Organic Chemistry

Z-Stereoselective Peterson olefination of ketones

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A highly-stereoselective method (90 % of the *Z*-isomer) was developed for the Peterson olefination of ketones with neryiacetone (**1**) as an example. The method is based on the introduction of a PhS group, which is removed after completion of the reaction, at the ketone C(3) atom.

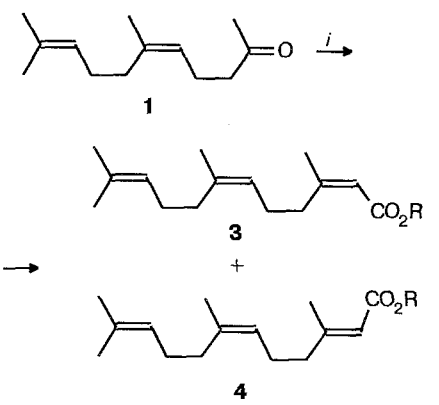
Key words: olefination of ketones, stereoselective synthesis, Peterson reaction, 2*Z*- and 2*E*-4-phenylthiofarnesoles and 2*Z*- and 2*E*-4-phenylthiofarnesoates.

The Peterson olefination of carbonyl compounds[1,2] is a convenient method for the elongation of a carbon chain that is frequently used in directed organic synthesis. The conditions for this reaction involving aldehydes that provide 95—98 % *Z*- or *E*-stereoselectivity have been established (examples can be found in Refs. 3, 4 and 5, respectively). However, the stereoselective olefination of ketones could be performed only in the case of some of their sterically hindered representatives.[6—9]

The approach described in the present work makes it possible to perform the Peterson olefination of isoprenoid ketones with 90 % *Z*-stereoselectivity.*

In order to carry out the complete synthesis of polyprenols,[11,12] a method for highly-stereoselective transformation of type **1** ketones into α,β-unsaturated esters **3** would be very useful. In connection with this problem, we studied the Peterson variant of this transformation involving alkyl[trialkyl(aryl)silyl]acetates (**2**).

It was found that the factors determining the stereochemical result of the olefination of aldehydes (the volume of



(1)

i. $Me_nPh_{3-n}SiCH_2CO_2R^1$ (**2**), B

2a: n = 3, R = Me; **2e**: n = 2, R = Bu^t;
2b: n = 3, R = Et; **2f**: n = 1, R = Et;
2c: n = 3, R = Bu^t; **2g**: n = 1, R = Bu^t;
2d: n = 2, R = Et; **2h**: n = 0, R = Bu^t.

† Deceased.

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Table 1. Effect of the structure of silylacetates **2** and the nature of the base (B) on the stereochemistry of reaction (1)

Entry	2	B	Yield of 3+4 (%)	3/4
1	**a**	Pr^i_2NLi	90	60:40
2	**b**	Pr^i_2NLi	93	55:45
3	**c**	$(Me_3Si)_2NK$	75	53:47
4	**f**	Pr^i_2NLi	60	65:35
5	**g**	Pr^i_2NLI	80	65:35
6	**h**	Pr^i_2NLi	75	58:42

Scheme 1

substituents in the organosilicon reagent[3,4,8] and the nature of the base used for generating a carbanion from the latter[3,8]) virtually do not affect the ratio of the stereoisomers formed from ketone **1** (Table 1).

It is well known[1,2] that the stereochemical result of the Peterson reaction is determined at the stage of the formation of its primary products, the alcoholates of β-hydroxysilanes (**5A,B**), whose ratio depends primarily on the spatial interaction of the substituted silyl group with the substituent closely approaching it (R^3 or R^2, Scheme 1). The transformation of compounds **5A,B** into the target products under the basic conditions created in this reaction occurs as stereospecific *syn*-elimination[13] to give esters **3** and **4**, respectively. Obviously, steric nonequivalence of the substituents at the carbonyl group of the aldehydes reacting with silyl reagent **2** should give alcoholates **5A** (R^3 = H) and subsequently esters **3**. On the other hand, the condensation of compound **2** with ketones whose α- and α′-positions are occupied by groups of similar volumes results in mixtures of **5A,B** and hence in mixtures of isomeric esters **3** and **4**.

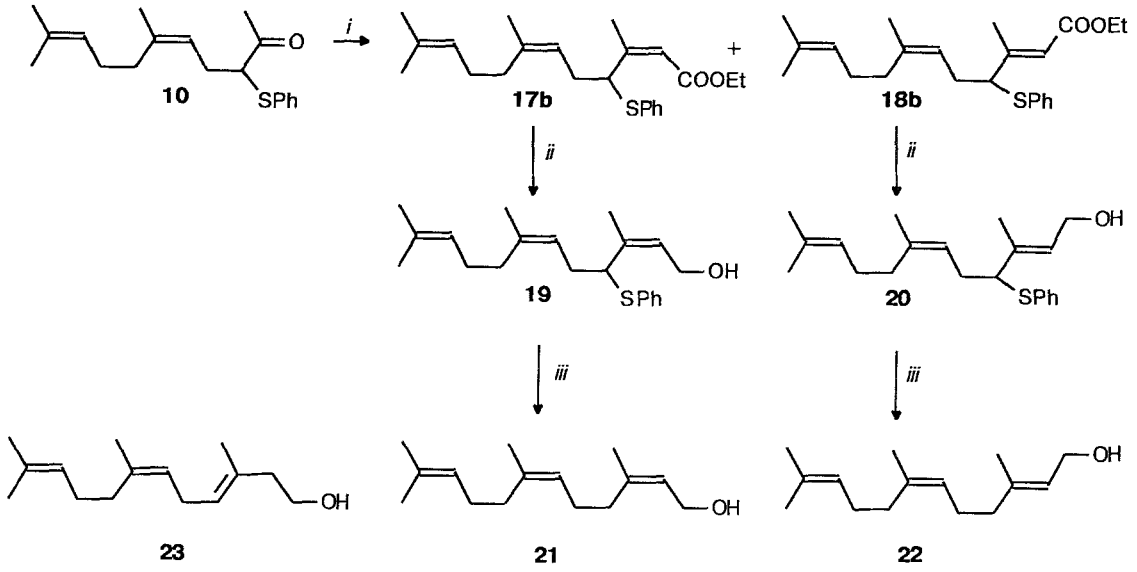
Based on the above considerations, we assumed that the stereoselectivity of Peterson *Z*-olefination of methylketones can be increased significantly by introducing a bulky substituent, which can be easily cleaved from the reaction products, at the C-3 position of their molecules. We studied the possibility of this approach using ketone **1** and the phenylthiyl group as the bulky substituent.

