Pergamon

Tetrahedron Vol. 51, No. 14, pp. 4011-4020, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00142-5

Organoaluminum-Promoted Cycloaddition of Trialkylsilylketene with Aldehydes: A New, Stereoselective Approach to *cis*-2-Oxetanones and 2(Z)-Alkenoic Acids

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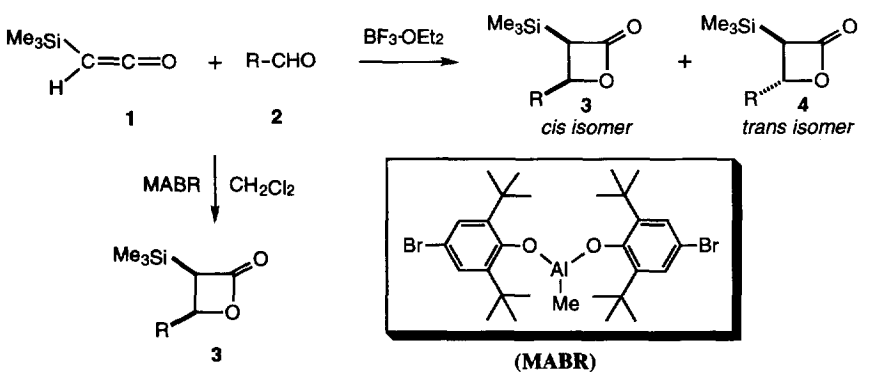
Abstract: The exceptionally bulky methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) can be successfully utilized as a highly efficient Lewis acid for achieving high stereoselectivity in the cycloaddition of trialkylsilylketene with aldehydes. This method serves as a highly effective route to the synthesis of *cis*-2-oxetanones from saturated aldehydes, and the synthesis of 2(Z)-alkenoic acids from aromatic and α,β-unsaturated aldehydes.

Introduction

There are essentially four reactions which ketenes undergo: cycloaddition, nucleophilic addition, dimerization, and polymerization.[1] Among these, the most synthetically useful reaction is the cycloaddition to yield versatile four-membered ring compounds. For example, cycloaddition of ketenes with aldehydes gives 2-oxetanones (β-lactones),[2] which are versatile and useful synthetic intermediates in the preparation of alkenes,[3] allenes,[4] carboxylic acid derivatives including amino acids,[5] and polymers.[6] Despite the availability of many different stereoselective approaches to 2-oxetanone synthesis,[2] however, the stereoselective cycloaddition of ketenes and aldehydes has never been developed to a useful level due to the lack of a satisfactory Lewis acid.[7] In fact, Brady reported that $BF_3{\cdot}OEt_2$-promoted cycloaddition of trimethylsilylketene[8] with saturated aldehydes gave rise to a mixture of *cis*- and *trans*-2-oxetanones without any stereoselectivity.[9] We now disclose a new method for effecting such cyclizations in a highly stereoselective manner under the influence of exceptionally bulky methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) as a promising Lewis acid (Scheme 1).[10-13]

Scheme 1



Results and Discussion

Cycloaddition of Silylketene with Saturated Aldehydes. First, we investigated the effect of various Lewis acids on the cycloaddition of equimolar quantities of trimethylsilylketene (**1**) with propionaldehyde **2** (R = Et) to afford a mixture of *cis*- and *trans*-4-ethyl-3-(trimethylsilyl)-2-oxetanones, **3** and **4** (R = Et). Attempted reaction of silylketene **1** and aldehyde **2** (R = Et) in CH_2Cl_2 with catalytic $BF_3{\cdot}OEt_2$ afforded cycloadducts, **3** and **4** (R = Et) in a ratio of 70:30. This result is better than that of Brady's previous observation, where the *cis/trans* ratio of cycloadducts is 55:45 in the absence of solvent. Et_2AlCl gave better selectivity (*cis/trans* = 92:8), while $SnCl_4$ resulted in low yield of 2-oxetanones due to partial decomposition under the reaction conditions. In marked contrast, exceptionally bulky organoaluminum reagent, MABR produced *cis*-2-oxetanone **3** (R = Et) exclusively in 82% yield.[8] None of the *trans* isomer **4** (R = Et) was detected by TLC and ^1H NMR analyses.

