# Photooxidative dehydrogenation of $\Delta^8$-drimen- and $\Delta^8$-11-homodrimen-7-ones into $\alpha,\alpha'$- dienones

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An efficient two-step procedure for photooxidative dehydrogenation of drimane and 11-homodrimane compounds containing an 8-en-7-one structural unit into $\alpha,\alpha'$-dienones was elaborated. The method is based on the transformation of ketones into the respective enol acetates followed by photosensitized oxygenation. Methyl 7-oxo-11-homodrima-5,8-dien-12-oate, 5,6-dehydro-7-ketoisodrimenine, 11-acetoxydrima-5,8-dien-7-one and 11,12-diacetoxydrima-5,8-dien-7-one were prepared in high yields starting from methyl 7-oxo-11-homodrim-8-en-12-oate, 7-oxoisodrimenine, 11-hydroxydrim-8-en-7-one and 11,12-diacetoxydrim-8-en-7-one, respectively.

**Key words:** photosensitized oxygenation, photooxidative dehydrogenation, drim-8-en-7-ones, drima-5,8-dien-7-ones, methyl 7-oxo-11-homodrim-8-en-12-oate, methyl 7-oxo-11-homodrim-5,8-dien-12-oate.

Aimed at preparing 11-homodrimane derivatives with oxygen-containing functional groups at the C(6) and C(9) atoms from readily available methyl 7-oxo-11-homodrim-8-en-12-oate (**1**),[1] we studied the photooxidative oxygenation of the enol acetate derived from **1**, namely, methyl 7-acetoxy-11-homodrima-6,8-dien-12-oate (**2**), in the presence of tetraphenylporphyrin ($H_2$tpp). We took into account the fact that conjugated 1,3-dienes preferably react with singlet oxygen according to the [4+2]-cycloaddition pattern to give endoperoxides.[2,3] However, data from elemental and spectral analyses convincingly demonstrated that the reaction product formed in high yield (93%) was not endoperoxide (**3**). The molecule contained no peroxide or acetate groups, but the ester function retained and a dienone group appeared (IR and $^1$H and $^{13}$C NMR data). Hence, the product was identified as methyl 7-oxo-11-homodrima-5,8-dien-12-oate (**4**) (Scheme 1). Previously, we have synthesized this compound[1] by dehydrogenation of oxo ester **1** with selenium dioxide. The physicochemical and spectral characteristics of compound **4** prepared from oxo ester **1** by these two methods were fully identical. It is noteworthy that photosensitized oxygenation of enol ester **2** is a more efficient and convenient route to dienone ester **4**, because the reaction of oxo ester **1** with $SeO_2$ gave not only the target product **4**, but also organoselenium by-products that are difficult to separate.

It was of interest to elucidate whether the two-step transformation of oxo ester **1** into dienone ester **4** that we found is common to enones of the *trans*-decalin series with similar structures, in particular, drimane compounds. Therefore, we used this approach to prepare natural oxo lactone **7** isolated from the moss *Porella cordeana*.[4] 7-Oxoisodrimenine (**5**) served as the starting compound.[5] Enol acetate **6** was photooxidized with oxygen in the presence of $H_2$tpp to give the target compound **7** in high yield (69%). When Bengal Rose was used as the photosensitizer instead of $H_2$tpp, the yield of the reaction product decreased to 57%. This synthesis has been described previously.[6]

Then we investigated photooxidative dehydrogenation of 11-hydroxydrim-8-en-7-one (**8**).[7] Its reaction with isopropenyl acetate in the presence of TsOH did not proceed to completion even on long-term refluxing and afforded a complex mixture of compounds in which the desired 7,11-diacetoxydrima-6,8-diene (**9**) was the major component. Its structure was confirmed by data from elemental and spectral analyses data. A two-step route to diacetoxy diene **9** from hydroxy ketone **8** proved to be more efficient and convenient. Compound **8** was ace-