Ketone **1** remains unchanged after treatment with Et_3N in DMF at 20—130 °C.[14,15] However, it readily undergoes enolization when treated with lithium diisopropylamide (LDA) or sodium bis(trimethylsilyl)amide[16] to give mixtures of enolates **6** and **7** in ~9 : 1 ratio, as established from the composition of the products of silylation (**8**, **9**) of the mixture of enolates **6** and **7** (^{1}H NMR data). We managed to find the conditions for

Scheme 2

i. $(Me_3Si)_2NNa$; *ii.* Me_3SiCl; *iii.* $(PhS)_2$.

Scheme 3



i. **2b**, LDA; *ii.* $[AlH_3]$; *iii.* $Na/NH_3/Et_2O$/DB-18/C/6.

phenylthiylation of the **6/7** mixture (Scheme 2) which make it possible to obtain, in 60 % yield, 3-phenylthioketone **10**, which contains no admixture of regioisomer **11** and is easily separated by flash chromatography from the products of bis- and trisphenylthiylation (**12—14**).

The structure of the hitherto unknown ketone **10** was confirmed by elemental analysis and spectral methods. For example, its ^1H NMR spectrum contains a singlet of the MeCO group (δ 2.27) and a triplet of the CHSPh group (δ 3.63), which correspond to the signals at δ 28.9 and 57.9 in the ^{13}C NMR spectrum, along with signals of the C_{10}-isoprenoid moiety and Ph group. The structures of ketones **12—14** were also established by spectral methods. The IR spectra of these compounds contain intense absorption bands of the C=O group. The ^1H NMR spectra of compounds **12** and **13** contain signals of two Ph groups along with signals of the C_{10}-isoprenoid moiety. The former are accompanied by a signal of MeCO (δ 2.47), whereas signals from the protons at the C atom linked with the PhS groups are not observed. The ^1H NMR spectrum of ketone **13** does not contain a signal of the MeCO group but displays a triplet of the CH_2CO group (δ 2.76) and a singlet at δ 4.95 attributed to the proton at C(1). This is in good agreement with the literature data for 1-methoxy-1-phenylthiopropan-2-one.[17] In addition to the signals of three Ph groups and the C_{10}-isoprenoid moiety, the ^1H NMR spectrum of ketone **14** contains characteristic signals of the protons at C(1) (a singlet at δ 5.43) and at C(3) (a triplet at δ 4.02) shifted 0.4—0.5 ppm downfield relative to the signals of the corresponding protons in the ^1H NMR spectra of ketones **13** and **10**, respectively.

The data obtained allow us to assume that the predominant formation of compound **10** under the conditions used results from a higher rate of phenylthiylation of the minor (see above) enolate **7** compared to that of **6**. A similar regularity has been observed previously during the alkylation of asymmetric ketones.[14] In addition, these data allow us to assume that the absence of 1-phenylthioketone **11** in the reaction products is due to the high rate of phenylthiylation of the corresponding enolate (**15**) into ketone **13** (Scheme 2), which is consistent with the absence of 1,3-bis(phenylthio)ketone **16** and the presence of tris(phenylthio)ketone **14** in the mixture of phenylthiylation products.

The reaction of ketone **10** with deprotonated ethyl(trimethylsilyl)acetate **2b** results in a mixture of esters **17b** and **18b** (Scheme 3) in good yield and with 88 % *Z*-stereoselectivity (^1H NMR data). The structures of **17b** and **18b** were confirmed by elementary analysis and spectral data. For example, in agreement with the data for isomeric ethyl farnesoates,[18] the signal of the MeC(3) group in the ^1H NMR spectrum of compound **17b** is shifted ~0.25 ppm upfield relative to the similar signal in the spectrum of compound **18b**. Conversely, the signals of HC(2) are observed in the ^1H NMR spectrum of **17b** at a weaker field than in the spectrum of **18b** ($\Delta\delta \sim 0.2$ ppm). This characteristic difference between the ^1H NMR spectra of compounds **17b** and **18b** is also observed for the signal of HC(4) (δ ~ 5.7 and 3.5 ppm, respectively).

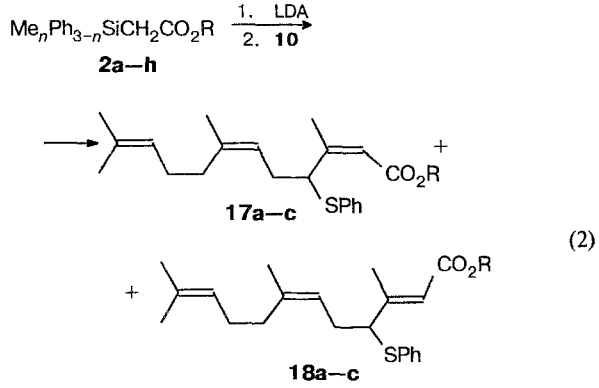
Similar regularities are observed in the ^1H NMR spectra of the methyl (**17a**, **18a**) and *tert*-butyl (**17c**, **18c**) analogs of **17b** and **18b** (see below). This provides a simple method for estimating the *Z*/*E* isomer ratios in their mixtures based on ^1H NMR spectral data.

Variations in the volumes of the substituents in organosilicon reagent **2** (Table 2) markedly affect the stereochemistry of the olefination of compound **10**. For

Table 2. Effect of the structure of reagent **2** on the stereochemistry of reaction (2)

Entry	2	Yield of 15+16 (%)	15/16
1	**a**	78	90:10
2	**b**	70	88:12
3	**c**	70	80:20
4	**d**	90	85:15
5	**e**	60	80:20
6	**f**	65	80:20
7	**g**	40	55:45
8	**h**	8	55:45

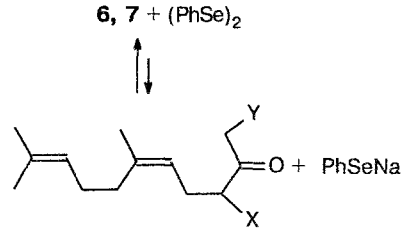
example, the maximum Z-stereoselectivity (90 %) was attained in the case of compound **2a**. Contrary to the literature data,[3,4] an increase in the volume of the substituents at the Si atom decreases the fraction of the Z-isomer in the mixture only slightly or does not affect it at all (*cf.* entries 2, 4, and 6, as well as 3 and 5 in Table 2). The volume of substituent R is of greater importance. For example, the use of reagents **2c,e,g,h** results in a noticeable decrease in stereoselectivity, or even in complete loss of stereoselectivity (entries 7 and 8). This is quite reasonable taking into account that the stereocontrol in the reaction studied appears at the stage of alcoholates **5**, for which the probability of the formation of isomer **5B** when $R^2 > R^3$ increases as the volume of R increases.