Other examples are listed in Table 1. Several characteristic features of the reaction have been noted. (1) MABR is the reagent of choice for the present cycloaddition (entries 4, 7, 9), and use of another Lewis acid, methylaluminum bis(2,6-diphenylphenoxide) (MAPH) allowed total recovery of the starting materials (entry 5). (2) α-Monosubstituted and α,α-disubstituted aldehydes are selectively transformed to *cis*-2-oxetanones with MABR (entries 4 and 7). This selectivity is dramatically lowered by changing to a bulky α,α,α-trisubstituted aldehyde such as pivalaldehyde (entry 9 *vs.* 4). (3) This reaction is not applicable to the ketonic substrates. Attempted reaction of trimethylsilylketene (**1**) and isopropyl methyl ketone with MABR in CH_2Cl_2 resulted in the greatest recovery of the starting ketone.

Table 1. Stereoselective Cycloaddition of Trimethylsilylketene and Saturated Aldehydes [a]

entry	aldehyde	Lewis acid (equiv)	conditions (°C, h)	% yield of **3** and **4** [c] (*cis/trans* ratio) [d]
1	CH_3CH_2-CHO	$BF_3{\cdot}OEt_2$ [b]	-20, 3.5; 0, 0.5	42 (70 : 30)
2		Et_2AlCl (1)	-78, 1.5	71 (92 : 8)
3		$SnCl_4$ (1)	-78, 2	6 (92 : 8)
4		MABR (1)	-78, 2	82 (100 : 0)
5		MAPH (1)	-78, 1; -40, 1; -20, 1; 0, 2	0
6	*c*-C_6H_{11}-CHO	$BF_3{\cdot}OEt_2$ [b]	-20, 1; 0, 0.5	52 (41 : 59)
7		MABR (1)	-78, 1; -40, 1.5	88 (90 : 10)
8	$(CH_3)_3C$-CHO	$BF_3{\cdot}OEt_2$ [b]	-20, 0.5; 0, 0.5	42 (4 : 96)
9		MABR (1)	-20, 0.5; 0, 1.5	53 (21 : 79)

[a] The reaction of aldehydes with trimethylsilylketene (1.1 equiv) was carried out in CH_2Cl_2 solvent. [b] Catalytic $BF_3{\cdot}OEt_2$ was utilized. [c] Isolated yield. [d] Determined by ^1H NMR analysis.

The effect of trialkylsilyl substituents in silylketenes on the stereoselectivity of the cycloaddition was also examined. Switching the trimethylsilyl substituent in **1** to the bulkier triethylsilyl and *tert*-butyldimethylsilyl substituents[14] lowered the *cis* selectivity with MABR, but increased the *trans* selectivity with $BF_3{\cdot}OEt_2$ as shown in Table 2.

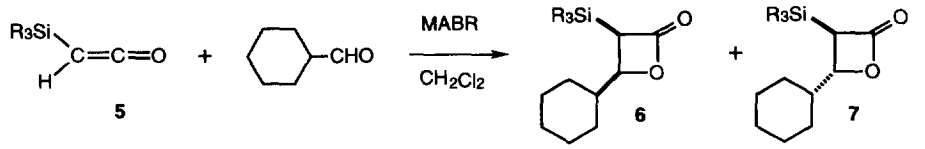


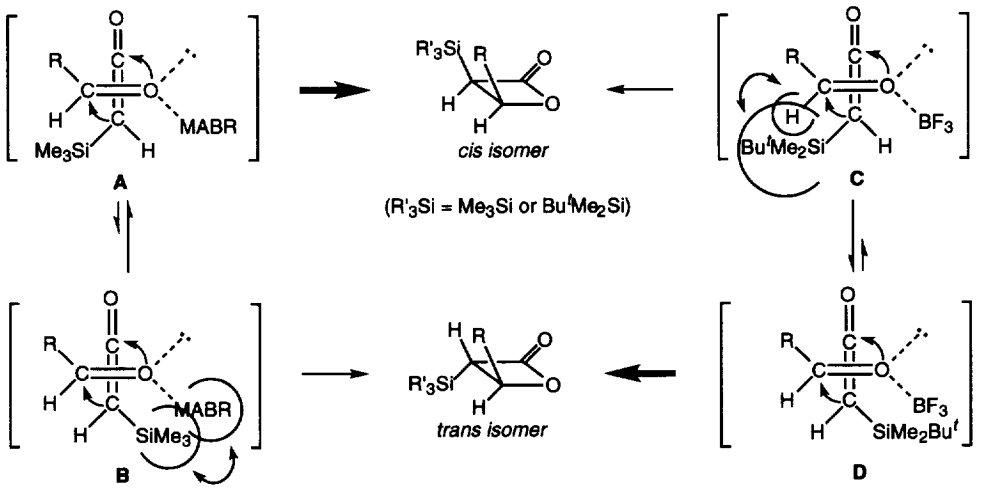
Table 2. Effect of Trialkylsilyl Substituents in Silylketene **5** [a]