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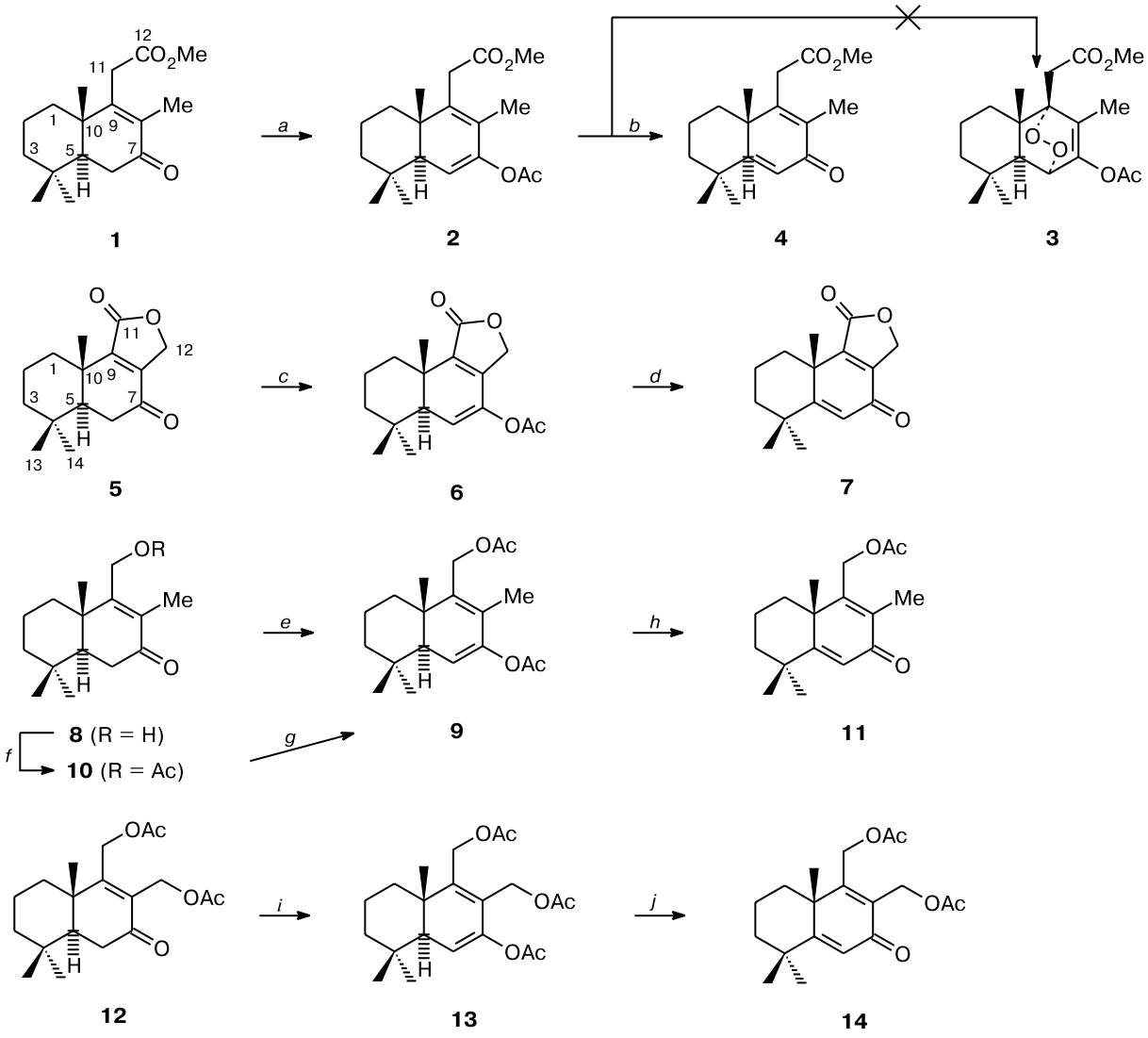
**Scheme 1**




**Reagents and conditions:** *a*. $H_2C$=C(Me)OAc, TsOH, Ar, Δ, 3 h, 98.5%; *b*. $O_2$, *h*ν, $H_2$tpp, $CCl_4$, 20 °C, 5 h, 90%; *c*. $H_2C$=C(Me)OAc, TsOH, Δ, 2 h, 75%; *d*. $O_2$, *h*ν, $H_2$tpp, $CCl_4$, 12 °C, 14 h, 69%; *e*. $H_2C$=C(Me)OAc, $C_6H_6$, TsOH, Δ, 6 h, 59%; *f*. $Ac_2O$, Py, 20 °C, 24 h, 97%; *g*. $H_2C$=C(Me)OAc, TsOH, Δ, 6 h, 72.6%; *h*. $O_2$, *h*ν, Bengal Rose, $CCl_4$, 20 °C, 20 h, 63%; *i*. $H_2C$=C(Me)OAc, TsOH, Ar, Δ, 6 h, 99%; *j*. $O_2$, *h*ν, $H_2$tpp, $CCl_4$, 20 °C, 4 h, 52.5%.