(2)

The reductive desulfurization of esters **17b** and **18b** or their methyl and *tert*-butyl analogs *via* alcohols **19** and **20** (Scheme 3) under conditions minimizing the formation of homoallyl alcohols (**23**)[19] gives good yields of Z,Z- (**21**) and E,Z-farnesol (**22**), respectively.

With the aim of possibly further increasing the Z-stereoselectivity of the olefination of isoprenoid ketones, it seemed interesting to study the reaction of compound **2a** with the Se-analog (**24**) of ketone **10**. However, we found that under the conditions used for obtaining **10**, compound **24** was formed as a mixture with its regioisomer (**25**) (~1 : 1). The overall yield of the isomers did not exceed 10 %, probably due to a sharp shift of the equilibrium of reaction (3) toward the formation of the starting products in the case of organoselenium compounds (*cf.* Ref. 20).



(3)

24: X = SePh, Y = H;
25: X = H; Y = SePh.

Although we managed to phenylselenate compound **1** *via* enolates **6** and **7** in ~ 40 % yield *in situ* using PhSeBr, this reaction also gave a mixture of ketones **24** and **25** (Scheme 4) in ~2 : 1 ratio, which could only be separated by HPLC. The olefination of the resulting compound **24** with deprotonated silylacetates gives a good yield of esters **26** and **27** in ~9 : 1 ratio (^{1}H NMR data), which was also attained in the case of the more accessible ketone **10**.

The structures of esters **26** and **27** and ketones **24** and **25** were established by spectral methods, as described above for the corresponding organosulfur compounds. Thus, the replacement of sulfur by selenium in the reaction studied merely results in complications and does not give any advantages.

It should be noted in conclusion that when this study was in progress, we noticed a work by Sato *et al.*[21] who reported that the olefination of aldehydes with ethyl (trimethylgermyl)acetate (**28**) occurs with E-stereoselectivity exceeding 98 %. In view of this, we studied the reaction of compound **28** with ketone **10**. However, in this case we obtained a mixture of esters **17b** and **18b** in ~ 3 : 2.2 ratio.

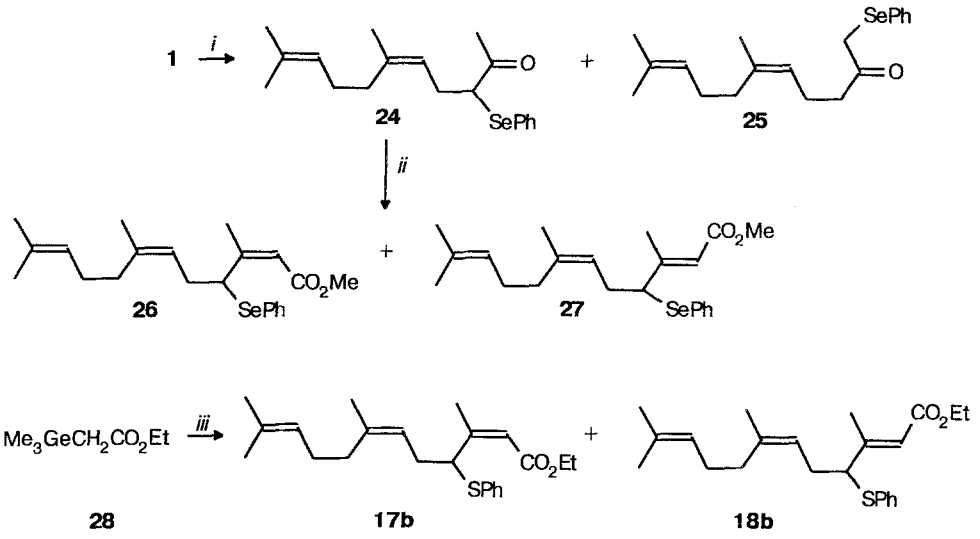
We are now studying the possibility of using the above approach for the synthesis of natural compounds.

Experimental

The ether and THF used in this study were kept over KOH, successively distilled from Na and $LiAlH_4$, refluxed with benzophenone sodium-ketyl until a stable blue color appeared, and finally distilled directly into the reaction flask. HMPA was dried with P_2O_5, distilled *in vacuo*, and stored over molecular sieves 4A. Bis(trimethylsilyl)amine was distilled and stored over molecular sieves 4A.

IR spectra were obtained in CCl_4 solutions on a Perkin-Elmer 577 spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ relative to $SiMe_4$ on a Bruker WM-250 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer with a working frequency of 75.5 MHz. Mass spectra (EI, 70 eV) were obtained on a Varian MAT CH-6 instrument. Preparative flash chromatography was performed on silica gel L (40—100 μm, Chemapol, Czech Republic). TLC was carried out on Silufol plates (Kavalier, Czech Republic) in the ether—

Scheme 4



i. $(Me_3Si)_2NNa$, then $(PhSe)_2$ or PhSeBr;
ii. $Me_3SiCH_2CO_2Me$/LDA; *iii.* LDA, then **10**

hexane, 1 : 9 (a), ether—hexane, 1 : 1 (b), ether—hexane, 1 : 19 (c) systems or in benzene (d). Analytic and preparative HPLC was performed on Armospher Sil 10 (150×4, 10 μm, a) or Silasorb 600 (250×6, b) columns in the heptane—ethyl acetate system (97 : 3, v/v) using RIDK-102 as the detector; the flow rate of the eluent was 6 mL min^{-1}.

Nerylacetone (1) was obtained from linalool according to the procedure in Ref. 22 followed by rectification of the 5*Z*-/5*E*-isomer mixture on a packed column with an efficiency of 120 theoretical plates. The physicochemical properties of the compound agree completely with those reported in the literature.[23]

Methyl and ethyl [trialkyl(aryl)silyl]acetates (2a, 2b, 2d, 2f) were obtained by the procedure in Ref. 24. Their physicochemical properties agree completely with those reported previously.[24,25]

***tert*-Butyl (trimethylsilyl)- (2c) and *tert*-butyl (methyldiphenylsilyl)- (2g) acetates** were obtained by the procedure in Ref. 26. Their physicochemical properties agree completely with those reported previously.[26,27]

***tert*-Butyl (dimethylphenylsilyl)acetate (2e)** was obtained similarly to compound **2g** as a colorless oil and purified by chromatography on SiO_2; yield 68 %; R_f 0.35 (a). ^1H NMR, δ: 0.42 (s, 6 H, Me_2Si), 1.36 (s, 9 H, Me_3C), 2.07 (s, 2 H, CH_2), 7.45 (m, 5 H, Ph).