entry	silylketene **5**	Lewis acid (equiv)	conditions (°C, h)	% yield of **6** and **7** [c] (*cis*/*trans* ratio) [d]
1	$Me_3SiCH{=}C{=}O$	$BF_3{\cdot}OEt_2$ [b]	-20, 1; 0, 0.5	52 (41 : 59) [e]
2		MABR (1)	-78, 1; -40, 1.5	88 (90 : 10) [e]
3	$Et_3SiCH{=}C{=}O$	$BF_3{\cdot}OEt_2$ [b]	-20, 0.5; 0, 0.5	70 (44 : 56)
4		MABR (1)	-78, 1; -40, 2	78 (79 : 21)
5	*t*-$BuMe_2SiCH{=}C{=}O$	$BF_3{\cdot}OEt_2$ [b]	-20, 1; 0, 0.5	62 (4 : 96)
6		MABR (1)	-78, 1; -40, 1; -20, 1	56 (60 : 40)

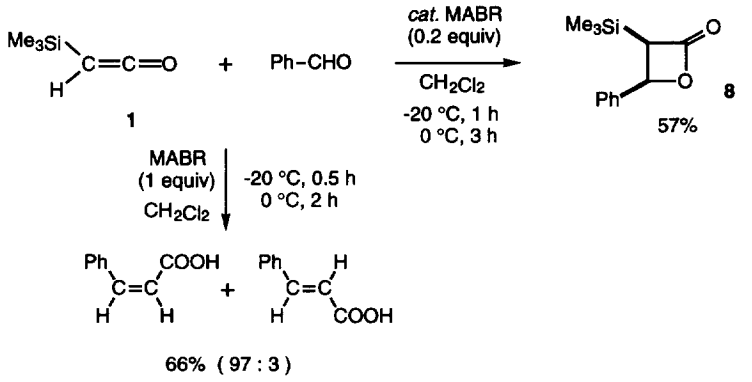
[a] The reaction of aldehydes with trialkylsilylketene (1.1 equiv) was carried out in CH_2Cl_2 solvent. [b] Catalytic $BF_3{\cdot}OEt_2$ was utilized. [c] Isolated yield. [d] Determined by ^1H NMR analysis. [e] Entries 1 and 2 are identical to entries 6 and 7, respectively, in Table I.

It has been suggested that in the [2+2] cycloaddition of ketene and aldehyde, ketene behaves as nucleophile.[15] Thus, the reaction occurs *via* the highest occupied molecular orbital (HOMO) of the ketene and the lowest unoccupied molecular orbital (LUMO) of the aldehyde. The use of a Lewis acid, upon complexation with the aldehyde, will induce a decrease in the activation energy of the reaction. Assuming, for example, that the Lewis acid coordinates to the aldehyde using the lone pair *anti* with respect to the substituent R, a large steric repulsion is produced between the Lewis acid and the trimethylsilyl group in transition state **B** as shown in Scheme 2. Hence, the equilibrium shifts from the transition state **B** to **A**, which gives a *cis* isomer preferentially. In the case of *t*-butyldimethylsilylketene, a repulsion between *t*-butyldimethylsilyl group and aldehydic hydrogen is not negligible in transition state **C**, and becomes a predominant factor with $BF_3{\cdot}OEt_2$ as a small Lewis acid, affording a *trans* isomer almost exclusively *via* a favorable transition state **D**. This is in accordance with the result of the *ab initio* calculations conducted by Cossio et al.,[16] where they reported that Lewis acid catalyzed [2+2] cycloaddition between ketenes and carbonyl compounds is a two-stage concerted process in which the catalyst is oriented *exo* with respect to the 2-oxetanone ring being formed.

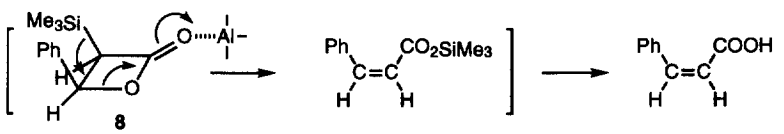
Scheme 2



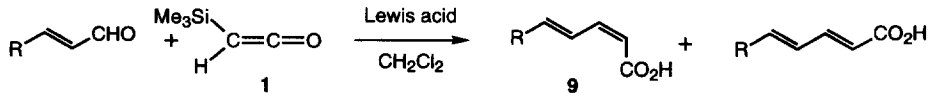
Cycloaddition of Silylketene with Aromatic and α,β-Unsaturated Aldehydes. When this cycloaddition reaction is applied to aromatic aldehydes such as benzaldehyde, we observed that the course of the cycloaddition with benzaldehyde depends strongly on the equivalency of MABR. For example, catalytic use (20 mol%) of MABR gave *cis*-2-oxetanones exclusively, while stoichiometric use resulted in further conversion to (*Z*)-cinnamic acid. In the case of aromatic aldehydes, the lactone C-O bond of the resulting cycloadduct **8** is rather weak compared to saturated aldehydes because of the adjacent phenyl group, inducing the facile ring-opening/desilylation sequences of the intermediary β-lactone **8** under the influence of MABR as illustrated in Scheme 3.