tylated with an $Ac_2O$—Py mixture under standard conditions to give the known 11-acetoxydrim-8-en-7-one (**10**)[7] (yield 97%) whose treatment with isopropenyl acetate in the presence of TsOH gave enol acetate **9** in 70% overall yield. In this case, the formation of enol acetate is more unambiguous and the reaction product could readily be purified by chromatography.

Photooxygenation of diacetoxy diene **9** in the presence of $H_2$tpp proceeded in relatively low yield (36%). In this case, Bengal Rose was a more efficient photosensitizer, ensuring an acceptable yield (63%) of 11-acetoxydrima-5,8-dien-7-one (**11**). Its structure was confirmed by the data from elemental and spectral analyses. In particular, the spectral characteristics of the dienone structural fragment were similar to those found for compounds **4** and **7**.

11,12-Diacetoxydrim-8-en-7-one (**12**) was also subjected to sensitized photooxidative dehydrogenation.[7] TsOH-catalyzed transformation of **12** into enol acetate with isopropenyl acetate afforded 7,11,12-triacetoxydrima-6,8-diene (**13**) in quantitative yield. Photosensitized oxygenation of compound **13** occurred most smoothly in the presence of $H_2$tpp to give 11,12-diacetoxydrima-5,8-dien-7-one (**14**) in 52.5% yield. Its structure was established by elemental and spectral

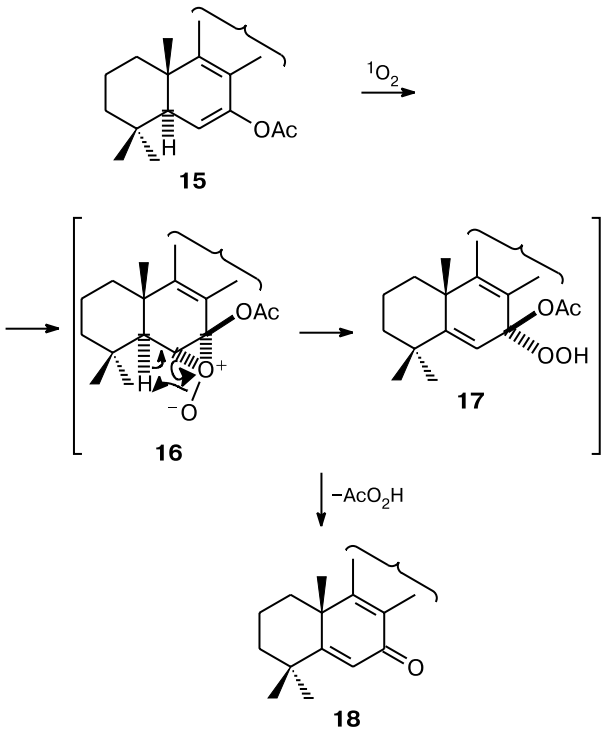
analyses. Apart from the major product, the reaction afforded a complex mixture of minor products, which were not further studied.

Thus, we demonstrated that the transformation of drimane and 11-homodrimane derivatives containing an 8-en-7-one structural fragment into 5,8-dien-7-ones upon the reaction of the corresponding enol acetates with singlet oxygen is of general character. It is noteworthy that in the absence of photosensitizers, enol acetates do not react with oxygen, *i.e.*, their dehydrogenation is caused by singlet oxygen. This method is a convenient alternative to $SeO_2$-induced dehydrogenation of these compounds.