***tert*-Butyl (triphenylsiylyl)acetate (2h)** was obtained similarly to compound **2g** as a colorless oil and purified by chromatography on SiO_2; yield 73 %; R_f 0.27 (c). ^1H NMR, δ: 1.15 (s, 9 H, Me_3C), 2.68 (br.s, 2 H, CH_2), 7.45 (m, 15 H, Ph).

Olefination of compound 1 with alkyl (trialkyl(aryl)silyl-acetates 2. An example representative of Table 1. A solution of compound **2b** (7.0 g, 43.3 mmol) in THF (10 mL) was added dropwise under argon to a stirred solution (−70 °C) of LDA (43 mmol) in a THF—hexane mixture (10 : 1, 33 mL). The mixture was stirred for 1 h and then treated with compound **1** (6.9 g, 36 mmol) at the same temperature. The reaction mixture was stirred at −70 °C for 1 h, the temperature was increased to ~20 °C over a period of 2 h, and stirred for an additional 1 h. $NaHSO_4 \cdot 2H_2O$ (7.9 g) was added, and stirring was continued for 15 min. The mixture was filtered, and the filtrate was washed with saturated NH_4Cl. Subsequent standard work-up and chromatography on SiO_2 (100 g) gave 8.5 g (90 %) of ethyl farnesoate as a mixture (~3 : 2) of 2*Z*/2*E*-isomers. ^1H NMR, δ: 1.23 and 1.25 (2t, 3 H, $\underline{Me}CH_2$, J_1 = J_2 = 7 Hz), 1.60 (s, 3 H, *cis*-MeC(11)); 1.68 (s, 6 H, *trans*-MeC(7,11)), 1.85 (d, 1.8 H, MeC(3) of the *Z*-isomer, J = 1.5), 2.08 (m, 4 H, CH_2), 2.16 (m, 4 H, HC(5), HC(4) and MeC(4) of the *E*-isomer), 2.62 (t, 1.2 H, HC(4) of the *Z*-isomer, J = 8 Hz); 4.13 and 4.15 (2q, 2 H, CH_2O, J_1 = J_2 = 7), 5.1 (m, 2 H, HC=C), 5.6 (br.s, 1 H, HC(2)).

6,10-Dimethyl-3-phenyltioundeca-5*Z*,9-dien-2-one (10), 6,10-dimethyl-3,3-diphenyltioundeca-5*Z*,9-dien-2-one (12), 6,10-dimethyl-1,1-diphenyltioundeca-5*Z*,9-dien-2-one (13), and 6,10-dimethyl-1,1,3-triphenyltioundeca-5*Z*,9-dien-2-one (14). Phenanthrene (2.67 g, 15 mmol) and bis(trimethylsilyl)amine (4.8 g, 30 mmol) were added simultaneously with stirring under argon (~20 °C) to a mixture of ether (20 mL), THF (20 mL), and Na (0.68 g, 29.6 g-at.), and the mixture was stirred at ~20 °C until the sodium dissolved completely (2.5 h). The solution was then cooled to −70 °C, and a solution of compound **1** (3.88 g, 20 mmol) in ether (5 mL) was added dropwise. The reaction mixture was stirred at −70 °C for 15 min, the temperature was increased to ~20 °C, and the mixture was stirred for an additional 2.5 h. The resulting solution was cooled to −5 °C, HMPA (10 mL) was added, and the mixture was stirred for 30 min. A solution of $(PhS)_2$ (5 g, 23 mmol) in a mixture of THF (10 mL) and HMPA (6 mL) was added at the same temperature, and the mixture was stirred for an additional 1 h. The reaction mixture was poured into a stirred (0 °C) mixture of 10 % HCl (20 mL) and ether (50 mL), the resulting mixture was stirred for 15 min, and the organic layer was separated. Ordinary work-up gave 12 g of a yellow oil, which was chromatographed on SiO_2 (200 g). Gradient elution from hexane to benzene (up to 50 % of the latter) with analysis of the fractions by ^1H NMR spectroscopy gave 0.86 g of a mixture of ketones **13**, **14**, and **12** in the ratio of ~1 : 1 : 0.17 (fraction 1), 0.20 g of a mixture of ketones **13**, **14**, **12**, and **10** in the ratio of ~1 : 0.5 : 1 : 0.2 (fraction 2), 0.40 g of a mixture of ketones

13, **14**, **12**, and **10** in the ratio of ~1 : 0.5 : 4.5 : 4 (fraction 3), 0.55 g of a mixture of ketones **13**, **12**, and **10** in the ratio of ~1 : 3.6 : 12 (fraction 4), 0.60 g of a mixture of ketones **12** and **10** in the ratio of ~1 : 6.5 (fraction 5), 1.28 g of pure compound **10**, 0.28 g of a mixture of ketones **10** and **1** in the ratio of ~1 : 1 (fraction 6), 0.33 g of a mixture of ketones **10** and **1** in the ratio of ~1 : 14 (fraction 7), and finally, 0.75 g of pure compound **1**. Repeated chromatography of fractions 3—6 gave an additional amount of compound **10** (1.22 g), whose overall yield was 60 % with respect to the reacted **1** and the conversion was 70 %. Ketone **10**, b.p. 120°C (0.07 Torr). (bath), R_f 0.38 (d). Found (%): C, 75.44; H, 8.79; S, 10.71. $C_{19}H_{26}OS$. Calculated (%): C, 75.44; H, 8.66; S, 10.60. IR, ν/cm^{-1}: 3080—2860, 1710, 1700, 1660, 1475, 1450, 1440, 1380, 1360, 1320, 1210, 1150, 1120, 1070, 1030 730, 690, 670. ^1H NMR, δ: 1.65 (s, 3 H, *cis*-Me), 1.72 and 1.74 (2 s for 3 H, *trans*-Me), 2.07 (m, 4 H, HC(7, 8)), 2.27 (s, 3 H, MeCO), 2.50 (m, 2 H, HC(4)), 3.65 (t, 1 H, HC(3), J = 7 Hz), 5.15 (m, 2 H, HC(5,9)), 7.35 (m, 5 H, Ph). ^{13}C* NMR, δ: 17.7 (*cis*-MeC(10)), 23.4 (MeC(6)), 25.7 (*trans*-MeC(10)), 26.4 (C-4), 26.9 (C-8), 28.9 (MeCO), 32.2 (C-7), 57.9 (C-3), 120.4 (C-5), 124.0 (C-9), 132.1 (C-10), 138.7 (C-6), 205.2 (C-2). MS, *m/z*: 302 (M^+), 301, 259, 258, 232, 192, 164, 122, 108, 68. Repeated chromatography of fraction 1 gave 0.32 g of compound **13** and 0.30 g of **14** containing no admixtures (according to ^1H NMR and HPLC data). Ketone **13**, R_f 0.58(d). ^1H NMR, δ: 1.65 (s, 3 H, *cis*-Me), 1.72 and 1.74 (2 s for 3 H, *trans*-Me), 2.07 (m, 4 H, HC(7, 8)), 2.30 (dt, 2 H, HC(4), $J_1 = J_2$ = 7.5 Hz), 2.76 (t, 2 H, HC(3), J = 7.5 Hz), 4.95 (s, 1 H, HC(1)), 5.10 (m, 2 H, HC(5,9)), 7.35 (m, 10 H, Ph). ^{13}C NMR, δ: 17.3 (*cis*-MeC(10)), 22.5 (C-4), 23.3 (MeC(6)), 25.7 (*trans*-MeC(10)), 26.5 (C-8), 31.8 (C-7), 38.9 (C-3), 64.6 (C-1), 123.1 (C-5), 124.1 (C-9), 131.7 (C-10), 136.7 (C-6), 201.7 (C-2). Ketone **14**, R_f 0.50(d). ^1H NMR, δ: 1.65 (s, 3 H, *cis*-Me), 1.72 and 1.74 (2 s for 3 H, *trans*-Me), 2.10 (m, 4 H, HC(7, 8)), 2.52 (dd, 2 H, HC(4), $J_1 = J_2$ = 7 Hz), 4.02 (t, 1 H, HC(3), J = 7 Hz), 5.15 (t, 1 H, HC(9), J = 7 Hz), 5.28 (t, 1 H, HC(5), J = 7 Hz), 5.43 (s, 1 H, HC(1)), 7.40 (m, 15 H, Ph).