Scheme 3



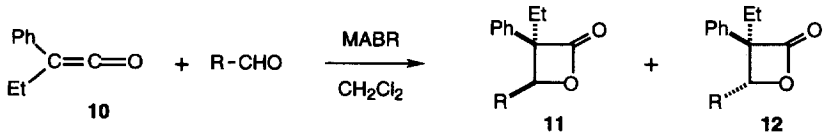
This finding led us to develop a new stereoselective route to the synthesis of 2(*Z*)-2,4-alkadienoic acids starting from α,β-unsaturated aldehydes. Here the selectivity is far superior to that with an ordinary Lewis acid, $BF_3{\cdot}OEt_2$.[7]



MABR : R = Pr, 77% (100 : 0)
R = Ph, 71% (100 : 0)

$BF_3{\cdot}OEt_2$: R = Pr, 62% (89 : 11)
R = Ph, 51% (82 : 18)

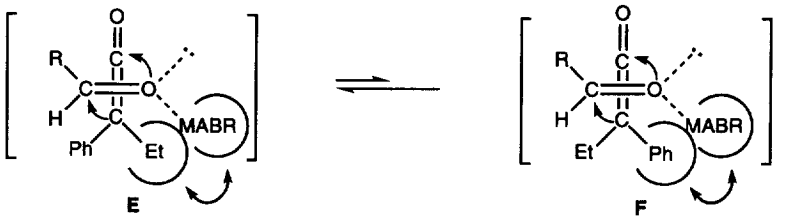
Cycloaddition of Dialkylketene with Aldehydes. Application of the present methodology to disubstituted ketene such as ethylphenylketene upon reaction with acetaldehyde and benzaldehyde in the presence of MABR resulted in the formation of trisubstituted 2-oxetanones with moderate *cis* selectivity. This result is easily predictable by considering two possible transition states, **E** and **F** , the former being more favorable due to the less steric repulsion produced between the Lewis acid and the ethyl group as shown in Scheme 4.



MABR : R = Me, 43% (89 : 11)
R = Ph, 42% (73 : 27)

$BF_3{\cdot}OEt_2$: R = Me, 42% (66 : 34)
R = Ph, 50% (50 : 50)

Scheme 4



Experimental Section

General. Infrared (IR) spectra were recorded on a SHIMADZU FTIR-8100 spectrometers. ^{1}H NMR spectra were measured on a Varian Gemini-200 or Gemini-300 spectrometer. Analytical gas-liquid phase chromatography (GLC) was performed on Shimadzu GC-8A instruments equipped with a flame ionization detector and a capillary column of PEG-HT (0.25 X 25,000 mm) using nitrogen as carrier gas. All experiments were carried out under an atmosphere of dry argon. Mass spectra were performed on Shimadzu GC-17A equipped with PARVUM QP-5000. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel E. Merck 9385. Microanalyses were accomplished at the Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University.

In experiments requiring dry solvents, ether and THF were freshly distilled from sodium metal using benzophenone ketyl as indicator or purchased from Aldrich Chem. Co. Methylene chloride was stored over 4A molecular sieves. Triethylamine was stored over KOH pellets. Trimethylaluminum was obtained from Toso-Akzo Chem. Co. Ltd., Japan. Ethyl ethynyl ether (50 wt. % solution in hexane) was purchased from Aldrich Chem. Co. Other simple chemicals were purchased and used as such.

Preparation of Ketenes. Trimethysilyketene (**1**),[8d] triethylsilylketene **5** (R = Et),[14] *tert*-butyldimethylsilylketene **5** (R_3 = *t*-$BuMe_2$),[14] and ethylphenylketene (**10**)[17] were prepared according to the known literature procedures.