The above-mentioned pathway of reaction of diene enol acetates **2**, **6**, **9**, and **13** with singlet oxygen can be interpreted as follows (Scheme 2). Diene systems in these compounds contain an electron-rich 6,7-double bond. Since singlet oxygen is electrophilic,[2,8] it reacts with compounds of the type **15** according to the ene reaction pattern involving the 6,7-double bond to give peroxy epoxide **16** (see Ref. 8) rather than according to the [4+2]-cycloaddition route. Singlet oxygen is known[2,8–10] to be sensitive to steric factors and, hence, the addition at the 6,7-double bond should occur from the sterically more accessible α-side of type **15** molecules to give peroxy epoxide **16**. This is also favored by the stereoelectronic requirements of the stereospecific ene photosensitized oxygenation: the newly formed C—O bond and the cleaved allylic C—H bond should be *cis*-arranged, and the allylic C—H bond should be perpendicular to the $\Delta^6$-bond plane, as only in this case, can the electron pair of the cleaved C—H bond interact with π-bond electrons to give a new double bond.[2,8–12] Thus, in the case of compounds with structure **15**, the steric and stereoelectronic factors act in the same direction, thus promoting the stereospecific formation of peroxy epoxide **16**, which is then converted regioselectively into unstable allylic hydroperoxide **17**, which eliminates peracetic acid being converted into the final product **18**.

It is noteworthy that similar photosensitized oxidative dehydrogenation has been performed previously[13] with tricyclic diterpenes containing an aromatic ring C and an oxo group in position 7.

**Scheme 2**




## Experimental

Melting points were determined on a Boetius hot stage. IR spectra were recorded on a Specord 74 spectrophotometer in $CCl_4$. $^1H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ on a Bruker AM-400 spectrometer (400.13 and 100.13 MHz, respectively) using $Me_4Si$ as the internal standard. The chemical shifts are in the δ scale. The $^{13}C$ NMR signals were assigned using the DEPT technique and by comparison with the spectra of the known related compounds described previously.[4–7] Mass spectra (EI, 70 eV) were obtained on an AEI MS 902 mass spectrometer. Photooxygenation of solutions of compounds was carried out in glass pear-shaped flasks (15 mL, diameter 2 cm) with external irradiation from two fluorescent lamps (40 W) at a distance of 1 cm from the flask and bubbling of oxygen through the solution at a rate of 6 L $h^{-1}$. Column chromatography was carried out using Across silica gel (60/200 μm); TLC was carried out on Silufol plates (visualization by iodine vapor) and Sorbfil (visualization by an $H_2SO_4$-acidified methanolic solution of $Ce_2(SO_4)_3$).

**Transformation of methyl 7-oxo-11-homodrim-8-en-12-oate (1) into enol acetate (2).** *p*-Toluenesulfonic acid (15 mg) was added to a solution of oxo ester **1** (0.15 g, 0.42 mmol) in isopropenyl acetate (3 mL) and the mixture was refluxed for 3 h under argon. The reaction mixture was cooled and diluted with $H_2O$ (10 mL) and the products were extracted with ether (3×30 mL). The extract was washed with water, a saturated solution of $NaHCO_3$, and water, dried with anhydrous $Na_2SO_4$, filtered, and concentrated *in vacuo*. The liquid residue was chromatographed on a column with $SiO_2$ (11 g). Elution with hexane—$Et_2O$ (97 : 3) gave 0.17 g (yield 98.5%) of methyl 7-acetoxy-11-homodrima-6,8-dien-12-oate (**2**). Found (%): C, 71.48; H, 9.06. $C_{19}H_{28}O_4$. Calculated (%): C, 71.22; H, 8.81. IR, ν/cm$^{-1}$: 1160, 1751 ($CO_2Me$); 1205, 1732 (OAc); 1590, 1657 (conjugated >C=C< bonds). $^1H$ NMR, δ: 0.91 (s, 3 H) and 0.96 (s, 6 H) (C(4)$Me_2$ and C(16)$H_3$); 1.61 (s, 3 H, C(13)$H_3$); 2.19 (s, 3 H, OAc); 2.23 (d, 1 H, C(5)H, $J$ = 2.0 Hz); 3.07, 3.18 (both d, 1 H each, AB-system, C(11)$H_2$, $J$ = 10.9 Hz); 3.69 (s, 3 H, $CO_2Me$); 5.41 (d, 1 H, C(6)H, $J$ = 2.0 Hz). $^{13}C$ NMR, δ: 12.63 (C(13)); 15.07 (C(16)); 18.81 (C(2)); 20.72 (C(14)); 22.80 ($\underline{C}H_3COO$); 32.33 (C(15)); 32.87 (C(1)); 33.09(C(4)); 34.84 C(3)); 39.53 (C(10)); 40.69 (C(11)); 51.23 (C(5)); 51.95 ($COO\underline{C}H_3$); 113.98 (C(6)); 126.12 (C(7)); 139.94 (C(8)); 147.20 (C(9)); 169.65 ($CH_3\underline{C}OO$); 172.36 (C(12)). Found: M 320.1984.

