Synthesis of 5-[(*E*)-1-Alkenyl]-3(2*H*)-furanones by the Stereoselective Dehydration with Me_3SiCl

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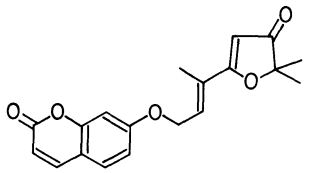
The stereoselective dehydration of 5-(2-hydroxyalkyl)-3(2*H*)-furanones is accomplished conveniently by the treatment with Me_3SiCl in acetonitrile to give 5-[(*E*)-1-alkenyl]-3(2*H*)-furanones.

5-(1-Alkenyl)-3(2*H*)-furanone is one of the important skeletons observed in natural products, e. g. geiparvarin (**1**)[1] and eremantholide A,[2] and hence much attention has been paid on their stereoselective synthesis. We previously reported a short step synthesis of **1**,[3] in which the (*E*)-olefinic side chain was introduced



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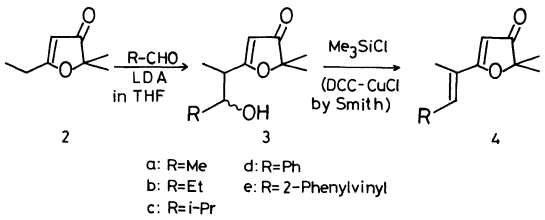
by the utilization of tiglic acid. Smith et al.[4] elaborated the olefinic moiety of **1** and the related 3(2*H*)-furanone **4** in a manner as shown in Scheme 1, which involves the aldol reaction of lithium enolate of 5-ethyl-2,2-dimethyl-3(2*H*)-furanone (**2**) with an appropriate aldehyde followed by the DCC-CuCl-catalyzed dehydration of the resulting diastereomeric mixture of 5-(2-hydroxyalkyl)-3(2*H*)-furanone (**3**) in refluxing benzene. However, the E/Z-stereoselectivity of the side chain of **4** is not satisfactory as cited in Table 1 and seems to be still open to further improvement. Recently, Tsuge et al.[5] have reported that the Horner-Emmons olefination of 5-[1-(diethoxyphosphoryl)-ethyl]-3(2*H*)-furanone with aldehydes gives **4a—e** with a considerable E selectivity. In the preceding paper of our laboratory concerning the stereoselective synthesis of polyenoic acids,[6] the Me_3SiCl-NaI reagent was successfully employed for the dehydration of acyclic allylic alcohol to produce a conjugated (E)-olefinic double bond. The fact stimulated us to examine the suitability of the reagent for the dehydration of **3**, and Me_3SiCl itself was found to be remarkably effective on the improvement of the stereoselectivity.

The present reaction merely involves stirring of a mixture of **3a—e** and 2.5 equiv of Me_3SiCl in acetonitrile at room temperature to give the desired product with sufficient purity after washing with aqueous sodium hydrogencarbonate. Addition of NaI to the reaction had no effect on the yield. The reaction time of 10—14 h is required, while the reaction for allylic alcohol **3e** was finished within 1 h. These results are summarized in Table 1. The olefinic side chains of **3a—e** thus obtained have only the E geometry, which was confirmed by the comparison of the ^1H NMR spectral data with those reported.[4b] Furthermore, their ^{13}C NMR spectral data summarized in Table 2 indicate the absence of (Z)-isomer definitely. The yields of the dehydration were also improved generally. The method seems to be more practical as compared with the reported one,[4] because the reagent is inexpensively available and the procedure is quite simple.

A possible mechanism for the present reaction is depicted in Scheme 2, which involves the formation of bis(trimethylsilyl)oxonium chloride intermediate **5**.[7] Subsequent elimination of hexamethyldisiloxane (**6**) from **5** would occur accompanying the abstraction of the reactive allylic proton by a chloride anion. Formation of **6** was confirmed by GLPC analysis.[8] The alcohols **3a—e** used were a diastereomeric mixture. Smith et al.[4] did not describe the detail of the isomeric



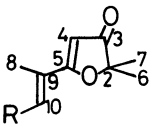
Scheme 1.