Repeated chromatography of fraction 3 gave 0.09 g of ketone **12** containing no admixtures (according to ^1H NMR and HPLC data), R_f 0.48(d). ^1H NMR, δ: 1.58 (s, 3 H, *cis*-MeC(10)), 1.72 (s, 3 H, *trans*-MeC(10)), 1.78 (s, 3 H, MeC(6)), 1.90 and 2.05 (2 m for 2 H, HC(7, 8)), 2.48 (d, 2 H, HC(4), J = 6 Hz), 2.50 (s, 3 H, MeCO), 5.02 (t, 1 H, HC(9), J = 7 Hz), 5.37 (t, 1 H, HC(5), J = 6 Hz), 7.40 (m, 10 H, Ph).

^1H NMR analysis of fractions 1—7 shows that the overall yield of ketone **12** is ~10 %, that of ketone **13** is ~10 %, and that of ketone **14** is ~7 % with respect to the reacted **1**; the conversion is 70 %.

6,10-Dimethyl-1-(phenylthio)undeca-5Z,9-dien-2-one (11). A solution of compound **1** (6.79 g, 35 mmol) in THF (10 mL) was added dropwise under argon to a stirred solution (0 °C) of LDA (40 mmol) in a THF—hexane mixture (4 : 1). The mixture was heated to 45 °C, stirred for 1 h at this temperature, and cooled to 0 °C. A solution of $(PhS)_2$ (7.63 g, 35 mmol) in HMPA (45 mL) was added dropwise, and the mixture was stirred for 1 h at −2 to 0 °C and poured into a solution of NH_4Cl cooled to 0 °C. Standard work-up gave 15.6 g of a light-yellow oil, which was chromatographed on SiO_2. Gradient elution from hexane to benzene gave 1.2 g of a mixture of ketones **12**, **14**, **10**, and **11** in the ratio of ~1 : 1 : 1 : 1, 2.25 g of a mixture of ketones **10** and **11** in the ratio of ~1 : 1, 2.0 g of a mixture of ketones **10**, **11**, and **1** in the ratio of ~1 : 1 : 6, and 2.8 g of the starting ketone **1**. HPLC of 2.25 g of the mixture of **10** and **11** (column a) gave 1.1 g of ketone **10** identical to the sample described above and 0.98 g of ketone **11** containing no admixtures (^1H NMR and HPLC data). Ketone **11**, R_f 0.55 (d). ^1H NMR, δ: 1.62 (s, 3 H, *cis*-Me), 1.68 and 1.70 (2s for 3 H, *trans*-Me), 2.02 (m, 4 H, HC(7, 8)), 2.25 (dt, 2 H, HC(4) $J_1 = J_2$ = 7.2 Hz), 2.62 (t, 2 H, HC(3), J = 7.2 Hz), 3.68 (s, 2 H, HC(1)), 5.08 (m, 2 H, HC(5, 9)), 7.3 (m, 5 H, Ph).

Olefination of compound 10 by silyl acetates 2 (an example representative of Table 2). Methyl 3,7,11-trimethyl-4-(phenylthio)dodeca-2Z,6Z,10-trienoate (17a) and its 2E-isomer (18a). A solution of silyl acetate **2a** (0.73 g, 5 mmol) in THF (3 mL) was added dropwise under argon to a stirred (−70 °C) solution of LDA (5.2 mmol) in a hexane—THF mixture (1 : 5). The mixture was stirred for 2 h at −70 °C, and a solution of compound **10** (0.95 g, 3.15 mmol) in THF (3 mL) was added dropwise at the same temperature. The mixture was stirred for an additional 2 h, heated to ~20 °C over a period of 1 h, and poured into a cooled NH_4Cl solution. Standard work-up gave 1.5 g of a light-yellow oil, which was chromatographed on SiO_2 (100 g). Gradient elution from hexane to benzene (up to 50 % of the latter) gave 0.69 g (70 %) of **17a** and 0.2 g of a mixture of **17a**, **18a**, and ketone **10** in the ratio ~1 : 5 : 7 (^1H NMR and HPLC data). Repeated chromatography of this mixture gave 0.06 g of pure ester **18a** (according to ^1H NMR and HPLC data). Ester **17a**, b.p. 195 °C (0.07 Torr; bath). Found (%): C, 73.84; H, 8.48; S, 8.86. $C_{22}H_{30}O_2S$. Calculated (%): C, 73.70; H, 8.43; S, 8.93. R_f 0.70 (d). IR, ν/cm^{-1}: 3080, 3060, 3020, 2975, 2950, 2930, 2920, 2860, 1710, 1640, 1580, 1480, 1440, 1380, 1370, 1260, 1200, 1180, 1160, 1150, 1110, 1090, 1050, 1030, 925, 870, 695. ^1H NMR, δ: 1.63 (s, 3 H, *cis*-Me), 1.72 (s, 6 H, *trans*-Me), 1.95 (s, 3 H, MeC(3)), 2.05 (m, 4 H, HC(8, 9)), 2.45 (m, 2 H, HC(5)), 3.50 (s, 3 H, MeO), 5.15 (m, 2 H, HC(6, 10)), 5.62 (br.s, 1 H, HC(2)), 5.68 and 5.70 (2 d, 1 H, HC(4), $J_1 = J_2$ = 9.5 Hz), 7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 17.4 (*cis*-Me-C(11)), 19.1 (Me-C(3)), 23.1 (Me-C(7)), 25.5 (*trans*-Me-C(11)), 26.3 (C-9), 30.7 (C-5), 32.0 (C-8), 47.5 (C-4), 50.5 (MeO), 118.3 (C-2), 120.8 (C-6), 124.0 (C-10), 131.4 (C-11), 137.4 (C-7), 156.95 (C-3), 165.9 (C-1). MS, *m/z*: 359, 358, 249, 248, 223, 222, 221, 194, 193, 190, 189, 179, 163, 162, 161, 154, 149, 147, 137, 135, 133, 125, 121, 109, 105, 97, 95, 94, 82, 81, 69, 41, 28. Ester **18a**, R_f 0.58 (d); ^1H NMR, δ: 1.63 (s, 3 H, *cis*-Me), 1.72 (br.s, 6 H, *trans*-Me), 2.07 (m, 4 H, HC(8, 9)), 2.22 (s, 3 H, MeC(3)), 2.45 (d d, 2 H, HC(5), $J_1 = J_2$ = 7.5 Hz), 3.50 (m, 4 H, MeO, HC(4)), 5.01 (m, 2 H, HC(6, 10)), 5.46 (br.s, 1 H, HC(2)), 7.35 (m, 5 H, Ph).

