Oxidation of Alcohols with Electrolytic Manganese Dioxide. Its Application for the Synthesis of Insect Pheromones

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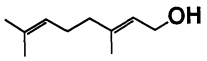
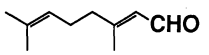
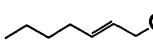
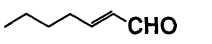
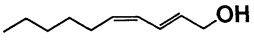
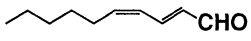
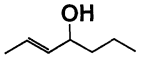
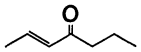
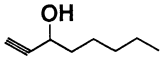
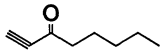
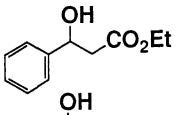
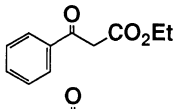
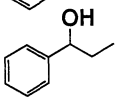
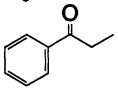
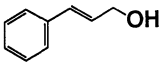
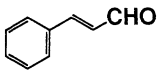
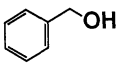
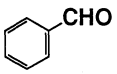
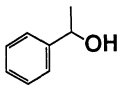
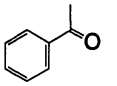
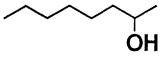
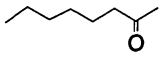
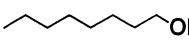
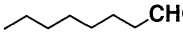
Oxidation of alcohols with electrolytic manganese dioxide under mild conditions afforded aldehydes and ketones in good yields. The method was applied for the syntheses of cystophorene [(3*E*, 5*Z*)-1,3,5-undecatriene] (**15**) and a sex pheromone of forest tent cater pillar [(5*Z*, 7*E*)-5,7-dodecadien-1-ol (**18**)].

There are a number of methods for the oxidation of primary alcohols to aldehydes. It was well-known that crystalline manganese dioxide is a poor oxidant. Activated manganese dioxide is a useful reagent for the oxidation of allylic alcohols to aldehydes.[1] However, its quality varies widely, the preparation is tedious, and the commercial reagent is expensive. On the other hand, electrolytic manganese dioxide (MnO_2) is less expensive and does not need to be purified. To our knowledge, the use of electrolytic manganese dioxide

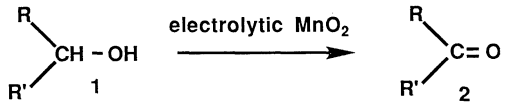
Table 1. Oxidation of Alcohols with Electrolytic Manganese Dioxide[a]

Alcohol		Reaction time/h	Product		Yield[b]/%
	**1a**	3		**2a**	100 (85)
	**1b**	0.5		**2b**	78
	**1c**[d]	1.5		**2c**	73
	**1d**	7		**2d**	63 (48)[c]
	**1e**	18		**2e**	59 (0)
	**1f**	10		**2f**	100 (12)
	**1g**	8		**2g**	76 (60)
	**1h**	2		**2h**	100
	**1i**	5		**2i**	78
	**1j**	4		**2j**	76 <81>
$CH_3(CH_2)_{11}CH_2OH$	**1k**	24	$CH_3(CH_2)_{11}CHO$	**2k**	36 (0) <32>
	**1l**	12		**2l**	31
	**1m**	48		**2m**	16

a) The reaction was carried out in hexane. Electrolytic MnO_2-1 (TKV) was used unless otherwise indicated. b) Isolated yield unless otherwise indicated. Yields in the oxidations of alcohols with electrolytic MnO_2-2 (*p*-EMD) and with activated manganese dioxide are shown in parentheses < > and ( ), respectively. c) Determined by GC. d) Prepared from ethyl (2*E*,4*Z*)-2,4-decadienoate: see Ref. 6.

for organic syntheses is quite few.[2]

We report here a new method for the oxidation of alcohols **1** to aldehydes or ketones **2** in good yields by using electrolytic manganese dioxide. This method is economical, efficient, and simple to operate and consists of treating a solution of alcohols in hexane with manganese dioxide. Two kinds of electrolytic manganese doxides (MnO_2-1 and MnO_2-2), of which pore sizes are different, were used. These results are shown in Table 1.



The oxidation was conducted mainly by using commercially available electrolytic MnO_2-1, and the yields were compaired with that of the oxidation by activated MnO_2, as shown in parenthesis.