Table 1. Yields of 5-[(*E*)-1-Alkenyl]-3(2*H*)-furanones (**4a—e**)

Compd	R	Reach time/h	Yield[a]	Smith's method[b]
			%	Yield/% (E/Z ratio)
4a	Me	14	66	54 (1:1)
4b	Et	12	80	73 (1:2)
4c	*i*-Pr	10	75	—
4d	Ph	10	66	60 (1:2)
4e	2-Phenylvinyl	1	77	55 (3:2)

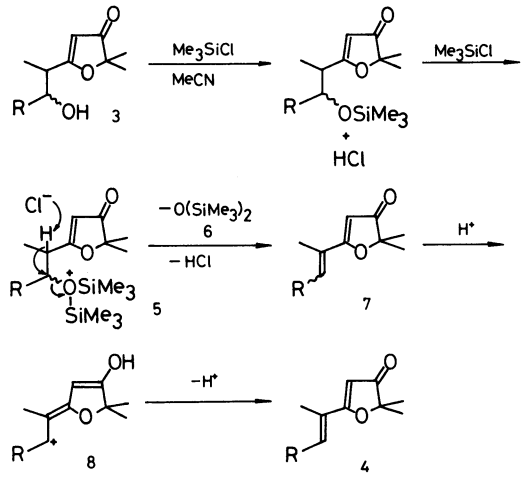
a) After purification by preparative TLC. b) DCC-CuCl in refluxing benzene. See Ref. 4.

Table 2. ^{13}C NMR Spectral Data of 5-[(*E*)-1-Alkenyl]-3(2*H*)-furanones ($CDCl_3$, ppm)

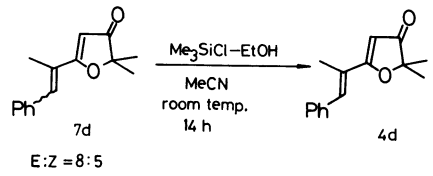


Compd	C-2	C-3	C-4	C-5	C-6,7	C-8	C-9	C-10	R
4a	88.1	207.2	98.5	184.5	23.1	12.7	126.6	133.1	14.2
4b	88.1	207.2	98.7	184.6	23.1	12.9	125.1	139.9	13.2, 21.9
4c	88.2	207.3	98.9	184.9	23.1	13.0	123.6	145.0	22.1, 27.8
4d	88.5	207.2	100.1	184.7	23.2	14.7	126.3	134.7	128.5,[a] 129.8,[a] 135.7
4e	88.2	206.9	99.7	184.0	23.2	13.5	125.1	134.3[b] 123.5[b] 139.4[b]	127.1,[a] 128.8,[a] 136.5
14	88.3	207.1	100.0	184.0	23.1	13.4	126.1	133.0[a,c] 127.0[c] 139.4[c]	14.0, 22.5, 27.3 34.2, 74.7, 128.4,[a] 129.6,[a] 130.3, 165.8
15	88.4	207.1	100.2	183.8	23.2	13.4	126.6[a]	132.5[d] 140.9[d]	13.9, 22.2, 28.6, 38.1, 62.2
17	88.5	207.3	100.3	183.9	23.2	13.2	127.5	125.4[e] 127.5[e] 136.5[e]	14.0, 22.5, 27.1, 71.3, 128.4,[a] 129.6,[a] 130.3, 133.0

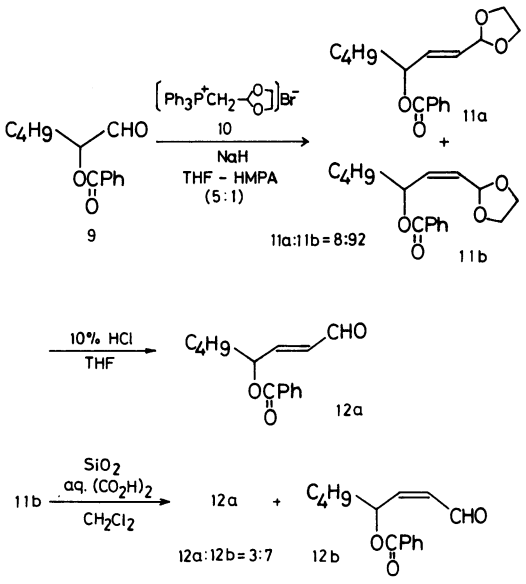
a) The signal due to overlapped two carbons with nearly double intensity. b, c, d, e) Assignment of olefinic carbons is interchangeable.



Scheme 2.



Scheme 3.



