Clay Montmorillonite: An Efficient, Heterogeneous Catalyst for Michael Reactions of Silyl Ketene Acetals and Silyl Enol Ethers with α,β-Unsaturated Carbonyl Compounds

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The Michael addition of silyl ketene acetals to α,β-unsaturated esters (enoates) is investigated. The reaction is catalyzed by clay montmorillonite (solid acid) most effectively among various, homogeneous and heterogeneous acid promoters. The montmorillonite-catalyzed reaction has several prominent features: (1) Not only α- or β-monosubstituted acrylates but also α,β- or β,β-disubstituted acrylates are applicable. (2) The highly regioselective 1,4-addition to a polyenoate is achievable. (3) The Michael adduct can be obtained in the form of a labile silyl ketene acetal owing to a simple work-up procedure. The Michael reaction of a silyl enol ether and silyl ketene acetals with α,β-unsaturated ketones (enones) is also described.

The Michael addition of an enolate to an α,β-unsaturated carbonyl system is one of the most important reactions for carbon-carbon bond formation.[1] However, its use in organic syntheses is occasionally restricted owing to a concurrent 1,2-addition reaction and polymerization of α,β-unsaturated carbonyl compounds. A new methodology to overcome these problems has been devised by the use of lithium enolates.[2,3] Another approach is to use silyl enol ethers and silyl ketene acetals as enolates. The Michael reaction of the silyl enol ethers with α,β-unsaturated ketones (enones) is generally performed with the aid of a stoichiometric amount of Lewis acid to afford 1,5-dicarbonyl compounds.[4,5] When the reaction is conducted thermally in acetonitrile,[6] under high pressure,[7] or by the use of $(Me_2N)_3S^+Me_3SiF_2^-$ [8] or $Ph_3C^+ClO_4^-$,[9] the intermediate adducts are isolable in the form of synthetically valuable silyl enol ethers.

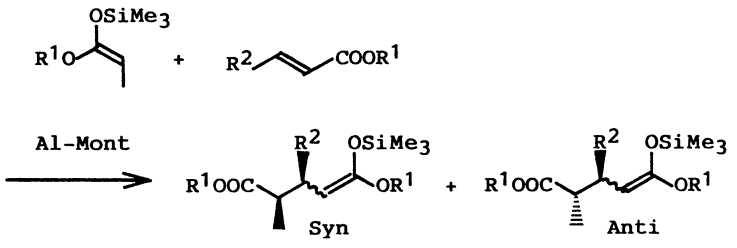
Concerning the Michael reaction of a silyl enol ether with an α,β-unsaturated ester (enoate), the reaction with acrylate was the only example with the yield being not so high.[4] The reaction of fumarate or crotonate with a cyclic silyl enol ether gave a [2+2]cycloaddition product.[10] The single example of Michael reaction of a silyl ketene acetal with an enoate was reported in the study of "Group Transfer Polymerization (GTP)" by the use of $(Me_2N)_3S^+Me_3SiF_2^-$ [11] or Lewis acids.[12] One-to-one addition of a silyl ketene acetal to an enoate has not been reported.

Recently we have shown that clay montmorillonite (sheet silicate) is an efficient, heterogeneous acid catalyst for the aldol reaction of silyl enol ethers[13] or silyl ketene acetals[14] with aldehydes or acetals. We have also demonstrated that the Michael reaction of silyl ketene acetals with enoates can be effectively accomplished by the use of clay montmorillonite.[15,16] In this paper, we provide a detailed description of the Michael reaction catalyzed by montmorillonite, and show its scope and limitations.

Results and Discussion

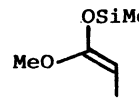
In the presence of aluminium ion-exchanged montmorillonite (Al-Mont),[17] the reactions of silyl ketene acetals derived from propionates with croton-

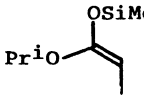
Table 1. The Al-Mont-Catalyzed Michael Reactions of Silyl Ketene Acetals Derived from Propionates with Enoates

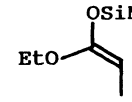


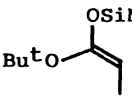
Entry	R^1	R^2	Temp/°C (Time/h)	Product	Yield/%	Syn : Anti
1	Me	Me	−78(0.5)	**23a**	84	27 : 73
2	Pr^i	Me	−60(0.5)	**24a**	90	55 : 45
3	Me	Ph	−50(0.5)	**25a**	91	61 : 39
4	Me	CH_3CH=CH	−50(0.5)	**26a**	96	39 : 61
5	Et	EtOOC	−78(0.5)	**27a**	85	42 : 58

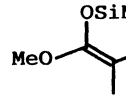
Reaction conditions: Nucleophile (1 mmol), Acceptor (1 mmol), Al-Mont (0.2 g), CH_2Cl_2 (4 ml).

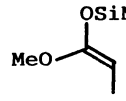
1: 

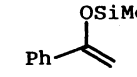
2: 

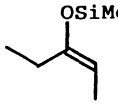
3: 

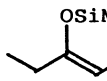
4: 

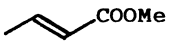
5: 

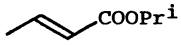
6: 

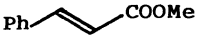
7: 

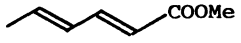
8: 

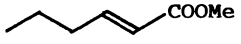
9: 

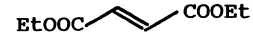
10: 

11: 

12: 

13: 

14: 

15: 

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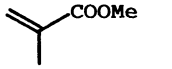
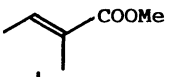
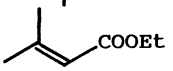
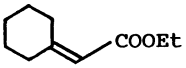
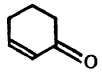
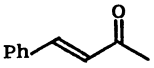
17: 

18: 

19: 

20: 

21: 

22: 

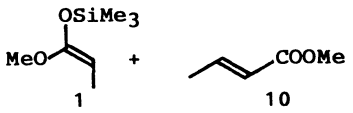
ate, cinnamate, sorbate, or fumarate were examined and the results are listed in Table 1. The reactions proceeded at low temperatures. After the reactions were complete, the solid catalyst of Al-Mont was easily removed through a Celite pad. Thereby the Michael products were isolated by simple distillation in the form of a trimethylsilyl ketene acetal. These products showed strong IR absorption around 1670 cm^{-1} ($\nu_{C=C}$), which is characteristic of the silyl ketene acetal structure.[18]

After the hydrolysis of the products with dilute HCl, the stereochemical assignment was made in comparison with authentic samples prepared via the conjugate addition of the corresponding lithium enolates.[3] Unfortunately the diastereoselectivities were low to moderate (1 : 1—3 : 1).