$C_{19}H_{28}O_4$. Calculated: M 320.1988. MS, $m/z$ ($I_{rel}$ (%)): 320 [$M^+$] (24), 278 [$M - C_3H_6$]$^+$ (100), 245 [$M - C_3H_7 - CH_3OH$]$^+$ (13), 205 [$M - C_3H_7 - CH_3OH - C_2O$]$^+$ (38), 149 [$M - C_8H_{12}O_2$]$^+$ (12), 135 [$M - C_9H_{13}O_2$]$^+$ (41).

**Photooxygenation of methyl 7-acetoxy-11-homodrima-6,8-dien-12-oate (2).** The photosensitizer $H_2$tpp (20 mg) was added to a solution of enol acetate **2** (0.2 g, 0.63 mmol) in dry $CCl_4$ (5 mL), and the solution was irradiated for 5 h at 20 °C with dry $O_2$ bubbling through. The solvent was evaporated *in vacuo*, the liquid (0.22 g) was chromatographed on a column with $SiO_2$ (10 g). Elution with hexane—ethyl acetate (95 : 5) gave 144 mg of methyl 7-oxo-11-homodrima-5,8-dien-12-oate (**4**), m.p. 111—112 °C (from hexane) (*cf.* Ref. 1: m.p. 114—115 °C). IR, ν/cm$^{-1}$: 826 (>C=C<$_H$); 1350, 1371 (C(4)$Me_2$); 1614, 1637 (dienone group >C=CH—C(=O)—C($CH_3$)=C<); 1167, 1715 ($CO_2$Me). $^1$H NMR, δ: 1.22, 1.29, 1.31 (all s, 3 H each, C(14)$H_3$, C(15)$H_3$, C(16)$H_3$); 1.86 (s, 3 H, C(13)$H_3$); 3.33, 3.47 (both d, 1 H each, AB-system, C(11)$H_2$, $J$ = 8.0 Hz); 3.68 (s, 3 H, $CO_2CH_3$); 6.33 (s, 1 H, C(6)H). $^{13}$C NMR, δ: 11.60 (C(13)); 18.13 (C(2)); 25.30 (C(16)); 28.63 (C(14)); 32.40 (C(15)); 34.37 (C(1)); 35.03 (C(3)); 37.35 (C(4)); 40.31 (C(11)); 43.83 (C(10)); 52.24 (COO<u>C</u>$H_3$); 123.96 (C(6)); 133.50 (C(8)); 155.05 (C(9)); 170.35 (C(5)); 172.35 (<u>C</u>$O_2CH_3$); 186.72 (C(7)). The chromatographic and spectral characteristics of compound **4** were identical to those for an authentic sample that we have prepared previously.[1]

Further elution with the same solvent gave 14.6 mg (7.3%) of the starting compound **2**. The yield of reaction product **4** with allowance for the recovery of the starting compound was 90%.

