

## Photooxidation with Simultaneous Reduction of Hydroperoxides with Tetrabutylammonium Borohydride. Synthesis of Perillenal from Myrcene \*

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The synthetic routes to 2-methyl-5-(3-furyl)-2-pentenal, perillenal (*1*), starting from 2-methyl-6-methylene-2,7-octadiene, myrcene (*2*), are described. Myrcene (*2*) was either photooxidized to a mixture of the allylic alcohols *3* and *4* or converted to the aldehyde *11* by oxidation with selenium dioxide followed by chromium trioxide dipyridine in acetic acid. The alcohols *3* and *4* and the aldehyde *11* were cyclized with singlet oxygen to the endoperoxides *5*, *6*, and *12*, respectively. The endoperoxides were converted to the furans *7*, *8*, and *1* by treatment with Fe(II). The secondary allylic furan *8* was converted to perillenal (*1*) by a one-step reaction involving an allylic rearrangement and an oxidation with pyridinium chlorochromate in the presence of *p*-toluenesulfonic acid in dichloromethane. A method for photooxidation and simultaneous reduction of hydroperoxides with tetrabutylammonium borohydride is presented.

The furanoid monoterpene *E*-2-methyl-5-(3-furyl)-2-pentenal (*1*), for which the name perillenal was adopted, has been shown to be the main volatile component of glands excised from males and females of the pine sawfly *Neodiprion sertifer* (Geoff.).<sup>1</sup> The identification was confirmed by comparison of spectral (MS) and chromatographic (GC) data with those of a synthetic sample prepared<sup>1</sup> according to a method described by Thomas,<sup>2</sup> who used compound *1* as an intermediate for the synthesis of some furanoid terpenes.

In order to investigate the biological significance of perillenal *1* by means of electrophysiological

measurements and field tests, there is a need for alternative and simple synthetic routes to this compound.