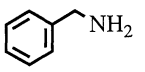
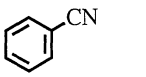
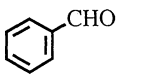
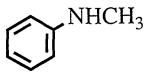
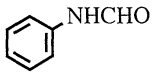
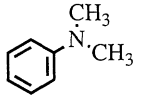
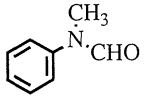
Table 1 shows that allylic alcohols can be easily oxidized to give allylic aldehydes in good yield. Especially, benzyl alcohols as well as vinylogous benzyl alcohol (**1h**) were oxidized with high yields to afford the corresponding ketones and aldehydes. In contrast with the oxidation by activated MnO_2, saturated alcohols were slowly oxidized to yield the corresponding aldehydes in low yields. The oxidation with electrolytic MnO_2 possessing larger pores was carried out representatively for 1-phenylethanol (**1j**) and tridecanol (**1k**), respectively. However, the yield in both cases were not much improved.

As shown in Table 2, both of aromatic and cyclic amines were also oxidized by electrolytic manganese dioxide (MnO_2-2) to give the corresponding amides in 15—38% yields. Treatment of benzylamine with electrolytic manganese dioxide gave a mixture of benzaldehyde (10% yield) and benzonitrile (71% yield). Hight and Wildman, however, reported that the oxidation of benzylamine with solid manganese dioxide gave benzaldehyde in 34% yield.[3] In order to clarify this discrepancy, we reinvestigated the above oxidation. When the reaction was carried out in an ambient atmosphere by the same procedure as shown in the literature,[3] benzaldehyde was obtained. However, the reaction under an atmosphere of nitrogen and absolute condition afforded benzonitrile (35% yield) along with another product which was not described in the literature.[3] This compound was identified as *N*-benzylphenylmethanimine(**6**) (33% yield) by spectral analysis. These results show that the oxidation of benzylamine with activated manganese dioxide produces phenylmethanimine at first, which is subsequently hydrolyzed with moisture existing in the flask to give benzaldehyde, as in Scheme 1. Further oxidation of phenylmethanimine will yield benzonitrile. Imine **6** seems to be produced by the condensation reaction of benzylamine and benzaldehyde. Actually, the structure was confirmed by the independent synthesis from the above reaction.

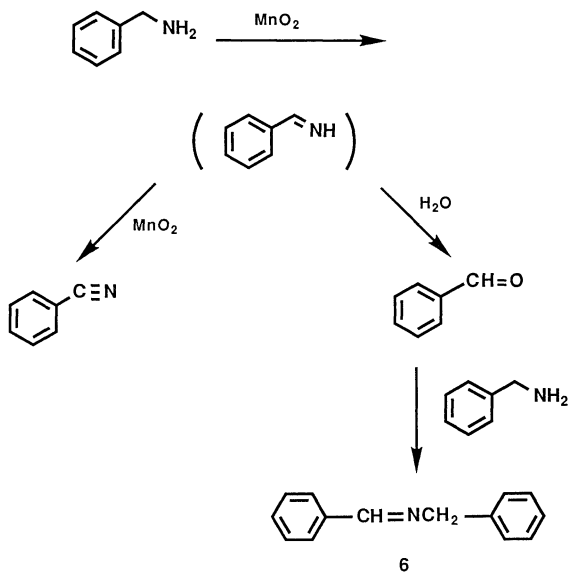
Oxidation of *N*-methylaniline (**7**) and *N*,*N*-dimethylaniline (**9**) with electrolytic manganese dioxide gave the corresponding formanilides, respectively. Oxidation of pyrrolidine also afforded pyrrolidone as a sole product although in a low yield. All of data show the electrolytic manganese dioxide is much active than the activated one.

Reactivity of electrolytic manganese dioxide was compared with that of activated one on the oxidation of 1-phenyl-1-propanol (**1g**) and the results were

Table 2. Oxidation of Amines with Electrolytic Manganese Dioxide

Amine		Reaction time/h	Product		Yield[a]/%
	**3**	24		**4**	68
				**5**	10
	**7**	24		**8**	38
	**9**	48		**10**	47
	**11**	74		**12**	15

a) Isolated yield. Electrolytic MnO_2-2 (*p*-EMD) was used.



Scheme 1.

shown in Fig. 1. The oxidation of the alcohol with electrolytic MnO_2 proceeds much faster than that of activated one.