Scheme 4.

ratio of **3a—e** and its participation in the geometry of the resulting **4a—e**. We confirmed that **3d** was ca. 1 : 1 diastereomeric mixture according to the ^{1}H NMR signals due to C-4 proton (δ 5.15 and 5.31), while the isomeric ratios of **3a—c** and **3e** were not clear by ^{1}H NMR analysis. Therefore, the initially formed dehydration product **7** should be a E, Z mixture. The (Z)-isomer of **7** would be converted to a thermodinamically more stable **4** at the acidic conditions[9] via the cationic intermediate **8**. The feasibility of the isomerization was exemplified by using a 8 : 5 E,Z mixture of **7d**,[4] which was readily converted to **4d** by the treatment with Me_3SiCl and EtOH in acetonitrile (Scheme 3).

As a preliminaly experiment for the synthetic study of a related natural product, we wished to confirm the applicability of the above reaction sequence to the stereospecific synthesis of 5-[(1*E*, 3*E*)-5-(benzoyloxy)-1-methyl-1,3-nonadienyl]-2,2-dimethyl-3(2*H*)-furanone (**14**) (Scheme 5) and its (1E, 3Z)-isomer **17** (Scheme 6). For the purpose, a stereoselective synthesis of the starting (*E*)- and (*Z*)-4-(benzoyloxy)-2-octenal (**12a** and **12b**) (Scheme 4) and their transformation to **14** and **17** with retention of the geometry are required.

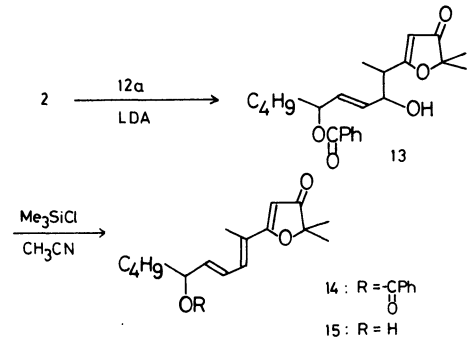
The Wittig reaction of 2-(benzoyloxy)hexanal (**9**)[10] with (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide (**10**)[11] in the presence of NaH in THF-HMPA (5 : 1) gave the (Z)-adduct **11b** stereoselctively (E : Z=8 : 92) in 48% yield (Scheme 4). The yield of **11b** was slightly increased to 52% by carring out the reaction in DMF-HMPA (3 : 1), while the yield of the (E)-isomer **11a** was also raised to 19%.

The treatment of the 8 : 92 mixture of **11a** and **11b** with 10% aqueous HCl-THF (1 : 1) afforded the (*E*)-aldehyde **12a** exclusively in 96% yield as a result of the isomerization Z to E. On the other hand, the hydrolysis of the (*Z*)-acetal **11b**, which was isolated by preparative TLC, with silica gel and 5% aqueous oxalic acid[12] in dichloromethane gave the (*Z*)-aldehyde **12b** (57% yield) together with the (E)-isomer **12a** (23% yield). They were separated chromatographycally. Further attempts to increase the ratio of **12b** by using other hydrolytic conditions such as *p*-TsOH[13] or (±)-10-camphorsulfonic acid monohydrate in acetone-H_2O resulted in unfruitfullness.

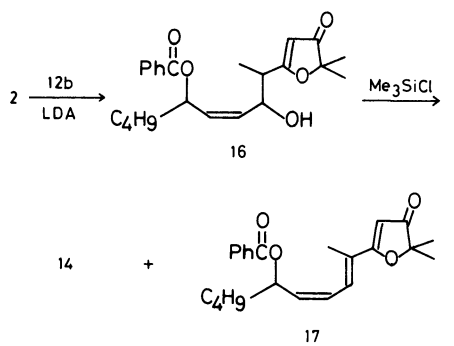
The reaction of lithium enolate of **2** with **12a** gave the aldol product **13** (54% yield). The dehydration with Me_3SiCl afforded **14** (61% yield) and its hydrolyzed product **15** (29% yield) under the acidic conditions (Scheme 5). The geometry of newly formed olefinic double bond of **14** and **15** was assigned to be E by the comparison of their ^{13}C NMR spectral data with those of **3a—e** (Table 2).

A similar aldol reaction of **2** with **12b** gave **16** (54% yield) with retention of the Z geometry (Scheme 6). However, at the subsequent dehydration step, the geomerty was partly inverted to give a 53 : 47 mixture of **14** and **17** (57% yield), which were separated by preparative HPLC. The E or Z geometry of the C-3 and C-4 double bond of the side chain is clearly distinguishable by the analysis of the coupling constants in the ^1H NMR spectra [**14**: $J_{3,4}$=14.5 Hz for E; **17**: $J_{3,4}$=12.0 Hz for Z]. Furthermore, in the ^{13}C NMR spectra (Table 2), the allylic carbon bearing a benzoyloxy group of the (Z)-isomer **17** appeared at 71.3 ppm, which was highly shielded as compared with that of the (E)-isomer **14** (74.7 ppm).