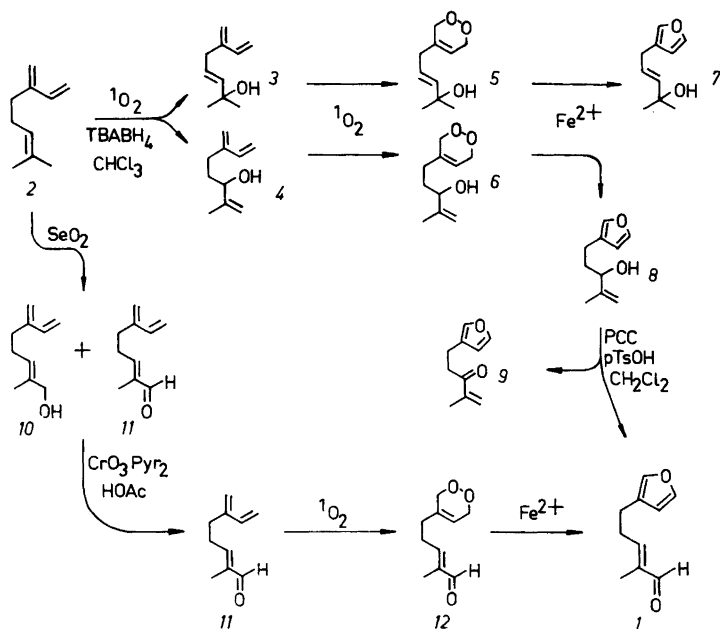
### DISCUSSION AND RESULTS

The preparative utility of the reactions of singlet oxygen with olefins was already emphasized by Schenk and his co-workers in their pioneering work on sensitized photooxygenations.\* Singlet oxygen reacts rapidly with tri- and tetrasubstituted double bonds and an allylic hydrogen in an ene-type reaction to give allylic hydroperoxides. With cyclic 1,3-dienes a facile Diels-Alder type reaction takes place. Although the formation of endoperoxides from open-chain 1,3-dienes and singlet oxygen is very slow due to conformational factors Kondo *et al.*<sup>4</sup> have recently shown that endoperoxide formation from 2-substituted butadienes is synthetically feasible. This is due to the slow rate of the competing ene-type reaction with mono- and disubstituted double bonds.<sup>4–6</sup> The endoperoxides can easily be converted to 3-substituted furans, *e.g.* by treatment with Fe(II) as shown by Herz,<sup>5</sup> thus providing attractive possibilities for the synthesis of perillenal (*1*), starting from the readily available 2-methyl-6-methylene-2,7-octadiene, myrcene (*2*).

Two different synthetic routes were followed. The first route, outlined in the upper part of Scheme 1, began with photooxidation of myrcene itself.<sup>4b,4c,8</sup> Due to the much greater reactivity of the trisubstituted double bond, a mixture of allylic

\* Part of this work was presented at the 8th Conference on Isoprenoids, Toruń, September 1979.

\* For comprehensive reviews of the reaction of singlet oxygen see Ref. 3.



Scheme 1.

hydroperoxides was rapidly formed. In our procedure the hydroperoxides were continuously reduced during irradiation (*vide infra*) to the corresponding alcohols 3 and 4.\* Extended irradiation gave a mixture of the endoperoxides 5 and 6. The mixture of 5 and 6 was converted to the furans 7 and 8 with  $\text{Fe}^{2+}$  according to Herz, and the products separated by column chromatography. A slight modification of Herz's procedure was introduced for the conversion of the endoperoxides. The solvent mixture (water—furan) was changed to water—acetone in order to avoid radical-induced reactions of furan.

The reaction sequence according to Scheme I could also be performed using a step-wise photooxidation procedure in which the alcohols 3 and 4 were first prepared and separated. The alcohol 4 was then subjected to a prolonged photooxidation followed directly by a transformation of the endoperoxide 6 to the furan alcohol 8. Such a step-wise procedure is convenient since fewer by-products are formed and the separation of the

reaction products can easily be performed by preparative chromatography. Furthermore, the alcohol 3, which is a by-product, is a useful starting material for a synthesis of ipsdienol, a pheromone component of the spruce bark beetle (*Ips typographus* L.).<sup>12</sup>

The necessary operations to obtain perillal (1) from compound 8 consisted of an allylic rearrangement and an oxidation. This was accomplished in one step\*\* by treating 8 with pyridinium chlorochromate (PCC)<sup>14</sup> in the presence of *p*-toluenesulphonic acid (pTsOH) in dichloromethane. In this reaction a minor amount (<20%) of ketone 9 was also formed. Although the isolated yield of pure 1 (*E:Z* > 98:2) was only  $\cong 35\%$  this method was preferred to alternative multistep sequences. When PCC in dichloromethane was used without addition of pTsOH for the treatment of 8, ketone 9 was formed as the major product together with trace amounts of 1.

A more direct route to perillal (1), outlined in the lower part of Scheme 1 has also been investigated. In this sequence the aldehyde was introduced prior to cyclization of the diene system in order to avoid the attack of singlet oxygen on the

\*The tertiary alcohol 3 has been identified as a constituent of the frass of *Ips paraconfusus* (Lanier)<sup>9</sup> and of guts of *Ips amitinus* (Eichh.).<sup>10</sup> It is also a plant constituent.<sup>11</sup> To our knowledge, 4 has not been described as a natural product although the corresponding ketone has been isolated from *Ledum palustre* (L.).<sup>11b</sup>

\*\*For an earlier example of the same type of reaction see Ref. 13.

trisubstituted double bond. This was done by oxidizing myrcene (2) with selenium dioxide<sup>15</sup> which gave a mixture of the alcohol 10 and the aldehyde 11. The mixture was subjected to oxidation with chromium trioxide dipyridine in acetic acid<sup>16</sup> to transform the alcohol 10 to aldehyde 11.