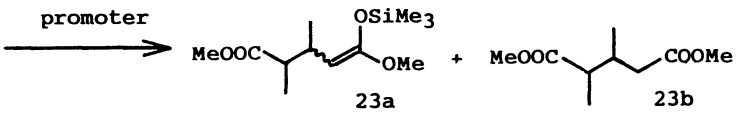
It is noteworthy that the present Michael addition to a polyenoate occurred regioselectively in the 1,4-fashion. In the case of methyl sorbate (Entry 4), the preferential 1,4-addition (98%) over 1,6-addition (2%) is notable because the addition of a lithium enolate gave a mixture (70 : 30) of 1,4- and 1,6-adducts in low yield (total yield 37%).[19]

For demonstrating the utility of the Al-Mont catalyst, representative, homogeneous acid promoters were employed for the same reaction (Table 2, Entries 2—6).[20] Compared with Al-Mont (Table 2, Entry 1), these promoters gave lower yield of the Michael product (**23a** or **23b**) due to deactivation during the reaction. For example, when Ph_3CClO_4 was added to the mixture of a silyl ketene acetal and an enoate in CH_2Cl_2, the yellow color of the trityl cation (Ph_3C^+) immediately disappeared at −78 °C, showing that Ph_3CClO_4 was destroyed.[21] In the case of CF_3SO_3H and $CF_3SO_3SiMe_3$, the Michael product was also isolated in the form of a silyl ketene acetal after the reaction mixture was

Table 2. The Michael Reaction of **1** with **10**[a]



1 10



23a 23b

Entry	Promoter (mol%)	Temp/°C (Time/h)	Product[b]	Yield/%	Syn : Anti
1	Al-Mont[c]	−78(0.5)	**23a**	84	27 : 73
2	CF_3SO_3H (5+5)[d]	−30(2)	**23a**	47	37 : 63
3	$CF_3SO_3SiMe_3$ (5+5)[d]	−30(2)	**23a**	46	39 : 61
4	Ph_3CClO_4 (5)	−50(2)	**23b**	38	35 : 65
5	$ZnBr_2$ (100)	−78(2)	**23b**	47	40 : 60
6	$BF_3 \cdot OEt_2$ (100)	−50(1)	—	0	—

a) **1** (1 mmol), **10** (1 mmol), CH_2Cl_2 (4 ml). b) Procedure for the isolation of products is described in the experimental section. c) Al-Mont (0.2 g) was used. d) The promoter was added in two portions.

quenched with organic amine (Entries 2 and 3).

In order to investigate the scope and limitations of the montmorillonite-catalyzed Michael reactions, we employed variously substituted silyl ketene acetals and enoates (Table 3). Concerning enoates, α- or β-monosubstituted and α,β- or β,β-disubstituted acrylates are applicable. Acrylate is the only case giving a Michael adduct in low yield and polymeric by-products (Entry 1). It should be noted that α,β- and β,β-disubstituted acrylates are reactive by the present method (Entries 3—5), while a lithium enolate of an ester is reported to have no reactivity to these disubstituted acrylates.[3a] In contrast to a silyl ketene acetal, a silyl enol ether is not reactive to enoates in the presence of Al-Mont (Entry 8).

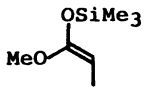
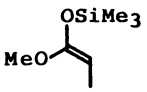
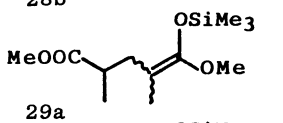
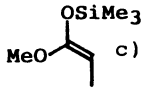
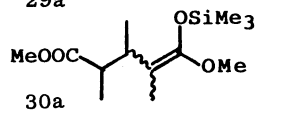
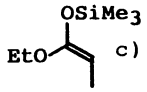
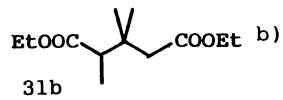
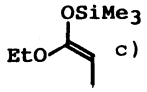
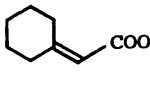
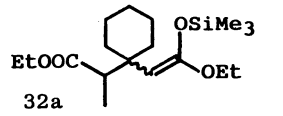
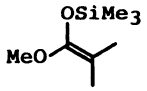
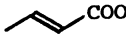
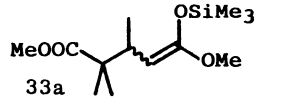
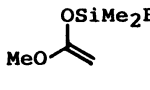
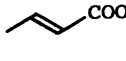
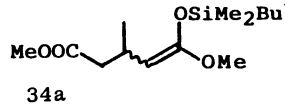
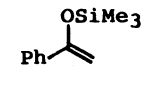
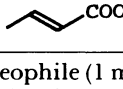
Even though the Al-Mont catalyst was dried at 120 °C/0.5 Torr (1 Torr=133.322 Pa) prior to use,[22] a small amount of water remained in the interlayer of the catalyst. When the Michael reaction was carried out at low temperature, the product could be obtained in the form of a labile silyl ketene acetal without being hydrolyzed. However, in some cases of a sterically hindered substrate a higher reaction temperature was required, and the product was partly hydrolyzed with the water in Al-Mont (Table 3, Entries 4 and 6).

The tandem reaction[23] of the Michael addition of a silyl ketene acetal to an enoate followed by the aldol reaction with an aldehyde was also successful to give a corresponding product in good yield without isolation of an intermediate, the silyl ketene acetal (Scheme 1).