Ethyl 3,7,11-trimethyl-4-(phenylthio)dodeca-2Z,6Z,10-trienoate (17b) and its 2E-isomer (18b) were obtained similarly to compounds **17a** and **18a** from LDA (15 mmol), compound **2b**, **2d**, or **2f** (15 mmol), respectively, and compound **10** (13.5 mmol). The yield and isomer ratio are presented in Table 2. Ester **17b**, b.p. 180 °C (0.08 Torr; bath). Found (%): C, 74.21; H, 8.47; S, 8.36. $C_{23}H_{32}O_2S$. Calculated (%): C, 74.14; H, 8.66; S, 8.60. R_f 0.37(a). IR, ν/cm^{-1}: 3080—2800, 1710, 1660, 1640, 1480, 1450, 1440, 1380, 1260, 1210, 1150, 1100, 1050, 1030, 870, 730, 695, 670. ^1H NMR, δ: 1.20 (t, 3 H, MeCH$_2$, J = 7.3 Hz), 1.65 (s, 3 H, *cis*-Me), 1.72 (br.s, 6 H, *trans*-Me), 1.94 (d, 3 H, MeC(3), J = 1.5 Hz), 2.08 (m, 4 H, HC(8, 9)), 2.45 (m, 2 H, HC(5)),

* The ^{13}C NMR spectrum of ketone **10** and the spectra of compounds **13**, **17**—**20**, **24**, and **25** (see below) also contain signals of the Ph group.

4.02 (q, 2 H, CH_2O, J = 7.3 Hz), 5.12 (m, 2 H, HC(6, 10)), 5.65 (d, 1 H, HC(2), J = 1.5 Hz), 5.70 and 5.73 (2d, 1 H, HC(4), $J_1 = J_2$ = 9.2 Hz), 7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 14.3 (MeCH$_2$) 17.7 (*cis*-Me-C(11)), 19.4 (Me-C(3)), 23.4 (Me-C(7)), 25.7 (*trans*-Me-C(11)), 26.5 (C-9), 30.9 (C-5), 32.2 (C-8), 47.7 (C-4), 59.6 (CH_2O), 119.0 (C-2), 121.1 (C-6), 124.2 (C-10), 132.1 (C-11), 137.7 (C-7), 156.6 (C-3), 165.8 (C-1). MS, *m/z*: 372 (M^+), 371, 302, 263, 262, 236, 235, 202, 161, 137, 109, 69. Ester **18b**, R_f 0.29 (a). ^{1}H NMR, δ: 1.25 (t, 3 H, MeCH$_2$, J = 7.3 Hz), 1.65 (s, 3 H, *cis*-Me), 1.72 (br.s, 6 H, *trans*-Me), 2.06 (m, 4 H, HC(8, 9)), 2.20 (d, 3 H, MeC(3), J = 1.5 Hz), 2.42 (m, 2 H, HC(5)), 3.56 (t, 1 H, HC(4), J = 7.5 Hz), 4.08 (q, 2 H, CH_2O, J = 7.3 Hz), 5.10 (m, 2 H, HC(6, 10)), 5.45 (d, 1 H, HC(2), J = 1.5 Hz), 7.30 (m, 5 H, Ph). ^{13}C NMR, δ: 14.3 (MeCH$_2$), 15.1 (Me-C(3)) 17.7 (*cis*-Me-C(11)), 23.4 (Me-C(7)), 25.4 (*trans*-Me-C(11)), 26.9 (C-9), 31.0 (C-5), 32.2 (C-8), 59.1 (C-4), 59.7(CH_2O), 117.6 (C-2), 120.9 (C-6), 124.0 (C-10), 133.2 (C-11), 138.1 (C-7), 156.6 (C-3), 166.3 (C-1).