The aldehyde 11 could be photooxidized to the endoperoxide 12, which on treatment with Fe<sup>2+</sup> gave perillenal (1), albeit the over-all yield of 1 (*E:Z*  $\cong$  3.5:1) from 11 was only 6%.

*Simultaneous oxidation and reduction.* In connection with this work we have developed a method for continuous reduction of hydroperoxides as they are formed in photooxidation reactions. In this way, the corresponding alcohols can be isolated without a build-up of potentially hazardous compounds. The substrate, *i.e.* myrcene, was photooxidized in the presence of tetrabutylammonium (TBA) borohydride, which proved to be surprisingly stable towards oxygen. Rose bengal was made soluble in chloroform by the formation of ion pairs with TBA ions.<sup>17</sup> A slight molar excess was added in portions to ensure proper reduction. Although relatively large amounts of TBA ions were added in this process, removal did not constitute a problem. Stripping off the chloroform, followed by the addition of diethyl ether and a concentrated solution of potassium iodide in water caused precipitation of easily filtered TBA iodide.

The use of TBA borohydride provided an additional benefit. Initial attempts to photooxidize myrcene dissolved in various solvents, with light > 320 nm led to serious bleaching of rose bengal. This problem was obviated by the method described above.

## EXPERIMENTAL

UV measurements were obtained using a Beckman DU instrument connected to Optilab Multiblank 171 and Multilog 802 units. NMR spectra were recorded at 200 MHz in CDCl<sub>3</sub> with TMS as internal standard using a Bruker model WP 200 unless specified. A Finnigan model 4021 connected to an INCOS data system was used to record GC-MS spectra which are reported as stored in the INCOS MS-library. Analytical GLC was performed on a PYE GCV instrument with an FID detector connected to an integrator (Spectra Physics Minigrator). Merck 60 silica gel 0.040–0.063 mm, dry packed in 2.54 cm i.d. columns was used for liquid chromatography. The solvent, light petroleum b.p. 40–60 °C with stepwise increased

amounts of EtOAc, was delivered by a metering pump at a rate of 100 ml/min. B.p.'s are uncorrected. Irradiations were carried out in a Rayonet reactor equipped with 16 RPR 350 nm lamps or by using a Wisconsin Black Box<sup>18</sup> (WBB) fitted with a 1000 W AH-6-B high pressure mercury arc employing a filter combination of 2 cm concentrated water solution of copper sulfate and 1 mm soft glass to cut off light < 320 nm. Stock solutions of solubilized rose bengal were made by mixing 1.50 g rose bengal and 0.97 g TBA bromide per liter chloroform followed by filtration to remove insoluble residue.

*Tetrabutylammonium (TBA) borohydride.* This reagent was prepared according to Brändström.<sup>19</sup> A suspension of 340 g (1.0 mol) of TBA hydrogen sulfate and 50 g (1.25 mol) of sodium hydroxide in 250 ml of water were mixed and cooled to room temperature. Dichloromethane, 500 ml, and 40 g (1.1 mol) of sodium borohydride in 100 ml of water were added and the mixture was agitated a few minutes. Precipitated sodium sulfate was removed by filtration using glass wool. The upper dichloromethane layer was separated and the aqueous layer extracted with 250 ml of dichloromethane (lower layer). After drying with anhydrous K<sub>2</sub>CO<sub>3</sub> and filtration, 250 ml of toluene were added and the solvents were removed by reduced pressure and by heating < 50 °C. The crystals were washed with ethyl ether and recrystallized from ethyl acetate, m.p. 126 °C.