**Synthesis of 7,11-diacetoxydrima-6,8-diene (9).** ***A.*** *p*-Toluenesulfonic acid (5 mg) was added to a solution of 11-hydroxydrim-8-en-7-one (**8**) 60 mg (0.25 mmol) in a mixture of isopropenyl acetate (1.5 mL) and anhydrous benzene (1.5 mL) and the mixture was refluxed for 4 h. The solvent was evaporated *in vacuo*, and the residue was dissolved in $Et_2O$ (15 mL). The solution was washed with a saturated solution of $NaHCO_3$ (2×2 mL) and water (3×2 mL), dried with anhydrous $Na_2SO_4$, and filtered. The solvent was evaporated *in vacuo*. The residue (75 mg) was chromatographed on a column with $SiO_2$ (2 g). Elution with light petroleum—$Et_2O$ (3 : 1) gave 48 mg (yield 59%) of diacetoxy diene **9**. Found (%): C, 71.41; H, 8.43. $C_{19}H_{28}O_4$. Calculated (%): C, 71.22; H, 8.81. IR, ν/cm$^{-1}$: 1230, 1740 (OAc); 1650 (conjugated >C=C< bond). $^1$H NMR, δ: 0.82, 0.87, 0.94 (all s, 3 H each, C(13)$H_3$, C(14)$H_3$, C(15)$H_3$); 1.58 (s, 3 H, C(12)$H_3$); 1.95, 2.08 (both s, 3 H each, 2 OAc); 4.57 (s, 2 H, C(11)$H_2$); 6.34 (d, 1 H, C(6), $J$ = 2.6 Hz). $^{13}$C NMR, δ: 11.92 (C(12)); 15.73 (C(15)); 18.44 (C(2)); 20.37, 20.82 (both <u>C</u>$H_3$COO); 22.53 (C(14)); 32.11 (C(1)); 32.78 (C(4)); 34.43 (C(13)); 38.62 (C(3)); 40.47 (C(10)); 51.19 (C(5)); 59.68 (C(11)); 115.85 (C(6)); 129.00 (C(7)); 139.69 (C(8)); 146.76 (C(9)); 169.30, 170.73 (both $CH_3$<u>C</u>OO).

***B.*** *p*-Toluenesulfonic acid (6 mg) was added to a solution of 11-acetoxydrim-8-en-7-one (**10**)[7] (0.2 g, 0.72 mmol) in isopropenyl acetate (1.5 mL), and the mixture was refluxed for 6 h (TLC monitoring). Ether (10 mL) was added. The solution was washed with a saturated solution of $NaHCO_3$ (2×5 mL) and water (2×5 mL), dried with anhydrous $Na_2SO_4$, filtered, and concentrated *in vacuo*. The residue (232 mg) was chromatographed on a column with $SiO_2$ (7 g). Elution with light petroleum—$Et_2O$ mixture (3 : 1) gave 167 mg (yield 72.6%) of diacetoxydiene **9**, whose chromatographic and spectral characteristics were identical to those given above.

**Photooxygenation of 7,11-diacetoxydrima-6,8-diene (9).** ***A.*** The photosensitizer $H_2$tpp (3 mg) was added to a solution of 7,11-diacetoxydrima-6,8-diene (**9**) (32 mg, 0.1 mmol) in dry $CCl_4$ (1.5 mL) and the solution was photooxygenated at 20 °C for 20 h. The reaction mixture was filtered, and the solvent was evaporated *in vacuo*. The residue (26 mg) was chromatographed on a column with $SiO_2$ (2 g). Elution with light petroleum—$Et_2O$ (4 : 1) gave 10 mg (36%) of 11-acetoxydrima-5,8-dien-7-one (**11**). Found (%): C, 73.82; H, 8.87. $C_{17}H_{24}O_3$. Calculated (%): C, 73.88; H, 8.75. IR, ν/cm$^{-1}$: 1218, 1739 (OAc); 1624, 1649 (the >C=C< group conjugated with the carbonyl group); 1690 (conjugated >C=O group). $^1$H NMR, δ: 1.22 (s, 3 H, C(13)$H_3$); 1.29 (s, 3 H, C(14)$H_3$); 1.34 (s, 3 H, C(15)$H_3$); 1.92 (s, 3 H, C(12)$H_3$); 2.08 (s, 3 H, OAc); 4.84 (s, 2 H, C(11)$H_2$); 6.34 (s, 1 H, C(6)H). $^{13}$C NMR, δ: 11.02 (C(12)); 18.00 (C(2)); 20.69 (<u>C</u>$H_3$COO); 25.13 (C(15)); 28.33 (C(13)); 32.32 (C(14)); 34.32 (C(1)); 37.35 (C(4)); 40.28 (C(3)); 43.29 (C(10)); 60.16 (C(11)); 123.78 (C(6)); 135.20 (C(8)); 154.70 (C(9)); 170.74, ($CH_3$<u>C</u>OO); 172.62 (C(5)); 186.93 (C(7)).