Preparation of MABR and MAPH. To a solution of 4-bromo-2,6-di-*tert*-butylphenol (2 equiv) in CH_2Cl_2 was added at room temperature a 1 *M* hexane solution of Me_3Al (1 equiv). The methane gas (~2 equiv) evolved immediately. The resulting solution was stirred at room temperature for 1 h and used as a solution of MABR in CH_2Cl_2 without any purification. MAPH was prepared *in situ* from Me_3Al and 2,6-diphenylphenol in CH_2Cl_2 in a similar manner as described above.

General Method for the Organoaluminum-Promoted Cycloaddition of Trialkylsilylketene with Aldehydes. To a solution of organoaluminum reagent (0.50 mmol) in CH_2Cl_2 (5 ml) was added an aldehyde (0.50 mmol) at -78 °C. Trialkylsilylketene (0.50 mmol) was added and the resulting mixture was stirred under the condition indicated in the tables. The reaction mixture was then poured into 1 *N* HCl and extracted with CH_2Cl_2. Evaporation of the solvent and purification of the residue by column chromatography gave the 2-oxetanones or 2(*Z*)-alkenoic acids.

General Method for the Cycloaddition of Trialkylsilylketene with Aldehydes Using Other Lewis Acids. To a solution of Lewis acid (0.50 mmol or catalytic amount) and aldehyde (0.50 mmol) in CH_2Cl_2 was added trialkylsilylketene (0.50 mmol) and the resulting mixture was stirred under the condition indicated in the tables. The reaction mixture was then poured into 1 *N* HCl and extracted with CH_2Cl_2. Evaporation of the solvent and purification of the residue by column chromatography gave the 2-oxetanones or alkenoic acids.

***cis*-4-Ethyl-3-(trimethylsilyl)-2-oxetanone 3 (R = Et):**[9] ^{1}H NMR ($CDCl_3$) δ 4.51 (1H, dt, *J* = 8.1, 6.0 Hz, Et-C<u>H</u>-O), 3.33 (1H, d, *J* = 6.0 Hz, Me_3Si-C<u>H</u>-C=O), 1.82 (2H, dq, *J* = 8.1, 7.3 Hz, CH_2), 1.07 (3H, t, *J* = 7.3 Hz, CH_3), 0.22 (9H, s, $(CH_3)_3$-Si); IR (liquid film) 2971, 1802, 1254, 1121, 1069, 965, 884, 851 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2Si$: C, 55.77; H, 9.36. Found: C, 55.70; H, 9.47.

***cis*- and *trans*-4-Ethyl-3-(trimethylsilyl)-2-oxetanone 3 and 4 (R = Et):**[9] ^{1}H NMR ($CDCl_3$) [*cis* isomer] δ 4.51 (1H, dt, *J* = 8.1, 6.0 Hz, Et-C<u>H</u>-O), 3.33 (1H, d, *J* = 6.0 Hz, Me_3Si-C<u>H</u>-C=O), 1.82 (2H, dq, *J* = 8.1, 7.3 Hz, CH_2), 1.07 (3H, t, *J* = 7.3 Hz, CH_3), 0.22 (9H, s, $(CH_3)_3$-Si) and [*trans* isomer] δ

4.21 (1H, dt, *J* = 6.6, 4.1 Hz, Et-C<u>H</u>-O), 2.93 (1H, d, *J* = 4.1 Hz, Me_3Si-C<u>H</u>-C=O), 1.91 (2H, dq, *J* = 7.3, 6.6 Hz, CH_2), 0.99 (3H, t, *J* = 7.3 Hz, CH_3), 0.17 (9H, s, $(CH_3)_3$-Si).

***cis*- and *trans*-4-Cyclohexyl-3-(trimethylsilyl)-2-oxetanone 3 and 4 (R = cyclohexyl):** ^1H NMR ($CDCl_3$) [*cis* isomer] δ 4.21 (1H, dd, *J* = 5.9, 10.4 Hz, *c*-Hex-C<u>H</u>-O), 3.29 (1H, dd, *J* = 5.9, 1.1 Hz, Me_3Si-C<u>H</u>-C=O), 0.83-2.09 (11H, m, *c*-Hex), 0.25 (9H, s, $(CH_3)_3$-Si) and [*trans* isomer] δ 3.93 (1H, dd, *J* = 4.1, 8.1 Hz, *c*-Hex-C<u>H</u>-O), 2.96 (1H, dd, *J* = 4.1, 0.9 Hz, Me_3Si-C<u>H</u>-C=O), 0.80-2.09 (11H, m, *c*-Hex), 0.16 (9H, s, $(CH_3)_3$-Si); IR (liquid film) 2930, 2855, 1802, 1453, 1254, 1129, 982, 914, 891, 847, 640 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_2Si$: C, 63.67; H, 9.79. Found: C, 63.59; H, 9.95.