The difference of the activity between activated manganese dioxide and electrolytic one can be discussed by the relationship of the corresponding pH and potential. Figure 2 shows that the plots of electrode potential versus solution pH fell on straight lines with the slopes of −60 mV/pH being very close to the theoretical pH response on electrode potential based on the reactions

$$MnO_2 + H^+ + e^- \longrightarrow MnOOH \quad \text{(in acidic solution)}, \tag{1}$$

and

$$MnO_2 + H_2O + e^- \longrightarrow MnOOH + OH^-, \quad \text{(in neutral and basic solution)}, \tag{2}$$

where H^+ and H_2O represent proton and water molecule, respectively, in aqueous solution trapped in the micropores of manganese dioxide, and e^- does electron released from reducing agent. The oxidation ability of manganese dioxide depends on the nature of the oxide and solution pH. The oxidation ability of the dioxides used was in order of electrolytic MnO_2-1 >electrolytic MnO_2-2>activated MnO_2 at a certain pH. The arrows in Fig. 2 show the pHs where the pH of solutions did not change by addition of the manganese dioxide powders to the solutions. The pHs which are named the equi-acid-base points (EABP)[4] of the dioxides used should agree with the pHs of solutions trapped in the micropores of the oxides. From the potentials at the EABPs the oxidation ability of the dioxides is predicted to be in order of electrolytic MnO_2-2>electrolytic MnO_2-1>activated MnO_2.

The present method was applied for the synthesis of cystophorene [(3*E*,5*Z*)-1,3,5-undecatriene] (**15**), isolated from the essential oil of Ferula galbaniflua.[5] The reaction sequence was shown in Scheme 2. Oxidation of (2*E*,4*Z*)-2,4-decadien-1-ol (**1c**)[6] with electrolytic manganese dioxide gave (2*E*,4*Z*)-2,4-decadienal (**2c**) in 73% yield, as shown in Table 1. The reaction of **2c** with methylenetriphenylphosphorane (THF, 0 °C, 1 h) afforded **15** in 69% yield after column chromatography. The spectral data were identical with those of the authentic sample.[5]

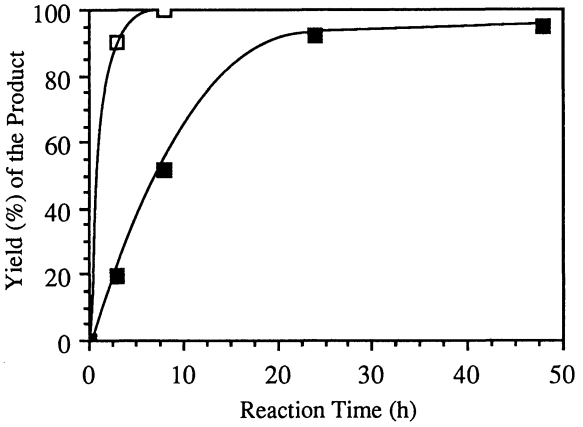


Fig. 1. Comparison of the reactivity of electrolytic MnO_2 and activated MnO_2 on the oxidation of 1-phenyl-2-propanol. □: Electrolytic MnO_2; ■: Activated MnO_2.