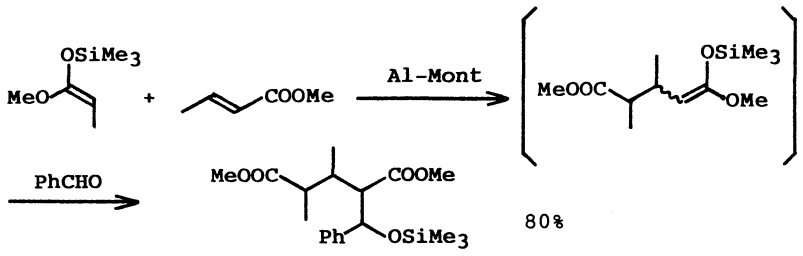
The Michael addition to enones was also achieved by the use of Al-Mont (Table 4). It is well-known that enones are more reactive than enoates in the 1,4-addition of alkylcopper reagents.[24] A similar trend was observed in the present Al-Mont-catalyzed reaction since enones reacted not only with silyl ketene acetals but also with a silyl enol ether in the 1,4-fashion.[25] The products were obtained in the form of a silyl enol ether. The behavior of diastereoselection of the reaction was similar to that of the reactions promoted by $TiCl_4$[5] and Ph_3CClO_4.[9b]

In conclusion, in spite of under heterogeneous con-

Table 3. The Michael Reactions of Enol Silanes with Enoates Catalyzed by Al-Mont[a]

Entry	Nucleophile	Acceptor	Temp/°C (Time/h)	Product	Yield/%
1			−78(0.5)	 28b	31
2			−50(1)	 29a	79
3			−30(1)	 30a	56
4			25(2)	 31b	71
5			15(9)	 32a	87
6			−10(1)	 33a	52[d,e]
7			−50(1)	 34a	86
8			0(1)	——	0

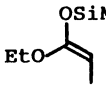
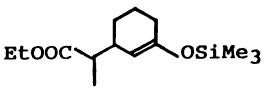
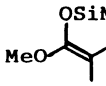
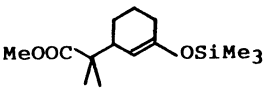
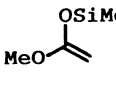
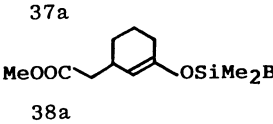
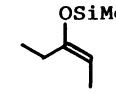
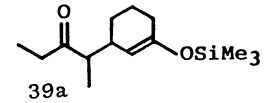
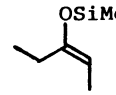
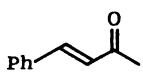
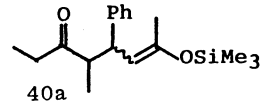
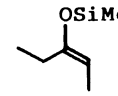
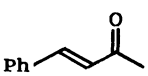
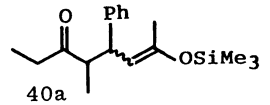
a) Reaction conditions: Nucleophile (1 mmol), Acceptor (1 mmol), Al-Mont (0.2 g), CH_2Cl_2 (4 ml). b) The product was isolated after the hydrolysis treatment. c) Silyl ketene acetal (1.5 mmol) was used. d) Al-Mont (0.5 g) was used. e) A hydrolyzed product (dimethyl 2,2,3-trimethylglutarate) was also obtained in 18% yield.



35a

Scheme 1.

Table 4. The Michael Reactions of Enol Silanes with Enones Catalyzed by Al-Mont[a)]

Entry	Nucleophile	Acceptor	Temp/°C (Time/h)	Product	Yield/%	Syn : Anti
1			−78(0.5)	 36a	87	57 : 43
2			−20(1)	 37a	86	—
3			−78(0.5)	 38a	95	—
4			−78(1)	 39a	83	38 : 62
5			−78(1)	 40a	98	29 : 71
6			−30(1)	 40a	81	21 : 79[b)]

a) Reaction conditions: Nucleophile (1 mmol), Acceptor (1 mmol), Al-Mont (0.2 g), CH_2Cl_2 (4 ml). b) 1,2-Dimethoxyethane was used as a solvent.

ditions, solid montmorillonite can facilitate the Michael additions of silyl ketene acetals and silyl enol ethers to enoates and enones. The montmorillonite proved to be an alternative to conventional, moisture-sensitive homogeneous acids which are frequently troublesome in manipulation and work-up.

Experimental

Measurement. ^1H NMR spectra were recorded in $CDCl_3$ with a Hitachi R-600 (60 MHz) spectrometer. ^{13}C NMR spectra were recorded in C_6D_6 with a JEOL JNM GX-500 (125 MHz) spectrometer. Infrared spectra were recorded in CCl_4 on a JASCO IRA-2 spectrometer. Analytical gas-liquid chromatography (GC) was done with a Shimadzu GC-8A instrument with a flame ionization detector and nitrogen carrier gas. The following capillary columns were used for analysis: OV-1 Bonded, 25 m×0.25 mm; PEG-HT Bonded, 25 m×0.25 mm. The flow rate of carrier gas was 2 ml min^{-1} (1.0 kg cm^{-2}). The following packed column was also used for monitoring the reaction: Silicone SE-30 on Uniport B, 1 m×3 mm.

Solvents and Reagents. Preparation of Aluminium ion-exchanged montmorillonite (Al-Mont) was previously described.[13)] Dichloromethane was distilled from P_2O_5 and stored over Molecular Sieves 3A. 1,2-Dimethoxyethane (DME) and diethyl ether were distilled from $LiAlH_4$ prior to use. $CF_3SO_3SiMe_3$ was distilled from CaH_2. $ZnBr_2$ was dried over flames at ca. 350 °C/0.5 Torr for 10 min. α,β-Unsaturated carbonyl compounds **10**,**13**,**15**—**18**,**21**, benzaldehyde, and CF_3SO_3H were purified by distillation. $BF_3 \cdot OEt_2$, **12**, and **22** were used without purification. Silyl enol ethers **7**,[26a)] **8** ($E:Z$=83 : 17)[26b)] and **9**[27)] were prepared according to the literatures. Enoates **11**[28a)] and **14**,**19**,**20**[28b)] were prepared by means of the known methods.