As described above, the present reaction offers a convenient and highly stereoselective synthetic method of 5-[1-(*E*)-alkenyl]-3(2*H*)-furanones and would be useful for other related systems.



Scheme 5.



Scheme 6.

Experimental

IR specra were measured with a JASCO A-102 spectrometer. ^1H NMR spectra (60 MHz) were measured with a JEOL JNM PMX 60 SI spectrometer. Both ^1H NMR (100 MHz) and ^{13}C NMR (25 MHz) spectra were taken on a JEOL FX-100 spectrometer using Me_4Si as an internal standard. GLPC analysis was done by using a Hitachi 163 gas chromatograph. HPLC analysis was carried out by using a Yanagimoto L-2000 high-performance liquid chromatograph. Elemental analyses were performed by Eiichiro Amano of our laboratory with a Yanagimoto MT-3 CHN recorder.

Hydroxy 3(2*H*)-furanones **3a—e**, **13**, and **16** were prepared from **2** and appropriate aldehydes by the procedure similar to that reported by Smith et al.[4] Sectral and analytical data of the new compounds **3c**, **13**, and **16** are shown.

5-(1,3-Dimethyl-2-hydroxybutyl)-2,2-dimethyl-3(2*H*)-furanone (3c): 28% yield; mp 113.5—114 °C (CCl_4); IR (KBr) 3400, 1680, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95, 0.98 (each with 3H, d, J=6 Hz), 1.26 (3H, d, J=7 Hz), 1.35 (6H, s), 1.73 (1H, m), 2.30 (1H, br s), 2.79 (1H, m), 3.54 (1H, m), 5.38 (1H, s). Found: C, 67.64; H, 9.42%. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50%.

General Procedure for the Dehydration of 5-(2-Hydroxyalkyl)- 3(2*H*)-furanone. To a solution of **3** (0.50 mmol) in acetonitrile (1 ml) was added chlorotrimethylsilane (136 mg, 1.25 mmol) through a syringe. The mixture was stirred at room temperature for the time indicated in Table 1. After the reaction was quenched by addition of water, the organic layer was extracted with ether, washed with aqueous sodium hydrogencarbonate and brine, dried ($MgSO_4$), filtered, and then concentrated under reduced pressure. The residual oil was purified by preparative TLC (Merck, Kieselgel PF_{254}, hexane-acetone, 3 : 1) to give **4** in the yield as shown in Table 1. The IR and ^1H NMR spectra of **4a—e** were consistent with those reported.[4,5] The spectral and analytical data of **4c**[5,14] are described below.

5-(1,3-Dimethyl-1-butenyl)-2,2-dimethyl-3(2*H*)-furanone (4c): Mp 68.5—69 °C (hexane); IR (KBr) 1695, 1640, 1560, 1175 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.06 (6H, d, J=7 Hz), 1.39 (6H, s), 1.89 (3H, d, J=1.3 Hz), 2.70 (1H, m), 5.47 (1H, s), 6.40 (1H, dq, J=9 Hz, and 1.3 Hz). Found: C, 74.36; H, 9.25%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

Isomerization of 7d to 4d. Chlorotrimethylsilane (33 mg, 0.3 mmol) was added to a mixture of **7d** (E: Z=8 : 5)[4] (29 mg,

0.13 mmol), EtOH (14 mg, 0.3 mmol), and acetonitrile (1 ml). After being stirred for 14 h at room temperature, the mixture was diluted with ether, washed with aqueous sodium hydrogencarbonate and water, dried over $MgSO_4$, and filtered. Removal of the solvent left **4d** (28 mg, 97%) with sufficient purity.