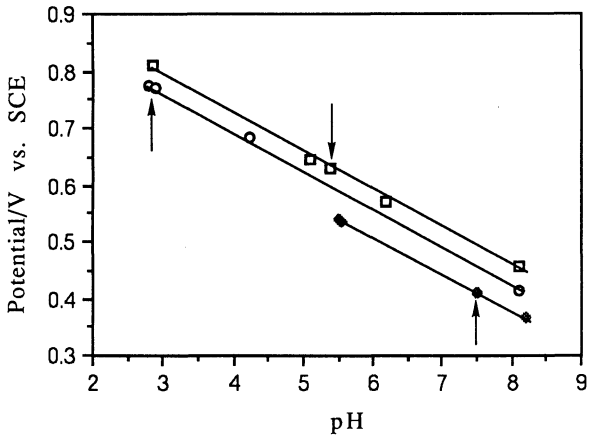
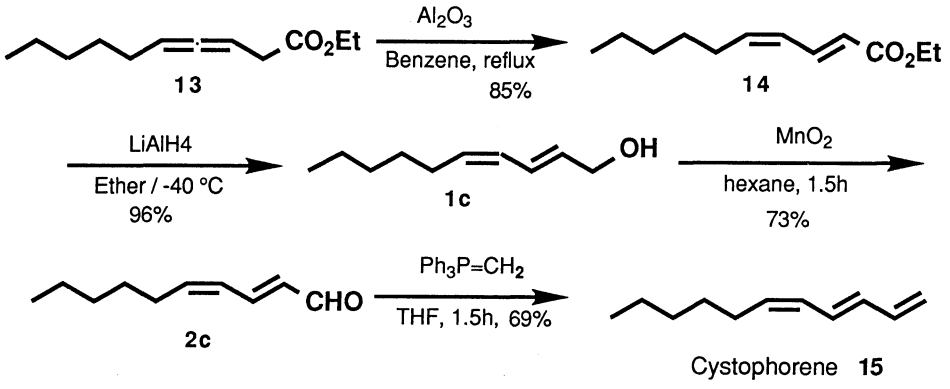
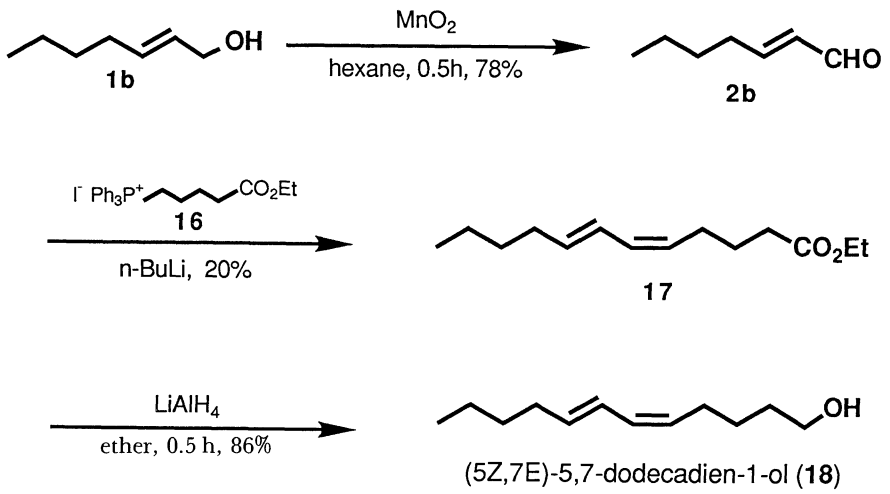


Fig. 2. Potential vs. pH plots for various MnO_2. □: Electrolytic MnO_2-1; ○: Electrolytic MnO_2-2; ◆: Activated MnO_2.



Scheme 2.



Scheme 3.

Furthermore the present procedure was applied for the synthesis of (5*Z*,7*E*)-5,7-dodecadien-1-ol (**18**), a sex pheromone of forest tent cater pillar.[7] The reaction sequences were shown in Scheme 3. Oxidation of (*E*)-2-hepten-1-ol (**1b**) with electrolytic MnO_2 afforded (*E*)-2-heptenal (**2b**) in 78% yield, which was condensed with 4-ethoxycarbonylbutyltriphenylphosphonium iodide (**16**) to give ethyl (5*Z*,7*E*)-5.7-dodecadienoate (**17**) in the low yield. Reduction of **17** with lithium aluminum hydride gave the sex pheromone (**18**) in 86% yield.

Experimental

The melting and boiling points are uncorrected. Elemental analyses were carrid out by Mr. Eiichiro Amano of our laboratory. IR spectra were obtained with a JASCO Model A-102 infrared spectrophotometer. ^{1}H NMR spectra (60 MHz) were recorded with a JEOL JNM-PMX60SI apparatus. ^{1}H NMR (100 MHz) and ^{13}C NMR spectra (25 MHz) were obtained with a JEOL JNM-FX100 apparatus, with $CDCl_3$ as a solvent. All chemical shifts are reported in δ unit downfield from the internal Me_4Si; *J* values are given in hertz. Mass spectra were obtained with ESCO EMD-05B apparatus.