*Exploratory irradiation of 2-methyl-6-methylene-2,7-octadiene, myrcene (2).* To a 0.1 M solution of myrcene dissolved in the stock solution of rose bengal in chloroform was added tetradecane as internal standard and an excess of TBA borohydride. Irradiations were carried out in the Rayonet reactor with a constant flow of oxygen bubbling through the solution. Before GLC monitoring (2 m, 4 mm, i.d., 10% Carbowax 20 M, 160 °C) withdrawn samples were filtered through basic alumina and eluted with ether. These investigations showed that a maximum yield of 38% of tertiary alcohol 3 and 36% secondary alcohol 4 could be obtained at 95% conversion of myrcene (2).

*2-Methyl-6-methylene-3,7-octadiene-2-ol (3) and 2-methyl-6-methylene-1,7-octadiene-3-ol (4).* Myrcene (2), 10 g (0.074 mol), was dissolved in 750 ml of the stock solution of rose bengal in chloroform and was irradiated in the WBB with a constant flow of oxygen bubbling through the solution. At 0, 30, 60 and 90 min of irradiation, portions of 10, 5, 2.5 and 2.5 g, in all 20 g (0.078 mol), of TBA borohydride were added. After 2 h of irradiation the chloroform was removed under reduced pressure (< 0.1 Torr). To the viscous residue was added 20 g (0.120 mol) of potassium iodide in 25 ml of water and 250 ml of ethyl ether. The mixture was then stirred for 1 h. The resulting crystals were separated by filtration and

washed with ether. The combined red ethereal layer was separated from the aqueous phase and dried with  $\text{MgSO}_4$ . After removal of the drying agent, 50 g of basic alumina were added and the ether was removed under reduced pressure. The red dry powder was poured on top of a column of 70 cm of silica gel with a top layer of 3 cm of basic alumina. After wetting the column with light petroleum (300 ml) the compounds were eluted by pumping 600 ml each of 0, 1.25, 2.5, 5 and 10 % of ethyl acetate in light petroleum. Elution was continued with 20% ethyl acetate in light petroleum. Of the two alcohols, the secondary alcohol 4 had the smaller retention volume. The yield of the reaction varied with the quality of the myrcene used. The best isolated yields obtained were 4.1 g of 3 (36%) and 3.3 g of 4 (27%). The analytical samples were further purified by distillation. Alcohol 3, b.p. 41 °C/0.3 Torr;  $n_D^{23}$  1.4835; MS:  $m/e$  (rel. int.) 137 (1.2), 134 (3.5), 119 (6.2), 95 (5.1), 93 (7.4), 91 (11.0), 85 (10.5), 81 (10.2), 80 (7.9), 79 (13.7), 77 (7.0), 67 (7.1), 59 (26.9), 55 (15.4), 53 (11.0), 43 (100), 41 (25.2); NMR:  $\delta$  6.35 (1H, dd,  $J = 17.6$  and 10.7 Hz, =CH-C=), 5.67 (2H, apparent s, CH=CH), 5.22 (1H, d,  $J = 17.6$  Hz, -HC=CH<sub>2</sub>, *trans*), 5.05 (1H, d,  $J = 10.6$  Hz, -HC=CH<sub>2</sub>, *cis*), 5.03 (1H, =CH<sub>2</sub>), 4.99 (1H, =CH<sub>2</sub>), 2.92 (2H, 5.9 Hz br., CH<sub>2</sub>), ~1.71 (1H, br., OH), 1.29 (6H, s, gem. CH<sub>3</sub>). Alcohol 4, b.p. 46 °C/0.2 Torr;  $n_D^{23}$  1.4820, lit.<sup>4c</sup> b.p. 85 °C/11 Torr; MS:  $m/e$  (rel. int.) 137 (3.3), 123 (4.4), 119 (4.2), 109 (5.1), 96 (6.7), 93 (10.4), 91 (10.5), 84 (21.7), 83 (9.2), 81 (11.8), 79 (21.0), 71 (27.5), 69 (28.3), 68 (19.0), 67 (29.8), 57 (11.1), 55 (24.5), 53 (27.1), 43 (64.7), 41 (100); NMR:  $\delta$  6.39 (1H, dd,  $J = 17.7$  and 10.7 Hz, =CH-C=), 5.26 (1H, d,  $J = 17.7$  Hz, -CH=CH<sub>2</sub>, *trans*), 5.07 (1H, d, partially obscured,  $J = 10.7$ , -CH=CH<sub>2</sub>, *cis*), 5.04 (2H, 3 Hz br. s, conj. =CH<sub>2</sub>), 4.98 (1H, 3.7 Hz br., =CH<sub>2</sub>), 4.87 (1H, 3 Hz br., =CH<sub>2</sub>), 4.11 (1H, apparent t,  $J \sim 6.5$  Hz, HO-CH), 2.3-2.2 (2H, m, =CH<sub>2</sub>-), 1.8-1.6 (2H, m, partially obscured, HO-CH-CH<sub>2</sub>-), 1.74 (3H, t,  $J = 1.2$  Hz, -CH<sub>3</sub>), ~1.6 (1H, OH).