***tert*-Butyl 3,7,11-trimethyl-4-(phenylthio)dodeca-2*Z*,6*Z*,10-trienoate (17c) and its 2*E*-isomer (18c)** were obtained similarly to compounds **17a** and **18a** from LDA (15 mmol), compound **2c**, **2e**, **2g**, or **2h** (15 mmol), respectively, and compound **10** (13.5 mmol). The yield and isomer ratio are presented in Table 2. Ester **17c**, b.p. 190 °C (0.04 Torr; bath). Found (%): C, 74.62; H, 9.07; S, 7.18. $C_{25}H_{36}O_2S$. Calculated (%): C, 74.94; H, 9.06; S, 7.89. R_f 0.43(a). IR, ν/cm^{-1}: 3080—2860, 1710, 1640, 1480, 1450, 1440, 1380, 1370, 1260, 1210, 1150, 1110, 1050, 1030, 970, 870, 790, 690, 670. ^{1}H NMR, δ: 1.42 (s, 9 H, Me_3C), 1.64 (s, 3 H, *cis*-Me), 1.72 (br.s, 6 H, *trans*-Me), 1.90 (d, 3 H, MeC(3), J = 1.5 Hz), 2.08 (m, 4 H, HC(8, 9)), 2.45 (m, 2 H, HC(5)), 5.18 (m, 2 H, HC(6, 10)), 5.57 (d, 1 H, HC(2), J = 1.5 Hz), 5.68 and 5.72 (2d, 1 H, HC(4), $J_1 = J_2$ = 8.5 Hz), 7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 17.7 (*cis*-Me-C(11)), 19.3 (Me-C(3)), 23.4 (Me-C(7)), 25.7 (*trans*-Me-C(11)), 26.5 (C(9)), 28.2 (Me_3C), 31.0 (C-5)), 32.2 (C-8), 47.4 (C-4), 78.9(CMe_3), 120.0 (C-2), 121.3 (C-6), 124.3 (C-10), 132.0 (C-11), 137.6 (C-7), 155.5 (C-3), 165.4 (C-1). MS, *m/z*: 401, 400 (M^+), 344, 234, 207, 206, 136, 69, 57. Ester **18c**, R_f 0.37 (a). ^{1}H NMR, δ: 1.43 (s, 9 H, Me_3C), 1.60 (s, 3 H, *cis*-Me), 1.70 (br.s, 6 H, *trans*-Me), 2.05 (m, 4 H, HC(8, 9)), 2.18 (d, 3 H, MeC(3), J = 1.5 Hz), 2.42 (dd, 2 H, HC(5), $J_1 = J_2$ = 7.2 Hz), 3.52 (t, 1 H, HC(4), J = 7.2 Hz), 5.10 (m, 2 H, HC(6, 10)), 5.35 (d, 1 H, HC(2), J = 1.5 Hz), 7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 14.9 (Me-C(3)), 17.7 (*cis*-Me-C(11)), 23.4 (Me-C(7)), 25.7 (*trans*-Me-C(11)), 26.5 (C-9), 28.3 (Me_3C), 31.0 (C-5), 32.2 (C-8), 59.1 (C-4), 79.8(Me_3C), 119.6 (C-2), 121.1 (C-6), 124.0 (C-10), 133.2 (C-11), 137.9 (C-7), 154.9 (C-3), 165.8 (C-1).

3,7,11-Trimethyl-4-(phenylthio)dodeca-2*Z*,6*Z*,10-trien-1-ol (19) and its 2*E*-isomer (20). A solution of $AlCl_3$ (0.21 g, 1.54 mmol) in ether (20 mL) cooled to 0 °C was added dropwise under argon to a stirred solution (−5 °C) of $LiAlH_4$ (0.55 *M*, 10 mL) in ether. The mixture was heated to 0 °C, stirred for 30 min, and cooled to −5 °C, then a solution of **17c** or **17a,b** (3.37 mmol) in ether (20 mL) was added dropwise. The reaction mixture was stirred for 30 min at 0 °C and for 1 h at ~20 °C and then poured into a solution of NH_4Cl cooled to 0 °C. Standard work-up gave 0.97 g of a colorless oil, which was chromatographed on SiO_2 (30 g). Gradient elution from hexane to ether gave 0.78 g (71 %) **19**, R_f 0.30 (b). IR, ν/cm^{-1}: 3620, 3080—2860, 1470, 1450, 1440, 1380, 1210, 1080, 1030, 990, 960, 730, 690, 670. ^{1}H NMR, δ: 1.62 (s, 3 H, *cis*-Me), 1.70 (br.s, 6 H, *trans*-Me), 1.80 (br.s, 3 H, MeC(3)), 2.05 (m, 4 H, HC(8, 9)), 2.32 and 2.45 (2 m for 1 H, HC(5)), 3.68 (m, 2 H, HC(1)), 4.05 (dd, 1 H, HC(4), $J_1 = J_2$ = 9 Hz), 5.10 (m, 2 H, HC(6, 10)), 5.42 (t, 1 H, HC(2), J = 6.8 Hz), 7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 17.7 (*cis*-Me-C(11)), 18.1 (Me-C(3)), 23.4 (Me-C(7)), 25.7 (*trans*-Me-C(11)), 26.5 (C-9), 30.6 (C-5), 32.2 (C-8), 50.8 (C-4), 58.1 (C-1), 121.4 (C-2,6), 124.0 (C-10), 134.4 (C-7,11), 137.9 (C-3). MS, *m/z*: 331, 330(M^+), 221, 203, 202, 194, 193, 175, 151, 135, 123, 83, 69.

Similarly, the reaction of $AlCl_3$ (0.11 g, 0.8 mmol), a solution of $LiAlH_4$ in ether (0.55 *M*, 5.8 mL), and compound **18c** (0.7 g, 1.75 mmol) gave 0.55 g (95 %) of compound **20**, R_f 0.32 (b). ^{1}H NMR, δ: 1.62 (s, 6 H, *cis*-Me), 1.70 (br.s, 6 H, *trans*-Me), 2.05 (m, 4 H, HC(8, 9)), 2.38 (dd, 2 H, HC(5), $J_1 = J_2$ = 7.5 Hz), 3.58 (t, 1 H, HC(4), J = 7.5 Hz), 3.97 (d, 2 H, HC(1), J = 7 Hz), 5.15 (m, 3 H, HC(2, 6, 10)), 7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 12.1 (MeC(3)), 17.7 (*cis*-MeC(11)), 23.5 (MeC(7)), 25.6 (*trans*-MeC(11)), 26.5 (C-9), 30.8 (C-5), 32.2 (C-8), 58.6 (C-1), 59.1 (C-4), 121.6 (C-2,6), 124.2 (C-10)), 133.5 (C-7,11), 137.3 (C-3).

2*Z*,6*Z*-Farnesol (21). A solution of compound **19** (200 mg, 0.6 mmol) in ether (5 mL) was added to a stirred (−70 °C) blue solution of Na (160 mg, 7 mg-at) in NH_3 (30 mL) containing dibenzo-18-crown-6 (20 mg, 0.05 mmol). The mixture was stirred for 1 h, then NH_4Cl was added until the solution became uncolored. Standard work-up gave 170 mg of a colorless oil, which was chromatographed on SiO_2 (15 g). Gradient elution from hexane to ether (up to 20 % of the latter) gave 130 mg of compound **21** containing ~8 % of an admixture of homoallylic alcohol **23** (^{1}H NMR data). HPLC (column a) gave 110 mg (83 %) of pure **21**, which was identical to the sample reported previously[27] (according to the IR and ^{1}H NMR data).