Silyl Ketene Acetals. These compounds should be free from amine for the present Michael reaction. They were prepared according to a minor modification of the standard procedure reported earlier.[18a,27)] The preparation of **3** is illustrative. To a stirred solution of 50 ml of hexane and 27

ml (0.19 mol) of diisopropylamine at 0 °C was added 100 ml (0.16 mol) of a 15% solution of butyllithium in hexane under nitrogen atmosphere. Hexane and excess amine were removed under reduced pressure at 0 °C. The flask was refilled with N_2 and residual white solids were redissolved in 50 ml of THF at 0 °C. The solution was cooled to −78 °C and a solution of 18 ml (0.16 mol) of ethyl propionate in 20 ml of THF was added over 10 min. After the mixture was stirred for 10 min, a solution of 20 ml (0.16 mol) of chlorotrimethylsilane in 20 ml of THF was added over 10 min. The reaction mixture was warmed to 0 °C over 1 h, diluted with 300 ml of cold pentane. The mixture was washed 15 times with 300 ml of ice-cold water and then with a 1 M (1 M=1 mol dm^{-3}) $Cu(OAc)_2$ solution until the aqueous layer became neutral. The organic layer was then washed with saturated brine and dried over Na_2SO_4. The solvent was removed with a rotary evaporator and the resulting crude product was purified by distillation to give 14 g (0.08 mol) of **3** (50%): bp 76—78 °C/55 Torr; *E*:*Z*=80:20 (isomeric ratio was determined by GC). **1** (*E*:*Z*=60:40) and **2** (*E*:*Z*=89:11) were similarly prepared. **4** (*E*:*Z*=32:68),[27] **5**,[18a] and **6**,[27] were prepared according to the known methods.

General Procedure for Al-Mont-Catalyzed Michael Additions of Silyl Ketene Acetals and Silyl Enol Ethers to α,β-Unsaturated Carbonyl Compounds. Al-Mont (0.2 g) in a 20 ml round-bottomed flask was dried at 120 °C and 0.5 Torr for 3 h in an oil bath, and cooled to −78 °C under nitrogen. A solution of an α,β-unsaturated carbonyl compound (1 mmol) in CH_2Cl_2 (4 ml) was added. After the mixture being stirred for 1 min, a solution of a silyl ketene acetal or a silyl enol ether (1 mmol) in CH_2Cl_2 (1 ml) was added at −78 °C. Then the mixture was stirred under the conditions listed in tables. The reaction was monitored by GC (SE-30, 1 m). As work-up, cold ether (−50 °C, 5 ml) was added, the montmorillonite was filtered off through a Celite pad and washed with ether. The organic layer was evaporated and distilled on a Kugelrohr apparatus to yield the Michael product.

If necessary, the Michael products in the form of silyl ketene acetals or silyl enol ethers were hydrolyzed as follows. One drop of 1 M HCl was added to a solution of the Michael product in methanol, ethanol, or THF at room temperature. The mixture was stirred for 0.5 h and quenched with aqueous $NaHCO_3$. Organic product was extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and the product was isolated by distillation in quantitative yield.

General Procedure for Homogeneous Acid Promoter-Mediated Reactions (Table 2, Entries 2—6). To a stirred solution of **1** (1 mmol) and **10** (1 mmol) in CH_2Cl_2 (4 ml) was added an appropriate amount of an acid promoter in CH_2Cl_2 (1 ml) under a nitrogen atmosphere at −78 °C. When the reaction was slow, the temperature was raised and/or the acid promoter was supplemented. The mixture was quenched with a few drops of triethylamine, diluted with ether, and poured into an aqueous $NaHCO_3$ solution. Organic products were extracted with ether. The extract was washed with water and with brine, and dried over Na_2SO_4. The products were purified by distillation.

Stereochemistry of Products. In comparison with the authentic samples (**23b**,[3b] **25b**,[3b] **26c**,[3b] **27b**,[3b] **36b**,[5] and **40b**,[9b]) prepared according to the known procedures, the relative configuration (syn or anti)[29] of the Michael products in the hydrolyzed form (1,5-dicarbonyl compounds) was assigned. Diastereomer ratios were determined by GC. The geometrical isomers (*E* or *Z*) of the Michael products in the form of a silyl ketene acetal or a silyl enol ether were not assigned.

Methyl 5-Methoxy-2,3-dimethyl-5-trimethylsiloxy-4-pentenoate (23a). Bp 110 °C (bath temp)/0.5 Torr; ^{1}H NMR ($CDCl_3$) δ=0.19 and 0.24 (two s, 3:7 ratio, 9H, CH_3Si), 0.96 (d, *J*=6.4 Hz, 3H, $C\underline{H}_3CHCH{=}C$), 1.10 (d, *J*=6.4 Hz, 3H, $C\underline{H}_3CHC{=}O$), 2.1—3.0 (m, 2H, $C\underline{H}C\underline{H}C{=}O$), 3.3—3.6 (m, 1H, CH=C), 3.51 (s, 3H, $CH_3OC{=}C$), and 3.68 (s, 3H, $CH_3OC{=}O$); IR (CCl_4) 1670 (C=C) and 1732 (C=O) cm^{-1}.

Dimethyl 2,3-Dimethylglutarate (23b). Obtained from **23a** by hydrolysis. A mixture of diastereomers (syn:anti=27:73): ^{1}H NMR ($CDCl_3$) δ=0.9—1.0 (m, 3H, $C\underline{H}_3CHCH_2$), 1.15 (d, *J*=6.4 Hz, 3H, $C\underline{H}_3CHC{=}O$), 2.2—2.6 (m, 4H, $CH_2C\underline{H}C\underline{H}$), and 3.70 (s, 6H, CH_3O); IR (CCl_4) 1735 (C=O) cm^{-1}; GC (PEG-HT, 100 °C) t_R 10.8 min (anti), 11.3 min (syn).