*2-Methyl-5-(3-furyl)-1-penten-3-ol* (8). The secondary alcohol 4, 6.727 g (44.26 mmol), was dissolved in 750 ml of the stock solution of rose bengal in chloroform and irradiated in the WBB for 24 h. The solvent was removed under reduced pressure with heating <40 °C. The last traces of solvent were removed at a pressure <1 Torr. The residue was dissolved in 150 ml of acetone and 12 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 300 ml of water were added. The mixture was stirred for 2 h. Most of the acetone was removed under reduced pressure before extraction with two portions of ethyl ether. The organic layer was washed with water and dried with  $\text{MgSO}_4$ . Filtration and solvent removal gave a red oil which was chromatographed on silica gel, yielding 1.342 g of starting material and 3.574 g of compound 9 (61 % of nonrecovered starting material). The analytical

sample was further purified by distillation. B.p. 80 °C/0.3 Torr;  $n_D^{23}$  1.4895; MS:  $m/e$  (rel. int.) 166  $\text{M}^+$  (1.8), 151 (2.8), 149 (2.0), 148 (17.4), 133 (5.2), 123 (3.8), 119 (3.6), 108 (3.8), 105 (3.6), 95 (22.8), 94 (11.4), 91 (4.5), 83 (7.7), 82 (100), 81 (66.8), 72 (9.9), 71 (23.5), 67 (13.9), 57 (9.6), 54 (8.7), 53 (25.3), 43 (41.5), 41 (60.3); NMR:  $\delta$  7.36 (1H, furan,  $\alpha$ -pos.), 7.24 (1H, furan,  $\alpha$ -pos.), 6.29 (1H, furan,  $\beta$ -pos.), 4.97 (1H, =CH<sub>2</sub>), 4.87 (1H, =CH<sub>2</sub>), 4.10 (1H, apparent t,  $J \approx 6$  Hz, HO-C-H), 2.52-2.45 (2H, m, fur.-CH<sub>2</sub>-), 1.86-1.78 (2H, m, HO-C-CH<sub>2</sub>-), 1.74 (3H, s, =-CH<sub>3</sub>),  $\approx 1.5$  (1H, OH).