***cis*- and *trans*-4-*tert*-Butyl-3-(trimethylsilyl)-2-oxetanone 3 and 4 (R = *t*-Bu):** ^1H NMR ($CDCl_3$) [*cis* isomer] δ 4.38 (1H, d, *J* = 6.6 Hz, *t*-Bu-C<u>H</u>-O), 3.35 (1H, d, *J* = 6.6 Hz, Me_3Si-C<u>H</u>-C=O), 1.03 (9H, s, *t*-Bu), 0.28 (9H, s, $(CH_3)_3$-Si) and [*trans* isomer] δ 3.98 (1H, d, *J* = 4.2 Hz, *t*-Bu-C<u>H</u>-O), 2.98 (1H, d, *J* = 4.2 Hz, Me_3Si-C<u>H</u>-C=O), 1.03 (9H, s, *t*-Bu), 0.28 (9H, s, $(CH_3)_3$-Si); IR (KBr) 2963, 1792, 1482, 1364, 1289, 1252, 1152, 1123, 1102, 986, 903, 864, 847, 708 cm^{-1}; Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 60.00; H, 10.24.

***cis*- and *trans*-4-Cyclohexyl-3-(triethylsilyl)-2-oxetanone 6 and 7 (R = Et):** ^1H NMR ($CDCl_3$) [*cis* isomer] δ 4.20 (1H, ddd, *J* = 1.1, 6.0, 10.4 Hz, *c*-Hex-C<u>H</u>-O), 3.37 (1H, dd, *J* = 1.2, 6.0 Hz, Et_3Si-C<u>H</u>-C=O), 0.94-2.07 (11H, m, *c*-Hex), 1.01 (9H, t, *J* = 7.8 Hz, 3 CH_3), 0.71-0.81 (6H, m, 3 CH_2) and [*trans* isomer] δ 4.01 (1H, dd, *J* = 4.1, 7.7 Hz, *c*-Hex-C<u>H</u>-O), 3.02 (1H, dd, *J* =0.8, 4.1 Hz, Et_3Si-C<u>H</u>-C=O), 0.94-2.07 (11H, m, *c*-Hex), 1.01 (9H, t, *J* = 7.8 Hz, 3 CH_3), 0.65-0.75 (6H, m, 2 CH_2); IR (liquid film) 2932, 2878, 2855, 1809, 1451, 1271, 1115, 1078, 1070, 982, 862, 841, 822, 716 cm^{-1}; MS: [*cis*] *m/z* (%) = $[M - CO_2]^+$ 224(5), 195(71), 167(60), 139(25), 111(12), 87(44), 83(17), 59(71), 44(100) and [*trans*] *m/z* (%) = $[M - CO_2]^+$ 224(5), 195(67), 167(56), 139(22), 111(10), 87(41), 83(12), 59(67), 44(100); Anal. Calcd for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51. Found: C, 67.05; H, 10.73.

***trans*-4-Cyclohexyl-3-(*tert*-butyldimethylsilyl)-2-oxetanone 7 (R_3 = *t*-BuMe$_2$):** ^1H NMR ($CDCl_3$) δ 4.00 (1H, dd, *J* = 4.1, 7.7 Hz, *c*-Hex-C<u>H</u>-O), 3.05 (1H, d, *J* = 4.1 Hz, *t*-$BuMe_2Si$-C<u>H</u>-C=O), 1.12-2.32 (11H, m, *c*-Hex), 0.98 (9H, s, *t*-Bu), 0.16 (3H, s, CH_3), 0.09 (3H, s, CH_3); IR (liquid film) 2930, 2857, 1809, 1728, 1451, 1255, 1115, 980, 843 cm^{-1}; Anal. Calcd for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51. Found: C, 67.07; H, 10.80.

***cis*- and *trans*-4-Cyclohexyl-3-(*tert*-butyldimethylsilyl)-2-oxetanone 6 and 7 (R_3 = *t*-BuMe$_2$):** ^1H NMR ($CDCl_3$) [*cis* isomer] δ 4.24 (1H, dd, *J* = 6.0, 9.6 Hz, *c*-Hex-C<u>H</u>-O), 3.44 (1H, d, *J* = 6.0 Hz, *t*-$BuMe_2Si$-C<u>H</u>-C=O), 1.12-2.32 (11H, m, *c*-Hex), 0.99 (9H, s, *t*-Bu), 0.23 (3H, s, CH_3), 0.18 (3H, s, CH_3) and [*trans* isomer] δ 4.00 (1H, dd, *J* = 4.1, 7.7 Hz, *c*-Hex-C<u>H</u>-O), 3.05 (1H, d, *J* = 4.1 Hz, *t*-$BuMe_2Si$-C<u>H</u>-C=O), 1.12-2.32 (11H, m, *c*-Hex), 0.98 (9H, s, *t*-Bu), 0.16 (3H, s, CH_3), 0.09 (3H, s, CH_3).