***B.*** The photosensitizer Bengal Rose (5 mg) was added to a solution of compound **9** (48 mg, 0.15 mmol) in dry $CCl_4$ (5 mL), and the solution was photooxygenated for 20 h at 20 °C. The reaction mixture was filtered and the solvent was evaporated *in vacuo*. The residue (50 mg) was chromatographed on a column with $SiO_2$ (2 g). Elution with a petroleum ether—$Et_2O$ mixture (4 : 1) gave 26 mg (yield 63%) of 11-acetoxydrima-5,8-dien-7-one (**11**) identical to the product obtained by method ***A***.

**Transformation of 11,12-diacetoxydrim-8-en-7-one (12) into enol acetate (13).** *p*-Toluenesulfonic acid (4 mg) was added to a solution of oxo diacetate **12**[7] (0.18 g, 0.535 mmol) in isopropenyl acetate (2 mL), and the mixture was refluxed under argon until the reaction was over (6 h, TLC monitoring). The reaction mixture was partitioned between $H_2O$ (5 mL) and $Et_2O$ (30 mL). The ethereal layer was separated and washed with a saturated solution of $NaHCO_3$ (4 mL) and water (2×10 mL), dried with anhydrous $Na_2SO_4$, filtered, and the solvent was evaporated *in vacuo*. The residue (0.26 g) was chromatographed on a column with $SiO_2$ (6.5 g). Elution with hexane—$Et_2O$ (91 : 9) gave 0.2 g (yield 99%) of 7,11,12-triacetoxydrima-6,8-diene (**13**) as a colorless liquid. Found (%): C, 66.89; H, 7.88. $C_{21}H_{30}O_6$. Calculated (%): C, 66.64; H, 7.99. IR, ν/cm$^{-1}$: 1220, 1730 (OAc); 1630 (conjugated >C=C< bond). $^1$H NMR, δ: 0.94, 0.98, 1.08 (all s, 3 H each, C(13)$H_3$, C(14)$H_3$, C(15)$H_3$); 2.01, 2.06, 2.19 (all s, 3 H each, 3 OAc); 4.67, 4.72 (both d, 1 H each, AB-system, C(11)$H_2$, $J$ = 12.0 Hz); 4.75 (s, 2 H, C(12)$H_2$); 5.56 (d, 1 H, C(6)H, $J$ = 2.0 Hz).

**Photooxygenation of 7,11,12-triacetoxydrima-6,8-diene (13).** The photosensitizer $H_2$tpp (15 mg) was added to a solution of triacetate **13** (0.16 g, 0.42 mmol) in dry $CCl_4$ (10 mL). The mixture was photooxygenated for 4 h (TLC monitoring). The reaction mixture was filtered and the solvent was evaporated *in vacuo*. The liquid residue (0.21 g) was chromatographed on a column with $SiO_2$ (10 g). Elution with hexane—AcOEt (19 : 1) mixture gave 74 mg (yield 52.5%) of 11,12-diacetoxydrima-5,8-dien-7-one (**14**). IR, ν/cm$^{-1}$: 1237, 1740 (OAc); 1663 (conjugated >C=O bond). $^1$H NMR, δ: 1.24, 1.33, 1.40 (all s, 3 H each, C(13)$H_3$, C(14)$H_3$, C(15)$H_3$); 2.04, 2.07 (s, 3 H each, 2 OAc), 4.94 (s, 2 H, C(12)$H_2$); 4.95, 4.99 (both d, 1 H each, AB-system, C(11)$H_2$, $J$ = 9.8 Hz). $^{13}$C NMR, δ: 17.92 (C(2)); 20.60

($OCO\underline{C}H_3$); 20.92 ($OCO\underline{C}H_3$); 25.40 (C(15)); 28.58 (C(13)); 31.66 (C(14)); 33.86 (C(1)); 37.52 (C(4)); 40.03 (C(3)); 43.78 (C(10)); 57.16 (C(12)); 59.36 (C(11)); 124.05 (C(6)); 133.25 (C(8)); 160.40 (C(9)); 170.30 ($O\underline{C}OCH_3$); 170.79 ($O\underline{C}OCH_3$); 173.07 (C(5)); 185.25 (C(7)).

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