(*Z*)-1-Butyl-3-(1,3-dioxolan-2-yl)-2-propenyl Benzoate (11b). To a cooled mixture (0 °C) of NaH (108 mg, 4.5 mmol), THF (7 ml), and HMPA (2 ml), was added **10**[11] (2.02 g, 4.7 mmol) quickly. The mixture was stirred at room temperature for 40 min, and then cooled to −78 °C. A solution of 2-(benzoyloxy)hexanal **9**[10] (560 mg, 2.55 mmol) in THF (3 ml) was introduced through a syringe. The mixture was allowed to warm to room temperature gradually and stirred for 2 d. After the reaction was quenched by addition of water, the organic layer was extracted with hexane-ether (1 : 1), washed with brine, dried ($MgSO_4$), filtered, and then concentrated. The precipitated $Ph_3P{=}O$ was removed by filtration with suction. The crude product was separated by preparative TLC (hexane-ether, 4 : 1) to give **11a** (R_f 0.22—0.30, 29 mg, 4% yield) and **11b** (R_f 0.30—0.42, 355 mg, 48% yield). **11a**: IR (neat) 1720, 1660, 1600 cm^{-1}. ^1H NMR (CCl_4) δ=0.7—2.0 (9H, m), 3.85 (4H, m), 5.1—6.1 (4H, m), 7.1—8.1 (5H, m); ^{13}C NMR ($CDCl_3$) δ=13.3 (q), 22.5 (t), 27.3 (t), 34.0 (t), 65.0 (t), 73.5 (d), 103.0 (d), 128.0 (d), 128.4 (d), 129.6 (d), 130.4 (s), 132.9 (d), 134.3 (d), 165.7 (s). Found: C, 70.15; H, 7.62%. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64%. **11b**: IR (neat) 1720, 1680, 1600 cm^{-1}; ^1H NMR (CCl_4) δ=0.7—2.0 (9H, m), 3.85 (4H, m), 5.2—6.0 (4H, m), 7.1—8.1 (5H, m); ^{13}C NMR ($CDCl_3$) δ=13.9 (q), 22.5 (t), 27.1 (t), 34.5 (t), 65.0 (t), 70.8 (d), 99.2 (d), 128.9 (d), 129.1 (d), 129.6 (d), 130.5 (s), 132.8 (d), 134.3 (d), 165.8 (s). Found: C, 70.11; H, 7.58%. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64%.

The reaction in DMF-HMPA was carried out in a similar way.

(*E*)-4-(Benzoyloxy)-2-octenal (12a). An 8 : 92 mixture of **11a** and **11b** (580 mg, 2 mmol), 10% HCl (3 ml), and THF (3 ml) was stirred for 3 h at room temperature. The organic layer was extracted with ether, washed with aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$), filtered, and then concentrated. The residual oil was purified by column chromatography (Silica gel 60, Katayama Chemical, Co. Ltd., hexane-acetone, 10 : 1) to give **12a** (470 mg, 96% yield): IR (neat) 1720, 1690, 1640, 1600 cm^{-1}; ^1H NMR (CCl_4) δ=0.8—2.1 (9H, m), 5.65 (1H, m), 6.13 (1H, dd, J=15, 8 Hz), 6.70 (1H, dd, J=15, 5 Hz), 7.3—8.1 (5H, m), 9.42 (1H, d, J=8 Hz); ^{13}C NMR ($CDCl_3$) δ=13.9 (q), 22.5 (t), 27.2 (t), 33.5 (t), 72.8 (d), 128.5 (d), 129.7 (d), 131.5 (d), 133.4 (d), 154.1 (d), 165.6 (s), 193.0 (d). Found: C, 73.25; H, 7.43%. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.57%.

(*Z*)-4-(Benzoyloxy)-2-octenal (12b). A mixture of silica gel (Merck Kieselgel PF_{254}, 5.0 g), 5% aqueous oxalic acid[11] (0.5 ml), and dichloromethane (8 ml) was stirred vigorously. To this was added a solution of **11b** (542 mg, 1.90 mmol) in dichloromethane (2 ml) and the resulting mixture was stirred for 6 h at room temperature. The mixture was neutralized by addtion of aqueous sodium hydrogencarbonate powder, dried ($MgSO_4$), filtered and then concentrated under reduced pressure. The residue was purified by preparative TLC (hexane-ether, 3 : 1) to give **12b** (R_f 0.57—0.67, 261 mg, 57% yield) and **12a** (R_f 0.38—0.54, 108 mg, 23% yield). **12b**: IR (neat) 1720, 1685, 1615, 1600 cm^{-1}; ^1H NMR (CCl_4) δ=0.7—2.1 (9H, m), 5.74—6.63 (3H, m), 7.1—8.2 (5H, m), 10.08 (1H, d, J=7 Hz); ^{13}C NMR ($CDCl_3$) δ=13.8 (q), 22.4 (t), 27.2 (t), 34.4 (t), 70.4 (d), 128.5 (d), 194.6 (d), 130.0 (s), 130.5 (d), 133.2 (d), 147.5 (d), 165.8 (s), 190.6 (d). Fond: C, 73.23; H, 7.57%. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37%.