***cis*-4-Phenyl-3-(trimethylsilyl)-2-oxetanone (8):** ^1H NMR ($CDCl_3$) δ 7.29-7.47 (5H, m. Ph-H), 5.71 (1H, d, *J* = 6.6 Hz, Ph-C<u>H</u>-O), 3.72 (1H, d, *J* = 6.6 Hz, Me_3Si-C<u>H</u>-C=O), -0.12 (9H, s, $(CH_3)_3$-Si); IR (KBr) 2957, 2922, 2899, 1801, 1495, 1453, 1360, 1252, 1161, 1109, 1076, 949, 846, 741, 704, 640; MS: *m/z* (%) = 220 (M^+, 25), 205(99), 161(75), 145(33), 131(100), 103(72), 75(80), 59(7), 45(48); Anal. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.32. Found: C, 65.34; H, 7.37.

***cis*- and *trans*-Cinnamic acid:** ^1H NMR ($CDCl_3$) [*cis* isomer] δ 7.54-7.68 (2H, m, Ph-H), 7.32-7.44 (3H, m, Ph-H), 7.07 (1H, d, *J* = 12.6 Hz, C<u>H</u>=CH-C=O), 5.97 (1H, d, *J* = 12.6 Hz, CH-C=O) and [*trans*

isomer] δ 7.81 (1H, d, *J* = 16.1 Hz, C<u>H</u>=CH-C=O), 7.52-7.62 (2H, m, Ph-H), 7.38-7.47 (3H, m, Ph-H), 6.47 (1H, d, *J* = 16.1 Hz, CH-C=O)

(2*Z*,4*E*)-5-Phenylpenta-2,4-dienoic acid 9 (R = Ph):[18] ^{1}H NMR ($CDCl_3$) δ 8.12 (1H, ddd, *J* = 0.9, 11.4, 15.9 Hz, C<u>H</u>-CH=CH-C=O), 7.54-7.57 (2H, m, Ph-H), 7.31-7.42 (3H, m, Ph-H), 6.89 (1H, dd, *J* = 0.9, 15.9 Hz, C<u>H</u>=CH-CH=CH-C=O), 6.88 (1H, t, *J* = 11.4 Hz, C<u>H</u>=CH-C=O), 5.78 (1H, dd, *J* = 0.9, 11.4 Hz, CH-C=O); IR (KBr) 2965, 2752, 1690, 1610, 1588, 1456, 1437, 1250, 1203, 1003, 960, 907, 756, 746, 700, 685 cm^{-1}; MS: *m/z* (%) = 174 (M^+, 15), 129(100), 115(10), 91(8), 77(16), 64(15), 51(27); Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.81; H, 5.93.

The authentic (2*E*,4*E*)-5-phenylpenta-2,4-dienoic acid[18,19] was prepared *via* two-carbon homologation of *trans*-cinnamaldehyde by $AgClO_4$-catalyzed addition of zirconocene complex, derived from hydrozirconation of ethoxyacetylene with $Cp_2Zr(H)Cl$, followed by acidic hydrolysis[20] and chlorite oxidation:[21] ^{1}H NMR ($CDCl_3$) δ 7.56 (1H, dd, *J* = 9.0, 15.3 Hz, C<u>H</u>-CH=CH-C=O), 7.49-7.52 (2H, m, Ph-H), 7.31-7.42 (3H, m, Ph-H), 6.88-6.99 (2H, m, C<u>H</u>=CH-C<u>H</u>=CH-C=O), 6.01 (1H, dd, *J* = 0.9, 11.4 Hz, CH-C=O).

(2*Z*,4*E*)-Octa-2,4-dienoic acid 9 (R = Pr): ^{1}H NMR ($CDCl_3$) δ 7.53 (1H, m, C<u>H</u>-CH=CH-C=O), 6.67 (1H, t, *J* = 11.4 Hz, C<u>H</u>=CH-C=O), 6.13 (1H, dt, *J* = 15.1, 7.1 Hz, C<u>H</u>=CH-CH=CH-C=O), 5.59 (1H, d, *J* = 11.4 Hz, CH-C=O), 2.21 (2H, q, *J* = 7.5 Hz, C<u>H</u>$_2$-CH=CH), 1.48 (2H, sextet, *J* = 7.5 Hz, CH_2), 0.94 (3H, t, *J* = 7.5 Hz, CH_3); IR (KBr) 2963, 2934, 2874, 1690, 1636, 1601, 1443, 1285, 1248, 1230, 963, 857 cm^{-1}; MS: *m/z* (%) = 140 (M^+, 30), 135(8), 97(100), 95(24), 89(22), 70(29), 55(60), 42(59); Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.52; H, 8.77.

