 g, 1 mmol) and dodecane (0.017 g, 0.1 mmol) in 10 mL of dry ether was degassed and irradiated for 8 hours at 253.7 nm. Ether was removed in vacuo and the crude mixture was analyzed by glc (column A). The gas chromatogram revealed five new product peaks, which were separated and collected by preparative glc (column E), as well as starting material. The identity of each peak (in order of

increasing retention time) was found to be: 13 (4.2%),  $^{1}$ H NMR (400 MHz) § 1.60 (3H, s), 1.65 (3H, s), 1.72 (3H, s), 2.24 (1H, p J = 7.3 Hz), 2.48 (1H, p J = 7.3 Hz), 3.01 (1H, t J = 7.6 Hz), 4.86 (1H, s), 4.87 (1H, m) and 4.99 (1H, tt J = 7.0, 1.0 Hz);  $^{13}$ C NMR (100 HHz) S 17.79, 20.39, 25.74, 28.93, 51.78, 53.20, 113.64, 121.05, 131.53, 142.39 and 112.95; IR (film) 2920 (m), 1120 (s), 1650 (v) and 1160 (m)  $cm^{-1}$ ; HS (m/e) 182 (H<sup>+</sup>), 139, 123, 122, 114, 107, 83, 82, 81, 69 (100) and 53; UV (methanol) end absorbance. 11 (5.9%),  $^{1}$ H NMR (400 MHz) & 0.75 (3H, s), 1.10 (3H, s), 1.11 (3H, s), 1.45, (1H, m), 1.55 (1H, m), 1.69 (1H, m), 2.30 (1H, s), 2.74 (1H, s) and 3.66 (3H, s); <sup>13</sup>C NMR (100 MHz) & 13.03, 16.97, 18.58, 23.62, 29.23, 43.18, 46.89, 50.09, 50.84, 53.25 and 112.78; IR (film) 2950 (s), 1120 (s), 1450 (s), 1440 (s), 1380 (s), 1050 (s) and 900 (m)  $cm^{-1}$ ; MS (m/e) 182 (M<sup>+</sup>), 123 (100), 122, 107, 81, 79, 67 and 55; UV (methanol) end absorbance . 12 (6.8%), <sup>1</sup>H NMR (400 HHz) & 0.91 (3H, d J = 7 Hz), 1.35-1.53 (2H, m), 1.71 (3H, s), 1.85-2.00 (2H, m), 2.41 (1H, br q J = 7 Hz, 2.78 (1H, t J = 9.2 Hz), 2.99 (1H, br q J = 8.4 Hz), 3.67 (3H, s), 4.70 (1H, br s) and 4.72 (1H, br s); <sup>13</sup>C NMR (100 MHz) & 16.90, 20.75, 30.58, 34.07, 36.94, 48.49, 51.19, 52.04, 109.37, 146.93 and 174.98; IR (film) 3050 (m), 2980 (s), 2875 (m,sh), 1120 (s), 1650 (s), 1440 (br, s), 1380 (br,s), 1170 (br, s) and 890 (s)  $cm^{-1}$ ; MS (m/e) 182 (M<sup>+</sup>), 167, 151, 139, 123, 114, 107, 83, 81, 69 (100) and 55. UV (methanol) end absorbance. 14 (5.7%), <sup>1</sup>H NMR (400 MHz) & 1.62 (3H, s), 1.69 (3H, s), 1.77 (3H, s), 2.71 (2H, t J = 7.2 Hz), 3.08 (2H, s), 3.68 (3H, s), 5.08 (1H, br t J = 7.2 Hz) and 5.33 (1H, br t J = 7.2 Hz); <sup>13</sup>C NMR(100 MHz) & 71.67, 23.91, 25.66, 27.23, 37.33, 51.78, 122.33, 127.78, 127.82, 132.00 and 171.96; IR (film) 2975 (s), 2918 (s), 2858 (s, sh), 1125 (s), 1436 (s), 1302 (m), 1259 (s) and 950 (m) cm<sup>-1</sup>; HS (m/e). 15 (41.6%), <sup>1</sup>H NHR (80 HHz) & 1.61 (3H, s), 1.67 (3H, s), 1.87 (3H, d J = 1.5 Hz), 2.16 (2H, m), 2.62 (2H, m), 3.67 (3H, s), 5.12 (1H, br t J = 7.2 Hz) and 5.63 (1H, s); <sup>13</sup>C NMR (20 MHz) & 17.39, 25.08, 25.50, 26.87, 33.44, 50.33, 115.91, 123.82, 131.82, 160.06 and 166.29; IR (film) 2970 (br,s), 1720 (s), 1650 (m), 1430 (m), 1220 (s), 1140 (s) and 1050 (v)  $cm^{-1}$ ; MS (m/e) 182 (M<sup>+</sup>), 123, 83, 82, 69 (100) and 53; UV (methanol)  $\lambda_{max}$  218 nm (x -  $\pi^{\circ}$ ),  $\epsilon$  = 3040 and 300 nm (n -  $\pi^{\circ}$ ),  $\epsilon$  = 25,  $\epsilon_{254}$  = 1350.