^{1}H NMR (500 MHz) spectra were obtained with a Varian VXR-500 instrument. Analytical determinations by GLC were performed on a Hitachi Model 163 gas chromatograph fitted with 10% Apiezone Grease L on Chromosorb W column (3 mm o.d. ×1 m). Column chromatography was accomplished with a 100—200 mesh Wakogel C-200. Hexane was dried over calcium chloride. Electrolytic MnO_2-1 (commonly named TKV) is commercially available from Mitsui Mining & Smelting Co., Ltd. Electrolytic MnO_2-2 (commonly named p-EMD) was donated by Mitsui Mining & Smelting Co., Ltd. Activated MnO_2 was obtained by the activation of commercially available MnO_2.[8] All MnO_2 were dried in vacuo before use. Alcohols **1a**, **1b**, **1i**, **1j**, **1k**, **1l** and **1m** were commercially available. (*E*,*Z*)-2,4-Decadien-1-ol (**1c**) was prepared by the method published by one of us.[6] (*E*)-2-Hepten-4-ol (**1d**) was obtained by the reaction of crotonaldehyde with propylmagnesium bromide: bp 100 °C/20 Torr (short-pass distillation) (1 Torr≈133.322 Pa); 79.1%.[9] 1-Octyn-3-ol (**1e**) was prepared by the method described in the literature.[10] Ethyl 3-hydroxy-3-phenylpropionate (**1f**) was obtained by the reaction of benzaldehyde with ethyl bromozincioacetate.[11] 1-Phenyl-1-propanol (**1g**) was prepared by the reaction of benzaldehyde with ethylmagnesium bromide:[12] bp 105 °C/20 Torr (short-pass distillation); 87% yield. First grade amines **3**, **7**, **9**, and **11** were used after distilled and dried over molecular sieves.

General Procedure of the Oxidation of Alcohols with MnO_2. Electrolytic MnO_2[13] was charged in a three-necked round bottom flask and the atmosphere was replaced with nitrogen gas. A solution of alcohols in dry hexane was added at room temperature and then the mixture was stirred at room temperature. When the starting material was consumed, the mixture was filtered and the filtrate was concentrated to give the desired product. Some experiments were representatively shown below.

Geranial. (a) To 1.15 g (13.2 mmol) of electrolytic MnO_2 was added a solution of 100 mg (0.649 mmol) of geraniol in 16 ml of hexane at 0 °C. The mixture was stirred at 0 °C[14] for 6 h. After filtration of the mixture, the filtrate was concentrated to give 109 mg (100%) of geranial. GLPC (column: 100 °C) showed one peak at R_t 7.43 min.

(b) To 1.15 g (13.2 mmol) of activated MnO_2 was added a solution of 100 mg (0.649 mmol) of geraniol in 16 ml of hexane at 0 °C. The mixture was stirred at 0 °C[14] for 6 h. After filtration of the mixture, the filtrate was concentrated to give 119 mg of a clean oil, whose GLPC analysis (column: 100 °C) showed two peaks at R_t 7.43 and 9.03 min with the intensity ratio of 7:3. Each peak was identified as geranial and geraniol, respectively.

(2*E*,4*Z*)-2,4-Decadienal (2c). To 5.6 g (64.4 mmol) of electrolytic MnO_2 was added a solution of 458 mg (2.97 mmol) of **1c** in 40 ml of dry hexane at room temperature. The mixture was stirred for 1.5 h, and then filtered. The filtrate was concentrated in vacuo to give crude **2c**. Purification with column chromatography (SiO_2, hexane) gave 329 mg (72.8%) of **2c**. Spectral data were consistent with those of an authentic sample.[6]

Oxidation of Benzylamine (3) with Activated MnO_2. A mixture of **3** (300 mg, 2.79 mmol), activated MnO_2 (4.50 g,

51.7 mmol), and chloroform (30 ml) was stirred for 24 h at room temperature under an atmosphere of nitrogen. After filtration, the solvent was evaporated, giving 270 mg of a crude product. Short-path distillation gave two fractions. First fraction (bp 105 °C (bath temperature)/15 Torr) afforded 110 mg of a mixture (91:8 by ^{1}H NMR) of benzonitrile (35% yield) and recovered benzylamine: IR (neat) 2230 (C≡N), 1598 (phenyl), 1490, 1442 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.51 (s, 0.16H, $C_6H_5C\underline{H}_2NH_2$), 3.84 (s, 0.16H, $C_6H_5CH_2N\underline{H}_2$), 7.1—7.9 (m, 4.95H, $C_6\underline{H}_5CH_2NH_2$ and $C_6\underline{H}_5CN$). The second fraction (bp 165 °C (bath temperature)/15 Torr) gave 90 mg (33% yield) of *N*-benzylphenylmethanimine (**6**): IR (neat) 3050 (phenyl), 2850, 1640 (C≡N), 1600, 1585, 1451, 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.78 (t, J=1 Hz, 2H, CH_2N=), 7.1—7.9 (m, 5H, C_6H_5), 8.33 (t, J=1 Hz, 1H, CH=N); MS (70 eV) m/z (rel intensity) 196 (21, M^+), 165 (5), 117 (27), 103 (56), 91 (100).