*2-Methyl-5-(3-furyl)-3-penten-2-ol* (7) and compound 8 from prolonged irradiation of myrcene (2). Starting with 10 g (0.074 mol of myrcene (2), the same procedure was followed as for the synthesis of 3 and 4 but irradiation was extended to 60 h. Silica gel chromatography gave 1.54 g of the two alcohols 3 and 4 and 1.90 g (14%) of the endoperoxides 5 and 6, which were collected in one fraction. The endoperoxides 5 and 6, 1.90 g (0.010 mol) dissolved in 50 ml of acetone, were mixed with 4.59 g (0.017 mol) of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dissolved in 75 ml of water and stirred for 2 h. The reaction mixture was worked up as described for the preparation of compound 6. The isolated yield of furans from endoperoxides was 1.44 g (87%). The furan alcohols 7 and 8 were separated by silica gel chromatography and further purified by bulb-to-bulb distillation. For NMR data of 6 see Ref. 4c. Compound 7 exhibits the following spectral data: MS:  $m/e$  (rel. int.) 166  $\text{M}^+$  (1.6), 151 (9.7), 149 (1.1), 148 (3.5), 133 (2.2), 123 (1.4), 109 (2.3), 105 (2.3), 95 (3.7), 94 (2.1), 91 (3.4), 85 (17.5), 82 (9.4), 81 (8.7), 79 (6.8), 77 (6.4), 72 (4.0), 59 (15.6), 57 (5.4), 55 (9.3), 53 (8.0), 43 (100), 41 (11.9); NMR:  $\delta$  7.36 (1 H, furan,  $\alpha$ -pos.), 7.22 (1H, furan,  $\alpha$ -pos.), 6.26 (1H, furan,  $\beta$ -pos.), 5.76-5.71 (2H, m, HC=CH), 3.16 (2H, d,  $J = 4.2$  Hz, CH<sub>2</sub>), ~1.5 (1H, br. s, OH), 1.32 (6H, s, gem., CH<sub>3</sub>).

*E-2-Methyl-5-(3-furyl)-2-pentenal*, *perillenal* (1) and *2-methyl-5-(3-furyl)-1-penten-3-one* (9). The secondary allylic furan alcohol 8 (2.490 g, 0.015 mol) was added to a stirred suspension of PCC<sup>14</sup> (6.465 g, 0.030 mol) and *p*-toluenesulfonic acid monohydrate (8.55 g, 0.045 mol) in 1500 ml of dichloromethane. The reaction mixture darkened rapidly. After 1 h, 100 ml of water and 200 ml of saturated sodium chloride solution were added and the layers separated. The dichloromethane layer was treated twice more in the same way and dried with  $\text{MgSO}_4$ . Silica gel chromatography gave 0.188 g (7.3%) of ketone 9 and 0.858 g (35%) of perillenal (1), with an E:Z ratio >98:2 as determined by GC (PYE GCV equipped with a capillary inlet system described in Ref. 20, 25 m i.d. 0.2 mm SE 30, 70-150 °C, 6 °C/min). Compound 1 was further purified by distillation. B.p. 76-77 °C/0.3 Torr;  $n_D^{23}$  1.5060. Perillenal (1) exhibits the following spectral data: MS:  $m/e$  (rel. int.) 164  $\text{M}^+$  (4.6), 149 (0.9), 146 (1.2), 136 (1.9), 135

(1.1), 107 (3.7), 94 (1.7), 91 (1.4), 82 (11.0), 81 (100), 77 (1.3), 65 (1.3), 55 (2.3), 54 (1.9), 53 (24.4), 51 (4.3), 41 (5.6), 40 (21.5); NMR:  $\delta$  9.69 (1H, CHO), 7.37 (1H, furan,  $\alpha$ -pos.), 7.26 (1H, furan,  $\alpha$ -pos.), 6.53–6.46 (1H, m, =CH), 6.28 (1H, furan,  $\beta$ -pos.), 2.64–2.57 (4H, m,  $\text{CH}_2\text{-CH}_2$ ), 1.73 (3H, s,  $\text{CH}_3$ ). For a 60 MHz spectrum of an *E*- and *Z*-mixture of *l* recorded in  $\text{CCl}_4$  see Ref. 2. Compound 9 exhibits the following spectral data: MS:  $m/e$  (rel. int.) 164  $\text{M}^{++}$  (11.0), 149 (1.5), 136 (1.3), 135 (2.6), 122 (1.0), 121 (2.2), 108 (1.3), 96 (5.0), 95 (61.9), 94 (8.9), 91 (2.7), 82 (3.6), 81 (37.4), 69 (23.2), 67 (10.0), 65 (5.0), 55 (5.0), 53 (13.2), 41 (100), 40 (6.4); NMR:  $\delta$  7.34 (1H, furan,  $\alpha$ -pos.), 7.25 (1H, furan,  $\alpha$ -pos.), 6.27 (1H, furan,  $\beta$ -pos.), 5.96 (1H, = $\text{CH}_2$ ), 5.77 (1H, = $\text{CH}_2$ ), 2.99–2.91 (2H, m, part of aa'bb'syst.), 2.80–2.72 (2H, m, part of aa'bb'syst.), 1.89 (3H, - $\text{CH}_3$ ).