Isopropyl 5-Isopropoxy-2,3-dimethyl-5-trimethylsiloxy-4-pentenoate (24a). Bp 130 °C (bath temp)/0.3 Torr; ^{1}H NMR ($CDCl_3$) δ=0.20 and 0.22 (two s, 9H, CH_3Si), 0.95 (d, *J*=6.4 Hz, 3H, $C\underline{H}_3CHCH{=}C$), 1.19 (d, *J*=6.0 Hz, 3H, $C\underline{H}_3CH{=}O$), 1.22 (d, *J*=6.0 Hz, 12H, $(C\underline{H}_3)_2CH$), 2.0—2.9 (m, 2H, $C\underline{H}C\underline{H}C{=}O$), 3.31, 3.44, 3.55, and 3.71 (four d, *J*=9.2, 9.3, 9.4, and 9.3 Hz, 1H, CH=C), 4.0—4.5 (m, 1H, $(CH_3)_2C\underline{H}OC{=}C$), and 4.98 (septet, *J*=6.0 Hz, 6H, $(CH_3)_2C\underline{H}OC{=}O$); IR ($CCl_4$) 1672 (C=C) and 1732 (C=O) cm^{-1}.

Diisopropyl 2,3-Dimethylglutarate (24b). Obtained from **24a** by hydrolysis. A mixture of diastereomers (syn:anti=55:45). ^{1}H NMR ($CDCl_3$) δ=0.9—1.1 (m, 6H, $C\underline{H}_3CH$), 1.23 (d, *J*=6.0 Hz, 12H, $(C\underline{H}_3)_2CH$), 2.1—2.6 (m, 4H, $CH_2C\underline{H}C\underline{H}$), and 5.01 (septet, *J*=6.0 Hz, 2H, $(CH_3)_2C\underline{H}$); IR (CCl_4) 1732 (C=O) cm^{-1}. Diastereomer ratio was determined in the form of **23b** after transesterification.

Methyl 5-Methoxy-2-methyl-3-phenyl-5-trimethylsiloxy-4-pentenoate (25a). Bp 150 °C (bath temp)/0.5 Torr; ^{1}H NMR ($CDCl_3$) δ=0.10, 0.13, 0.20, and 0.22 (four s, 9H, CH_3Si), 0.98, 1.00, 1.17, and 1.19 (four d, *J*=7.0, 7.0, 7.0, and 7.0 Hz, 3H, $C\underline{H}_3CH$), 2.4—3.1 (m, 1H, $CH_3C\underline{H}$), 3.4—4.1 (m, 8H, $C\underline{H}C{=}C$, $PhC\underline{H}$, and $C\underline{H}_3O$), and 7.24 (s, 5H, C_6H_5); IR (CCl_4) 1670 (C=C) and 1732 (C=O) cm^{-1}.

Dimethyl 2-Methyl-3-phenylglutarate (25b). Obtained from **25a** by hydrolysis. A mixture of diastereomers (syn:anti=61:39). ^{1}H NMR ($CDCl_3$) δ=0.96 and 1.18 (two d, 3:2 ratio, *J*=6.4, 7.0 Hz, 3H, $C\underline{H}_3CH$), 2.6—3.1 (m, 3H, $CH_2CHPhC\underline{H}$), 3.2—3.6 (m, 1H, $PhC\underline{H}$), 3.51, 3.56, and 3.72 (three s, 6H, CH_3O), and 7.26 (s, 5H, C_6H_5); IR (CCl_4) 1735 (C=O) cm^{-1}; GC (PEG-HT, 150 °C) t_R 24.0 min (syn), 24.5 min (anti).

Methyl 5-Methoxy-2-methyl-3-(1-propenyl)-5-trimethylsiloxy-4-pentenoate (26a). Bp 135 °C (bath temp)/0.8 Torr; ^{1}H NMR ($CDCl_3$) δ=0.19 (s, 9H, CH_3Si), 1.10 (d, *J*=6.6 Hz, 3H, $C\underline{H}_3CHC{=}O$), 1.66 (d, *J*=4.2 Hz, 3H, $C\underline{H}_3CH{=}CH$), 2.2—2.7 (m, 1H, $CHC{=}O$), 2.9—3.2 (m, 1H, $C\underline{H}CHC{=}O$), 3.2—3.7 (m, $CH{=}COSi$), 3.51 and 3.53 (two s, 3H, $CH_3OC{=}C$), 3.66 and 3.68 (two s, 3H, $CH_3OC{=}O$), and 5.3—5.5 (m, 2H, $C\underline{H}{=}C\underline{H}$); IR ($CCl_4$) 1670 (C=C) and 1730 (C=O) cm^{-1}.

Dimethyl 2-Methyl-3-(1-propenyl)glutarate (26b). Obtained from **26a** by hydrolysis. A mixture of diastereomers (syn:anti=39:61): ^{1}H NMR ($CDCl_3$) δ=1.11 and 1.13 (two d, *J*=6.6 and 6.6 Hz, 3H, $C\underline{H}_3CHC{=}O$), 1.66 (d, *J*=5.0 Hz, 3H, $C\underline{H}_3CH{=}CH$), 2.3—2.8 (m, 4H, $CH_2C\underline{H}C\underline{H}C{=}O$), 3.68 and 3.70 (two s, 6H, CH_3O), and 5.3—5.7 (m, $C\underline{H}{=}C\underline{H}$, 2H); IR

(CCl_4) 1730 (C=O) cm^{-1}; GC (PEG HT, 120 °C) t_R 10.6 min (anti), 10.9 min (syn).

Dimethyl 2-Methyl-3-propylglutarate (26c). Obtained from **26** by hydrogenation on Pd/C in methanol. A mixture of diastereomers: ^1H NMR ($CDCl_3$) δ=0.90 (t, J=6.0 Hz, 3H, CH_3CH_2), 1.10 and 1.13 (two d, 3:2 ratio, J=7.0 and 7.0 Hz, 3H, CH_3CH), 1.3 (br, 4H, CH_2CH_2), 2.2—2.9 (br, 4H, $CH_3CHCHCH_2C$=O), and 3.69 (s, 6H, CH_3O); IR (CCl_4) 1735 (C=O) cm^{-1}.