Independent Synthesis of *N*-Benzylphenylmethanimine (6). To a solution of **3** (30 mg, 0.28 mmol) in dry chloroform (5 ml) was added benzaldehyde (30 mg, 0.28 mmol) at room temperature. After the mixture was stirred for 1 h, the solvent was evaporated, giving 50 mg (91%) of **6**. IR and NMR spectra were identical with those of the sample described above.

Oxidation of Benzylamine (3) with Electrolytic MnO_2. A solution of **3** (100 mg, 0.935 mmol) in dry chloroform (15 ml) was stirred with electrolytic MnO_2-2 (1.50 g, 17.0 mmol) for 24 h at room temperature under an atmosphere of nitrogen. The mixture was filtered and the filtrate was concentrated to give 78 mg of an oil: IR (neat) 2250 (CN), 1750 (C=O), 1500, 1450 cm^{-1}; ^{1}H NMR (CCl_4) δ=7.25—7.80 (m, phenyl), 9.90 (s, CH=O). The GLC analysis (column: SE-30 (5 mm o.d.×1 m), 80 °C) showed two peaks at R_t 2.17 and 2.33 min with the intensity ratio of 6.7/1. Retention times of each peak were consistent with those of benzonitrile (71% yield) and benzaldehyde (10% yield).

Oxidation of *N*-Methylaniline (7) with Electrolytic MnO_2. A mixture of electrolytic MnO_2-2 (3.0 g, 34.4 mmol), *N*-methylaniline (**7**) (100 mg, 0.93 mmol), and dry chloroform (15 ml) was stirred for 24 h at room temperature under an atmosphere of nitrogen. After filtration, the solvent was evaporated to give 90 mg of a crude oil. Preparative TLC (SiO_2, hexane/ethyl acetate=1/1) gave 42 mg (38%) of formanilide (**8**). The ^{1}H NMR spectrum was identical with that of an authentic sample.

Oxidation of *N,N*-Dimethylaniline (9) with Electrolytic MnO_2. A mixture of electrolytic MnO_2-2 (3.6 g, 41 mmol), **9** (200 mg, 1.6 mmol), and dry chloroform (15 ml) was stirred for 2 d at room trmperature under an atmosphere of nitrogen. After filtration, the solvent was evaporated to give 190 mg of an oil. Distillation under reduced pressure gave 102 mg (47%) of *N*-methylformanilide (**10**): bp 100 °C/0.3 Torr. ^{1}H NMR spectrum and the retention time of the GLC were identical with those of an authentic sample.

Oxidation of Pyrrolidine (11) with Electrolytic MnO_2. A mixture of electrolytic MnO_2-2 (2.50 g, 28.7 mmol), pyrrolidine (100 mg, 1.4 mmol), and chloroform (15 ml) was stirred for 3 d at room temperature. After filtration, the solvent was evaporated to give 90 mg of an oil. Distillation of the crude product gave 20 mg (15%) of 2-pyrrolidone (**12**): bp 130 °C/5 Torr. Proton NMR spectrum was identical with that of an authentic sample.

Cystophorene (15). To a mixture of 211 mg (0.592 mmol) of triphenylmethylphosphonium bromide in dry THF (1.5 ml) was added 0.366 ml (0.6 mmol) of butyllithium at 0 °C. The mixture was stirred for 30 min, and then 90 mg of **2c** was added dropwise at 0 °C. After being stirred at 0 °C for 30 min, the mixture was poured into ice water and then acidified with 10% HCl. The organic layer was dried over $MgSO_4$. Removal of the solvent gave a clean oil, which was purified by column chromatography to give 61 mg (68.6%) of **15**.