Photolysis of Methyl Geranate with 1,2-Dimethylimidazole. A solution of methyl geranate, 3, (0.182 g, 1 mmol) and 1,2-dimethylimidazole (0.024 g, 0.24 mmol) in 10 mL of dry ether vas degassed and irradiated for 5 h with 254 nm light. At this time the photolysis mixture vas vashed with 5% HCl, saturated NaHCO, and brine. The ether was removed, after drying with MgSO4, in vacuo and the reaction mixture analyzed by glc (column A). In addition to products 13, 11, 12, 14, 15 and starting material 3, two new products were isolated by preparative glc (column D) and characterized spectroscopically. 16: <sup>1</sup>H NMR (400 MHz) & 1.61 (3H, s), 1.69 (3H, s), 2.12 (4H, s), 3.06 (2H, s), 3.68 (3H, s), 4.91 (1H, s), 4.95 (1H, s) and 5.10 (1H, br s); <sup>13</sup>C NHR (20 MHz) & 17.69, 25.69, 26.27, 36.01, 41.93, 51.67, 113.69, 123.87, 131.85, 142.43 and 171.81; IR (film) 2900 (s), 1740 (s), 1650 (v), 1440 (m), 1160 (m), 1020 (m) and 900 (m) cm<sup>-1</sup>; HS (m/e) 182 (H<sup>+</sup>), 122, 109 (100), 107, 95, 83, 81, 12, 67, 59, 55 and 53; UV (methanol) end absorption. 17, <sup>1</sup>H NMR (400 MHz) & 1.63 (3H, s), 1.69 (3H, d J = 1 Hz), 1.71 (3H, s), 2.12 (2H, t J = 7.5 Hz), 3.00 (2H, s), 3.68 (3H, s), 5.10 (1H, t J = 7.5 Hz) and 5.25 (1H, t J = 7.5 Hz);  $^{13}$ C NMR (100 MHz) & 16.20, 17.69, 25.64, 27.17, 44.79, 51.67, 122.41, 128.00, 128.21, 131.95 and 172.48; IR (film) 2975 (s), 2918 (s), 2858 (s, sh), 1125 (s), 1436 (s), 1302 (m), 1259 (s) and 950 (m) cm<sup>-1</sup>; HS (m/e) 182 (M\*), 135, 124 (100), 123, 111, 109, 107,95, 91, 81, 79, 72, 67, 55 and 53; UV (methanol) end absorption.

Photolysis of Methyl Geranate and Propiophenone in benzene. A solution of methyl geranate, 3, (0.100 g, 0.55 mmol) and propiophenone (0.4 g, 3 mmol) in 10 mL of dry benzene was irradiated for 20 h with 254 nm light. After removal of benzene in vacuo the mixture was analyzed by glc (column A) and was found to consist of 11 (19%), 12 (22.6%), 15 (26.6%) and starting material, 3 (26.7%). Photolysis of Methyl Geranate, (3), in Ether, Time versus Composition. A solution of methyl geranate (0.455 g, 2.5 mmol) and dodecane (42 mg, 0.25 mmol) in 25 mL of ether vas divided among 20 quartz photolysis tubes. After degassing, two tubes were vrapped in aluminum foll and all were placed into the Rayonet reactor and irradiated with 254 nm light. Two tubes were removed at each of the following time intervals: 0.5, 1, 2, 4, 8, 12, 18.5, 30 and 48 h. The tubes wrapped in aluminum foil were in the reactor for the entire 48 h. All samples were analyzed by glc (column 8). Analysis results are presented in the discussion and results section (Figure 1).

Photolysis of Hethyl (2E,6E)-3,7-Dimethyl-2,6-nonadienoate (4a) in Ether, Time versus Composition. A solution of 4a (0.196 g, 0.001 mol) and dodecane (0.019 g,  $1.1 \times 10^{-4}$ mol) in 10 mL of ether was divided among 10 quartz photolysis tubes. After degassing in the usual way, the tubes were placed into the Rayonet reactor and irradiated with 254 nm light. two tubes were removed at each of the following time interval: 1.3, 2, 4, 8 and 12 h. Samples were analyzed by glc (column B). Product identification was achieved by  $^{1}$ H NMR (400 MHz),  $^{13}$ C NMR (100 MHz),  $^{1}$ H -  $^{1}$ H (COSY-45) and  $^{1}$ H -  $^{13}$ C (HETCOR) correlations and DEPT: 4b (2Z, 6E methyl ester) <sup>1</sup>H NMR & 0.97 (3H, tJ = 7.4 Hz), 1.62 (3H, s), 1.89 (3H, s), 1.97 (2H, q J = 7.4 Hz, 2.16 (2H, m), 2.65 (2H, t J = 7.8 Hz), 3.67 (3H, s), 5.14 (1H, m) and 5.66 (1H, s); <sup>13</sup>C NMR & 12.68, 15.85, 25.34, 26.60, 32.28, 33.47, 50.73, 115.77, 122.04, 137.66, 160.55 and 166.75; 4c (2E, 6Z methyl ester) <sup>1</sup>H NMR \$ 0.96 (3H, t J = 7.5 Hz), 1.67 (3H, s), 2.01 (2H, q J = 7.5), 2.16 (7H, s), 3.68 (3H, s), 5.04 (1H, m) and 5.67 (1H, s);  $^{13}C$  NMR \$ 12.74, 18.84, 22.82, 24.77, 25.66, 41.24, 50.77, 115.19, 122.54, 138.28, 160.12 and 167.27; 4d (2Z, 6Z methyl ester) <sup>1</sup>H NMR & 0.97 (3H, t J = 7.5 Hz), 1.67 (3H, s), 1.89 (3H, s), 2.03 (2H, q J = 7.5 Hz), 2.16 (2H, m), 2.63 (2H, t J = 7.6 Hz), 3.68 (3H, s), 5.12 (1H, m) and 5.66 (1H, s); <sup>13</sup>C NMR & 12.81, 22.81, 24.69, 25.38, 26.43, 33.76, 50.74, 115.80, 122.55, 138.28, 160.42 and 167.27. Analysis results are presented in the results and discussion section (Figure 2).

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