The Michael Addition of Lithium Enolate of Methyl Propionate to 13.[3b] A solution of methyl propionate (2 mmol) in THF (5 ml) was added to a stirred solution of lithium diisopropylamide (2 mmol) in THF-HMPA (2 and 1 ml, respectively) at −78 °C. Then a solution of **13** (1.5 mmol) in THF (1.5 ml) was added and the mixture was stirred for 1 h at −78 °C. The reaction was quenched by adding saturated aqueous ammonium chloride. The organic layer was extracted with ether, washed with water and with brine, and dried over Na_2SO_4. The solvent was evaporated and the resulting crude product was distilled on a Kugelrohr apparatus to yield a mixture of 1,4-product **26b** (syn:anti=5:95) and 1,6-product **26d** in 37% yield (total yield). The ratio of **26b** to **26d** was 70:30 determined by GC. **26b** and **26d** were separated by column chromathography on silica gel using hexane-ether (4:1) as eluent.

Dimethyl 5,6-Dimethyl-3-heptenedioate (26d; 1,6-adduct). ^1H NMR ($CDCl_3$) δ=1.01 (d, J=7.0 Hz, 3H, CH_3CHCH=C), 1.11 (d, J=7.0 Hz, 3H, CH_3CHC=O), 2.2—2.6 (m, 2H, $CH_3CHCHCH_3$), 3.05 (d, J=5.6 Hz, 2H, CH_2C=O), 3.67 and 3.69 (two s, 6H, CH_3O), and 5.4—5.7 (m, 2H, CH=CH); IR (CCl_4) 1738 (C=O) cm^{-1}; GC (PEG-HT, 120 °C) t_R 16.5 and 17.1 min.

Diethyl 2-[2-Ethoxy-2-(trimethylsiloxy)ethenyl]-3-methylsuccinate (27a). Bp 145 °C (bath temp)/0.5 Torr; ^1H NMR ($CDCl_3$) δ=0.22 (s, 9H, CH_3Si), 1.17 (d, J=7.0 Hz, 3H, CH_3CH), 1.23 (t, J=7.0 Hz, 9H, CH_3CH_2O), 2.5—3.1 (m, 1H, CH_3CH), 3.5—3.8 (m, 2H, CHCH=C), and 3.8—4.3 (m, 6H, CH_3CH_2O); IR (CCl_4) 1668 (C=C) and 1725 (C=O) cm^{-1}.

Diethyl 3-Ethoxycarbonyl-2-methylglutarate (27b). Obtained from **27a** by hydrolysis. A mixture of diastereomers (syn:anti=42:58): ^1H NMR ($CDCl_3$) δ=1.19 (d, J=7.0 Hz, 3H, CH_3CH), 1.27 (t, J=7.0 Hz, 9H, CH_3CH_2O), 2.5—3.5 (m, 4H, $CHCHCH_2$), and 4.18 (q, J=7.0 Hz, 6H, CH_3CH_2O); IR (CCl_4) 1730 (C=O) cm^{-1}; GC (PEG-HT, 120 °C) t_R 14.2 min (syn), 14.9 min (anti).

Dimethyl 2-Methylglutarate (28b). Bp 105 °C (bath temp)/0.5 torr; ^1H NMR ($CDCl_3$) δ=1.17 (d, J=7.0 Hz, 3H, CH_3CH), 1.8—2.1 (m, 2H, CH_2CHCH_3), 2.3—2.7 (m, 3H, $CH_3CHCH_2CH_2$), and 3.67 (s, 6H, CH_3O); IR (CCl_4) 1742 (C=O) cm^{-1}.

Methyl 5-Methoxy-2,4-dimethyl-5-trimethylsiloxy-4-pentenoate (29a). Bp 115 °C (bath temp)/0.6 Torr; ^1H NMR ($CDCl_3$) δ=0.19 (s, 9H, CH_3Si), 1.10 (d, J=6.8 Hz, 3H, CH_3CH), 1.49 and 1.53 (two s, 1:2 ratio, 3H, CH_3C=C), 2.1—2.7 (m, 3H, CH_2CH), 3.48 and 3.52 (two s, 1:2 ratio, 3H, CH_3OC=C), and 3.67 (s, 3H, CH_3OC=O); IR (CCl_4) 1690 (C=C) and 1732 (C=O) cm^{-1}; ^{13}C NMR (C_6D_6) δ=0.0, 0.1, 14.2, 15.0, 16.7, 35.4, 35.7, 38.4, 38.6, 51.0, 56.1, 56.8, 92.0, 92.3, 151.6, 152.3, and 176.5; GC (OV-1, 150 °C) t_R 4.0 and 4.6 min (67:33).

Dimethyl 2,4-Dimethylglutarate (29b). Obtained from **29a** by hydrolysis. ^1H NMR ($CDCl_3$) δ=1.15 and 1.17 (two d, J=6.7 and 6.7 Hz, 6H, CH_3CH), 1.5—2.2 (m, 2H, CH_2), 2.2—2.8 (m, 2H, CH_3CH), and 3.67 (s, 6H, CH_3O); IR (CCl_4) 1741 (C=O) cm^{-1}; GC (OV-1, 120 °C) t_R 3.8 and 4.2 min (42:58). Found: C, 57.18; H, 8.72%. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.56%.

Methyl 5-Methoxy-2,3,4-trimethyl-5-trimethylsiloxy-4-pentenoate (30a). Bp 120 °C (bath temp)/0.4 Torr; ^1H NMR ($CDCl_3$) δ=0.19 and 0.21 (two s, 9H, CH_3Si), 0.9—1.2 (m, 6H, CH_3CH), 1.38 and 1.43 (two s, 2:1 ratio, 3H, CH_3C=C), 2.3—2.9 (m, 2H, CH), 3.47, 3.49 and 3.61 (three s, 3H, CH_3OC=C), and 3.67 (s, 3H, CH_3OC=O); IR (CCl_4) 1682 (C=C) and 1732 (C=O) cm^{-1}.