The authentic (2*E*,4*E*)-octa-2,4-dienoic acid was prepared *via* two-carbon homologation of *trans*-2-hexenal by $AgClO_4$-catalyzed addition of zirconocene complex, derived from hydrozirconation of ethoxyacetylene with $Cp_2Zr(H)Cl$, followed by acidic hydrolysis[20] and chlorite oxidation:[21] ^{1}H NMR ($CDCl_3$) δ 7.35 (1H, m, C<u>H</u>-CH=CH-C=O), 6.20 (2H, m, , C<u>H</u>=CH-C<u>H</u>=CH-C=O), 5.79 (1H, d, *J* = 15.1 Hz, CH-C=O), 2.17 (2H, q, *J* = 7.2 Hz, C<u>H</u>$_2$-CH=CH), 1.47 (2H, sextet, *J* = 7.5 Hz, CH_2), 0.93 (3H, t, *J* = 7.5 Hz, CH_3).

***cis*- and *trans*-3-Ethyl-4-methyl-3-phenyl-2-oxetanones 11 and 12 (R = Me):** ^{1}H NMR ($CDCl_3$) [*cis* isomer] δ 7.24-745 (5H, m, Ph-H), 4.71 (1H, q, *J* = 6.3 Hz, CH), 2.18 (2H, dt, *J* = 3.6, 7.4 Hz, CH_2), 1.17 (3H, d, *J* = 6.3 Hz, CH_3), 0.99 (3H, d, *J* = 7.4 Hz, CH_3) and [*trans* isomer] δ 7.24–7.45 (5H, m, Ph-H), 4.84 (1H,q, *J* = 6.5 Hz, CH), 1.91 (2H, dq, *J* = 14.8, 7.4 Hz, CH_2),1.66 (3H, d, *J* = 6.5 Hz, CH_3) 0.85 (3H, t, *J* = 7.4 Hz, CH_3); IR (liquid film) 2977, 2932, 1813, 1497, 1451, 1383, 1277, 1148, 1120, 1024, 837, 760, 702 cm^{-1}; MS: [*cis*] *m/z* (%) = $[M - CO_2]^+$ 208(48), 198 (23), 179 (30), 146 (100), 130 (12), 115 (67), 103 (14), 91 (30), 77 (18), 44 (62) and [*trans*] *m/z* (%) = $[M - CO_2]^+$ 208(33), 198 (17), 179 (23), 146 (100), 130 (15), 115 (56), 103 (15), 91 (27), 77 (17), 44 (50); Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.72; H, 7.49.

***cis*- and *trans*-3,4-Diphenyl-3-ethyl-2-oxetanones 11 and 12 (R = Ph):** ^{1}H NMR ($CDCl_3$) [*cis* isomer] δ 6.94-7.55 (10H, m, 2Ph-H), 5.55 (1H, s, CH), 2.31 (2H, ddq, *J* = 14.8, 29.5, 7.4 Hz, CH_2), 1.06 (3H, t, *J* = 7.4 Hz, CH_3) and [*trans* isomer] δ 6.94-7.55 (10H, m, 2Ph-H), 5.71 (1H, s, CH), 1.49 and 1.75 (2H, dq, *J* = 14.8, 7.4 Hz, CH_2), 0.65 (3H, t, *J* = 7.4 Hz, CH_3); IR (liquid film) 2975, 2938, 1825, 1497, 1449, 1254, 1219, 1113, 1076, 957, 893, 762, 700, 531 cm^{-1}; MS: [*cis*] *m/z* (%) = $[M - CO_2]^+$ 208(48), 198 (23), 179 (30), 146 (100), 130 (12), 115 (67), 103 (14), 91 (30), 77 (18), 44 (62) and [*trans*] *m/z* (%) = $[M - CO_2]^+$ 208(33), 198 (17), 179 (23), 146 (100), 130 (15), 115 (56), 103 (15), 91 (27), 77 (17), 44 (50); Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.91; H, 6.55.

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(*Received in Japan* 18 *January* 1995; *accepted* 13 *February* 1995)