*2-Methyl-6-methylene-2,7-octadienal* (11). Myrcene (2) was oxidized with selenium dioxide according to Delaby and Dupin<sup>15</sup> which gave a mixture of alcohol 10 and aldehyde 11. The mixture was distilled and the fraction b.p. 80–105 °C/1–5 Torr was subjected to oxidation with chromium trioxide dipyridine in acetic acid prepared according to Stensiö and Wachtmeister.<sup>16</sup> To 350 ml of a 1 M solution of the complex, cooled in an ice-bath, was added 10 g of the alcohol aldehyde mixture during 5 min. After additional 10 min the reaction mixture was poured into 500 ml of water and extracted with ether. The ether layer was washed with water and aqueous sodium carbonate. Drying with  $\text{MgSO}_4$  and work-up gave 6.5 g of yellow oil which was distilled to yield aldehyde 11 b.p. 45–55 °C/1 Torr. MS:  $m/e$  (rel. int.) 150  $\text{M}^{++}$  (4.8), 149 (1.1), 135 (5.4), 121 (4.1), 117 (2.9), 107 (4.0), 105 (3.4), 95 (6.0), 93 (44.5), 92 (31.1), 91 (23.1), 82 (8.4), 79 (24.1), 77 (13.5), 67 (21.6), 65 (15.5), 55 (27.8), 54 (10.2), 53 (22.5), 43 (13.9), 41 (100); NMR 60 MHz ( $\text{CDCl}_3$ ):  $\delta$  9.40 (1H, s, CHO), 6.40 (1H, dd,  $J=17.0$  and 10.5 Hz, =CH-C=), 6.42 (1H, m, =CH- $\text{CH}_2$ ), 5.20 (1H, d,  $J=17.0$  Hz, = $\text{CH}_2$ ), 5.08 (1H, d,  $J=10.5$  Hz, = $\text{CH}_2$ ), 5.01 (2H, br. s, = $\text{CH}_2$ ), 2.55–2.20 (2H, m,  $\text{CH}_2\text{-CH}_2$ ), 1.70 (3H, s,  $\text{CH}_3$ ).

*Perillenal* (1) from photooxidation of *2-methyl-6-methylene-2,7-octadienal* (11). Aldehyde 11 (1 g) was added to a solution of rose bengal (0.509 g) and TBA bromide (0.070 g) in 100 ml of a mixture of methanol (5%) in dichloromethane. The solution was irradiated in the Rayonet reactor for 19 h with a continuous flow of oxygen bubbling through the reaction mixture. Occasionally some rose bengal solution was added to make up for the bleaching of the sensitizer that occurred. The solvent was removed under reduced pressure and the residue was dissolved in 20 ml of THF. A slight excess of ferrous sulfate dissolved in 40 ml of water was added. The reaction mixture was left overnight. Water (300 ml) was then added and the reaction

mixture was worked up by extraction with ethyl ether. The ethereal phase was dried with  $\text{MgSO}_4$ . The solvent was removed under reduced pressure (10 mm) with heating <25 °C to yield 0.740 g of red oil. Silica gel chromatography using 10% ether in light petroleum as the eluent gave 0.059 g, 5% of an *E:Z* mixture (85:15) of perillenal (1).

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