Dimethyl 2,3,4-Trimethylglutarate (30b). Obtained from **31a** by hydrolysis. ^1H NMR ($CDCl_3$) δ=0.8—1.0 (m, 3H, CH_3CHCHC=O), 1.18 (d, J=7.0 Hz, 6H, CH_3CHC=O), 1.7—2.0 (m, 1H, CHCHC=O), 2.2—2.9 (m, 2H, CHC=O), and 3.67 (s, 6H, CH_3O); IR (CCl_4) 1732 (C=O) cm^{-1}.

Diethyl 2,3,3-Trimethylglutarate (31b). Bp 115 °C (bath temp)/0.5 Torr; ^1H NMR ($CDCl_3$) δ=1.07 (s, 6H, $(CH_3)_2C$), 1.12 (d, J=7.0 Hz, 3H, CH_3CH), 1.25 (t, J=7.0 Hz, 6H, CH_3CH_2), 2.32 (s, 2H, CH_2C=O), 2.55 (q, J=7.0 Hz, 1H, CH_3CH), and 4.12 (q, J=7.0 Hz, 4H, CH_3CH_2O); IR (CCl_4) 1725 (C=O) cm^{-1}. Found: C, 62.29; H, 9.69%. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63%.

1-(1-Ethoxycarbonylethyl)-1-[2-ethoxy-2-(trimethylsiloxy)-ethenyl]cyclohexane (32a). Bp 150 °C (bath temp)/0.4 Torr; ^1H NMR ($CDCl_3$) δ=0.20 and 0.25 (two s, 5:1 ratio, 9H, CH_3Si), 1.07 (d, J=7.0 Hz, 3H, CH_3CH), 1.25 (t, J=7.0 Hz, 3H, CH_3CH_2OC=O), 1.28 (t, J=7.0 Hz, 3H, CH_3CH_2OC=C), 1.2—1.8 (br, 10H, $(CH_2)_5$), 2.58 (q, J=7.0 Hz, 1H, CH_3CH), 3.07 (s, 1H, CH=C), 3.74 (q, J=7.0 Hz, 2H, CH_3CH_2OC=C), and 4.08 (q, J=7.0 Hz, 2H, CH_3CH_2OC=O); IR (CCl_4) 1670 (C=C) and 1722 (C=O) cm^{-1}.

1-(1-Ethoxycarbonylethyl)-1-(ethoxycarbonylmethyl)cyclohexane (32b). Obtained from **32a** by hydrolysis. ^1H NMR ($CDCl_3$) δ=1.10 (d, J=7.0 Hz, 3H, CH_3CH), 1.25 (t, J=7.0 Hz, 6H, CH_3CH_2O), 1.5 (br, 10H, $(CH_2)_5$), 2.44 and 2.48 (two s, 2H, CH_2C=O), 2.85 (q, J=7.0 Hz, 1H, CH_3CH), and 4.12 (q, J=7.0 Hz, 4H, CH_3CH_2O); IR (CCl_4) 1735 (C=O) cm^{-1}. Found: C, 66.71; H, 9.77%. Calcd for $C_{15}H_{26}O_4$: C, 66.64; H, 9.77%.

Methyl 5-Methoxy-2,2,3-trimethyl-5-trimethylsiloxy-4-pentenoate (33a). Bp 120 °C (bath temp)/0.5 Torr; ^1H NMR ($CDCl_3$) δ=0.21 and 0.26 (two s, 5:1 ratio, 9H, CH_3Si), 0.89 (d, J=6.8 Hz, 3H, CH_3CH), 1.09 and 1.14 (two s, 6H, $(CH_3)_2C$), 2.5—2.9 (m, 1H, $CHCH_3$), 3.34 and 3.57 (two d, 5:1 ratio, J=10.0 and 10.0 Hz, CH=C), 3.51 (s, 3H, CH_3OC=C), and 3.67 (s, 3H, CH_3OC=O); IR (CCl_4) 1668 (C=C) and 1725 (C=O) cm^{-1}.

Dimethyl 2,2,3-Trimethylglutarate (33b). Obtained from **33a** by hydrolysis. ^1H NMR ($CDCl_3$) δ=0.91 (d, J=6.7 Hz, 3H, CH_3CH), 1.13 (s, 6H, $(CH_3)_2C$), 1.7—2.1 (m, 1H, CH), 2.2—2.6 (m, 2H, CH_2), and 3.67 (s, 3H, CH_3O); IR (CCl_4) 1740 (C=O) cm^{-1}. Found: C, 57.18; H, 8.72%. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.56%.

Methyl 5-(*t*-Butyldimethylsiloxy)-5-methoxy-3-methyl-4-pentenoate (34a). Bp 135 °C (bath temp)/0.8 Torr; ^1H NMR ($CDCl_3$) δ=0.16 (s, 6H, CH_3Si), 0.96 (s, 9H, $(CH_3)_3CSi$), 1.01 (d, J=6.0 Hz, 3H, CH_3CH), 2.27 and 2.30 (two d, J=7.8 and 5.8 Hz, 2H, $CHCH_2CO$), 2.7—3.2 (m, 1H, $CHCH_3$), 3.38 and 3.63 (two d, J=8.6 and 8.6 Hz, CH=C), 3.48 (s, 3H, CH_3C=C), and 3.67 (s, 3H, CH_3C=O); ^{13}C NMR (C_6D_6) δ=−4.1, 22.0, 22.1, 25.1, 27.9, 42.8, 43.1, 50.7, 54.2, 54.6, 80.9, 86.9, 154.1, 156.9, and 172.4; IR (CCl_4) 1668 (C=C) and 1735 (C=O) cm^{-1}.

Found: C, 58.07; H, 9.94%. Calcd for $C_{14}H_{28}O_4Si$: C, 58.29; H, 9.78%.