5-[(*E*)-5-(Benzoyloxy)-2-hydroxy-1-methyl-3-nonenyl]-2,2-dimethyl-3(2*H*)-furanone (13). This compound was prepared in a manner similar to Smith's method[4] in 54% yield. **13**: IR (neat) 3450, 1720, 1700, 1660, 1580 cm^{-1}; ^1H NMR (CCl_4) δ=0.7—2.0 (18H, m), 2.78 (1H, m), 3.70 (1H, br s, OH), 4.36 (1H, m), 5.40 (1H, s), 5.4—5.9 (3H, m), 7.2—8.1 (5H, m). Found: C, 71.29; H, 7.91%. Calcd for $C_{23}H_{30}O_5$: C, 71.48; H, 7.82%.

5-[(1*E*,3*E*)-5-(Benzoyloxy)-1-methyl-1,3-nonadienyl]-3(2*H*)-furanone (14). A similar reaction of **13** (77 mg, 0.20 mmol) with Me_3SiCl (55 mg, 0.50 mmol) was done for 4 h at room temperature. The crude product was separated by preparative TLC (hexane-acetone, 3 : 1, developed twice) gave **14** (R_f 0.34—0.41, 45 mg, 61% yield) and **15** (R_f 0.41—0.46, 15 mg, 29% yield). **14**: IR (neat) 1720, 1695, 1635, 1605, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.7—2.0 (15H, m), 2.00 (3H, d, J=1.0 Hz), 5.57 (1H, s), 5.60 (1H, m), 6.13 (1H, dd, J=14.5, 6.9 Hz, C-4), 6.68 (1H, dd, J=14.5, 11.3 Hz, C-3), 7.04 (1H, dd, J=11.3 Hz, 1.0 Hz, C-2), 7.3—8.2 (5H, m). Found: C, 74.88; H, 7.79%. Calcd for $C_{23}H_{28}O$: C, 74.79; H, 7.66%. **15**: IR (neat) 3500, 1695, 1630, 1605, 1550 cm^{-1}: ^1H NMR (CCl_4) δ=1.33 (6H, s), 0.8—1.9 (9H, m), 2.01 (3H, s), 4.37 (1H, m), 5.45 (1H, s), 5.8—7.1 (3H, m). Found: C, 72.88; H, 9.32%. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15%.

5-[(*Z*)-5-(Benzoyloxy)-2-hydroxy-1-methyl-3-nonenyl]-2,2-dimethyl-3(2*H*)-furanone (16): 54% yield; IR (neat) 3450, 1720, 1700, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.7—2.0 (18H, m), 2.84 (1H, m), 3.70 (1H, br s, OH), 4.78 (1H, m), 5.46 (1H, s), 5.4—6.0 (3H, m), 7.2—8.1 (5H, m). Found: C, 71.63; H, 7.90%. Calcd for $C_{23}H_{30}O_5$: C, 71.48; H, 7.82%.

Compounds 14 and 17. The dehydration of **16** (72 mg, 0.19 mmol) with Me_3SiCl (51 mg, 0.47 mmol) was done for 2 h at room temperature in the usual way. The crude product was purified by preparative TLC (hexane-acetone, 3 : 1, developed twice) to give a mixture of **14** and **17** (R_f 0.51—0.56, 39 mg, 57% yield). The product ratio of **14** and **17** was determined to be 53 : 47 based on their weights isolated by using preparative HPLC (Yanagimoto column SA-I; 6 mmϕ×250 mm; hexane-ethyl acetate-ethanol, 100 : 2 : 1; 1.0 ml min^{-1}), which showed two peaks due to **14** (retention time: 29.2 min, 19 mg) and **17** (33.5 min, 17 mg). **17**: IR (neat) 1720, 1700, 1635, 1605, 1555 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.7—2.0 (15H, m), 2.0 (3H, s), 5.63 (1H, s), 5.95 (2H, m), 6.28 (1H, dd, J=12.0, 10.1 Hz, C-3), 7.3—8.2 (6H, m, phenyl and C-4). Found: C, 74.85; H, 7.71%. Calcd for $C_{23}H_{28}O_4$: C, 74.97, 7.66%.

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