2*E*,6*Z*-Farnesol (22) was obtained and purified similarly to compound **21**, yield 80 %. The IR and ^{1}H NMR spectral data are in agreement with those reported previously.[27]

6,10-Dimethyl-3-(phenylseleno)undeca-5*Z*,9-dien-2-one (24) and 6,10-dimethyl-1-(phenylseleno)undeca-5*Z*,9-dien-2-one (25). ***a.*** Using the procedure described above for compound **10**, the reaction of compound **1** (20 mmol), Na (28 mg-at), $(Me_3Si)_2NH$ (28 mmol), phenanthrene (14 mmol), and $(PhSe)_2$ (7 g, 32.1 mmol) gave 12.6 g of a yellow oil, which was chromatographed on SiO_2 (100 g). Gradient elution from hexane to benzene gave 0.92 g of a mixture of ketones **24**, **25**, and **1** in the ratio of ~1 : 1 : 2 and 1.96 g of a mixture of **24**, **25**, and **1** in the ratio of ~1 : 1 : 10. The former mixture was chromatographed under HPLC conditions (column b) to give 0.22 g of compound **24** and 0.20 g of **25** containing no admixtures (HPLC and ^{1}H NMR data). Ketone **24**, R_f 0.44 (d). ^{1}H NMR, δ: 1.60 (s, 3 H, *cis*-Me), 1.68 (br.s, 6 H, *trans*-Me), 2.02 (m, 4 H, HC(7, 8)), 2.23(s, 3 H, MeCO), 2.45 (m, 2 H, HC(4)), 3.62 (t, 1 H, HC(3), J = 7.5 Hz), 5.10 (m, 2 H, HC(5, 9)), 7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 17.4 (*cis*-MeC(10)), 23.2 (MeC(6)), 25.5 (*trans*-MeC(10)), 26.2 (C-8), 27.5 (C-1), 28.7 (C-4), 31.9 (C-7), 52.1 (C-3), 121.3 (C-5), 123.8 (C-9), 131.4 (C-10), 137.8 (C-6), 203.8 (C-2). Ketone **25**, R_f 0.55 (d). ^{1}H NMR, δ: 1.60 (s, 3 H, *cis*-Me), 1.66 and 1.68 (2s, 6 H, *trans*-Me), 2.02 (m, 4 H, HC(7, 8)), 2.28 (dt, 2 H, HC(4), $J_1 = J_2$ = 7 Hz), 2.60 (t, 2 H, HC(3), J = 7 Hz), 3.58 (s, 2 H, HC(1)), 5.10 (m, 2 H, HC(5, 9)), 7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 17.4 (*cis*-MeC(10)), 22.3 (C-3), 23.1 (MeC(6)), 25.5 (*trans*-MeC(10)), 26.3 (C-8), 31.6 (C-7), 35.8 (C-4), 40.7 (C-1), 123.1 (C-5), 124.0 (C-9), 131.2 (C-10), 136.2 (C-6), 205.1 (C- 2).

b. HMPA (10 mL) was added dropwise under argon at −7—−5 °C to a stirred solution of enolates **6,7**, which were obtained from Na (0.68 g, 29.6 g-at), phenanthrene (2.67 g, 15 mmol), and $(Me_3Si)_2NH$ (4.8 g, 30 mmol) in ether—THF (1 : 1, 40 mL) as described above for the synthesis of compound **10**. The mixture was stirred for 30 min at the same temperature and then cooled to −70 °C. After that, a solution obtained by treatment of a solution of $(PhSe)_2$ (6.86 g, 22 mmol) in THF (15 mL) by bromine (3.52 g, 22 mmol) at 5 °C was added. The reaction mixture was stirred for 1 h at −40 to −35 °C and poured into a mixture of ether (100 mL) and 10 % HCl (45 mL) cooled with ice. The mixture was stirred for 15 min, and the organic layer was separated. Ordinary work-up gave 12.7 g of an orange oil, which was chromatographed on SiO_2. Gradient elution from hexane to benzene gave 2.8 g (~40 %) of a mixture of ketones **24** and **25** in ~2 : 1 ratio, which were separated by HPLC (column b). Their physicochemical data were in agreement with the samples described above.

Olefination of ketone 24 with methyl (trimethylsilyl)acetate (2a). Treatment of compound **24** (−70 °C) with **2a** (0.36 g, 2.5 mmol) deprotonated by LDA, according to the procedure described above for **10** gave 0.4 g of a yellow oil, which was chromatographed on SiO_2 (100 g) to give 0.19 g of ester **26** and 0.04 g of a mixture of esters **26** and **27** in ~2 : 3.5 ratio (^{1}H NMR data).

Ester **26**, R_f 0.48 (d), ^{1}H NMR, δ: 1.65 (s, 3 H, *cis*-Me), 1.72 and 1.74 (2 s for 3 H, *trans*-Me), 1.95 (s, 3 H, MeC(3)), 2.07 (m, 4 H, HC(8, 9)), 2.48 (m, 2 H, HC(5)), 3.50 (s, 3 H, MeO), 5.10 (m, 2 H, HC(6, 10)), 5.53 (s, 1 H, HC(2)), 5.73 and 5.78 (2d, 2 H, H(4), $J_1 = J_2 = 8$ Hz), 7.40 (m, 5 H, Ph). Ester **27**, R_f 0.40 (d), ^{1}H NMR, δ: 1.65 (s, 3 H, *cis*-Me), 1.72 (br.s, 6 H, *trans*-Me), 2.07 (m, 4 H, HC(8, 9)), 2.26 (s, 3 H, MeC(3)), 2.48 (dd, 2 H, HC(5), $J_1 = J_2 = 8$ Hz), 3.49 (s, 3 H, MeO), 3.50 (t, 1 H, HC(4), $J = 8$ Hz), 5.10 (m, 2 H, HC (6, 10)), 5.32 (s, 1 H, HC(2)), 7.40 (m, 5 H, Ph).

Olefination of ketone 10 with ethyl (trimethylgermyl)acetate (28). A solution of ester **28** (1.03 g, 5.04 mmol; obtained by the procedure in Ref. 21) in THF (6 mL) was added dropwise under argon at −78 °C to a stirred solution of LDA (5.54 mmol). The mixture was stirred for 40 min, and a solution of ketone **10** (1.08 g, 3.6 mmol) in THF (5 mL) was then added dropwise. The reaction mixture was stirred for 30 min at −78 °C and heated to ~20 °C over a period of 1 h. Stirring was continued for an additional 1 h, and the mixture was cooled to 0 °C, poured into a NH_4Cl solution cooled with ice, and stirred for 15 min. The organic layer was separated. Standard work-up gave 1.6 g of a yellow oil, which was chromatographed on SiO_2 (60 g). Gradient elution from hexane to ether (up to 5 % of the latter) gave 0.79 g of a mixture of esters **17b**, **18b** and ketone **10** in a ratio of ~3 : 2.2 : 2. The overall yield of compounds **17b** and **18b** was 60 %.

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