Spectral data were consistent with those of an authentic sample.[5]

4-Ethoxycarbonylbutyltriphenylphosphonium Iodide (16). To a solution of 1.32 g (5.92 mmol) of triphenylphosphine in 20 ml of dry benzene was 1.07 g (4.18 mmol) of ethyl 5-iodopentanoate under an atmosphere of dry nitrogen. The mixture was heated at reflux temperature of benzene for 24 h. After removal of the solvent, hexane (50 ml) was added. The precipitate was collected by filtration, and washed with hexane to give 2.20 g (100%) of **16**.

Ethyl (5*Z*,7*E*)-5,7-Dodecadienoate (17). Dry *N,N*-dimethylformamide (DMF) (5 ml) was added to 600 mg (1.16 mmol) of **16** at −50 °C under an atmosphere of dry nitrogen. Butyllithium in hexane (0.935 ml, 1.49 mmol) was added dropwise, and then the mixture was stirred for 2 h. After a dropwise addition of **2b** (60 mg, 0.536 mmol), the mixture was stirrred for 2 h at −50—−60 °C, poured into ice water, and then acidified with 10% HCl. The organic materials were extracted with ether and the combined extracts were washed with water, and dried over $MgSO_4$. After evaporation of the solvent, column chromatography (SiO_2, hexane/ethyl acetate (100/1)) of the crude oil and further purification with HPLC (column: Unisil Q (10.7 mm o.d.×250 mm), eluent: hexane/ethyl acetate (50/1)) gave 20 mg (7.7%) of **17**: R_t 37.5 min; IR (neat) 3000, 2950, and 1750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.895 (t, J=7 Hz, 3H, CH_3), 1.255 (t, J=7.5 Hz, 3H, $OCH_2C\underline{H}_3$), 1.280—1.400 (m, 4H, $(CH_2)_2$), 1.720 (tt, J=6.2 Hz, 2H, $C\underline{H}_2CH_2CO_2$), 2.094 (dt, J=7.5 Hz, 2H, $C\underline{H}_2CH$-), 2.209 (dt, J=7.5 Hz, 2H, $CH_2C\underline{H}_2CH_2CO_2$), 2.310 (t, J=7.5 Hz, 2H, $C\underline{H}_2CO_2$), 5.260 (dt, J=10.7 and 7.5 Hz, 1H, =C(5)H), 5.675 (dt, J=15.0 and 7.5 Hz 1H, =C(8)H), 5.984 (dd, J=10.9 and 10.7 Hz, 1H, =C(6)H), 6.263 (dd, J=11.04 and 15.0 Hz, 1H, =C(7)H); ^{13}C NMR ($CDCl_3$) δ=14.0, 14.2, 22.3, 24.9, 27.0, 31.5, 32.6, 33.7, 60.2, 125.3, 128.3, 129.7, 135.3, 173.7.

(5*Z*,7*E*)—5,7-Dodecadien-1-ol (18).[7] To a stirred mixture of lithium aluminumhydride (2 mg, 0.05 mmol) and dry ether (1 ml) was added dropwise a solution of **17** (20 mg, 0.0893 mmol) at −40 °C. After the mixture was stirred for 30 min at −40 °C, it was poured into ice water and neutralized with 10% HCl. The organic materials were extracted with ether, and the combined extracts were washed with water, dried over $MgSO_4$. Evaporation of the solvent gave 14 mg (86%) of **18**: IR (neat) 3300, 2950, 2850 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.87 (t, J=7.5 Hz, 3H, CH_3), 1.27—1.38 (m, 4H, $CH_3C\underline{H}_2C\underline{H}_2$), 1.44 (m, 2H, $C\underline{H}_2CH_2CH_2OH$), 1.58 (m, 2H, $C\underline{H}_2CH_2OH$), 2.08 (m, 2H, =C(8)-$C\underline{H}_2$), 2.18 (m, 2H, C(4)$\underline{H}_2$), 3.63 (t, J=7.0 Hz, $C\underline{H}_2OH$), 5.27 (dt, J=7.5 and 10.5 Hz, 1H, =C(5)H), 5.64 (dt, J=7.5 and 15.0 Hz, 1H, =C(8)H), 5.79 (dd, J=10.5 and 11.00 Hz, 1H, =C(7)H), 6.26 (dd, J=11.0 and 15.0 Hz, 1H, =C(6)H).

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