Dimethyl 3-Methylglutarate (34b). Obtained from **34a** by hydrolysis. ^{1}H NMR ($CDCl_3$) δ=1.03 (d, J=6.0 Hz, 3H, $C\underline{H}_3CH$), 2.37 (br, 5H, $C\underline{H}_2C\underline{H}C\underline{H}_2$), and 3.70 (s, 6H, CH_3O); IR (CCl_4) 1732 (C=O) cm^{-1}. Found: C, 54.88; H, 8.25%. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10%.

The Tandem Michael-Aldol Reaction of 1, 10, and Benzaldehyde. Al-Mont (0.2 g) in a 20 ml round-bottomed flask was dried at 120 °C and 0.5 Torr for 3 h in an oil bath, and cooled to −78 °C under nitrogen. A solution of **10** (1 mmol) in CH_2Cl_2 (4 ml) was added. After the mixture being stirred for 1 min, a solution of **1** (1 mmol) in CH_2Cl_2 (1 ml) was added at −78 °C. After stirring for 30 min, a solution of benzaldehyde (1 mmol) in CH_2Cl_2 (1 ml) was added at −78 °C. The temperature was raised to 0 °C, and the mixture was stirred for 1 h. After the addition of cold ether (−50 °C, 5 ml), the montmorillonite was filtered off through a Celite pad and washed with ether. The organic layer was evaporated and distilled on a Kugelrohr apparatus to yield the product of **35a** in 80% yield.

Dimethyl 2,3-Dimethyl-4-[α-(trimethylsiloxy)benzyl]-glutarate (35a). Bp 170 °C (bath temp)/0.5 Torr; ^{1}H NMR ($CDCl_3$) δ=−0.08 and −0.05 (two s, 9H, CH_3Si), 0.7—1.3 (m, 6H, $C\underline{H}_3CH$), 1.8—3.1 (m, 3H, $CH_3C\underline{H}C\underline{H}(CH_3)C\underline{H}C$=O), 3.3—3.8 (m, 6H, CH_3O), 4.8—5.1 (m, 1H, PhCH), and 7.30 and 7.33 (two s, 5H, C_6H_5); IR (CCl_4) 1732 (C=O) cm^{-1}.

Dimethyl 2,3-Dimethyl-4-(α-hydroxybenzyl)glutarate (35b). Obtained from **35a** by hydrolysis. ^{1}H NMR ($CDCl_3$) δ=0.8—1.5 (m, 6H, $C\underline{H}_3CH$), 1.8—3.2 (m, 4H, $CH_3C\underline{H}C\underline{H}$-$(CH_3)C\underline{H}C$=O and OH), 3.45 and 3.68 (br s, 6H, CH_3O), 4.80—5.25 (m, 1H, PhC$\underline{H}$), and 7.35 (br s, 5H, C_6H_5); IR (CCl_4) 1740 (C=O) and 3520 (OH) cm^{-1}.

Ethyl 2-(3-Trimethylsiloxy-2-cyclohexenyl)propanoate (36a). Bp 135 °C (bath temp)/0.4 Torr; ^{1}H NMR ($CDCl_3$) δ=0.17 (s, 9H, CH_3Si), 1.09 (d, J=6.4 Hz, 3H, $C\underline{H}_3CH$), 1.24 (t, J=7.0 Hz, 3H, $C\underline{H}_3CH_2$), 1.5—2.6 (m, 8H, aliphatic CH), 4.15 (q, J=7.0 Hz, 2H, $CH_3C\underline{H}_2O$), and 4.71 and 4.85 (two br, 1 : 1 ratio, 1H, CH=C); IR (CCl_4) 1660 (C=C) and 1725 (C=O) cm^{-1}.

Ethyl 2-(3-Oxocyclohexyl)propanoate (36b). Obtained from **36a** by hydrolysis. A mixture of diastereomers (syn : anti=57 : 43): ^{1}H NMR ($CDCl_3$) δ=1.15 and 1.18 (two d, J=6.4 Hz and 6.4 Hz, 3H, $C\underline{H}_3CH$), 1.28 (t, J=7.0 Hz, 3H, $C\underline{H}_3CH_2$), 1.6—2.6 (m, 10H, aliphatic CH), and 4.16 (q, J=7.0 Hz, 3H, $CH_3C\underline{H}_2O$); IR (CCl_4) 1710 (C=O) and 1730 (C=O) cm^{-1}; GC (PEG-HT, 120 °C) t_R 14.2 min (syn), 14.9 min (anti). The authentic sample of **36b** was prepared by means of $TiCl_4$-mediated reaction[5] of **4** with **21** followed by transesterification.

Methyl 2-Methyl-2-(3-trimethylsiloxy-2-cyclohexenyl)propanoate (37a). Bp 130 °C (bath temp)/0.2 Torr; ^{1}H NMR ($CDCl_3$) δ=0.18 (s, 9H, CH_3Si), 1.11 (s, 6H, CH_3C), 1.4—2.8 (m, 7H, aliphatic CH), 3.68 (s, 3H, CH_3O), and 4.71 (br, 1H, CH=C); IR (CCl_4) 1658 (C=C) and 1725 (C=O) cm^{-1}.

Methyl 2-[3-(*t*-Butyldimethylsiloxy)-2-cyclohexenyl)acetate (38a). Bp 140°C (bath temp)/0.5 Torr); ^{1}H NMR ($CDCl_3$) δ=0.11 (s, 6H, CH_3Si), 0.91 (s, 9H, $(CH_3)_3CSi$), 1.5—2.1 (m, 6H, $C\underline{H}_2C\underline{H}_2C\underline{H}_2$); 2.27 and 2.29 (two d, J=7.8 and 6.2 Hz, 2H, CH_2C=O), 2.4—2.8 (m, 1H, C$\underline{H}$CH=C), 3.69 (s, 3H, CH_3O), and 4.80 (br, 1H, CH=C); IR (CCl_4) 1662 (C=C) and 1735 (C=O) cm^{-1}.

2-(3-Trimethylsiloxy-2-cyclohexenyl)-3-pentanone (39a). Bp 130 °C (bath temp)/0.2 Torr; ^{1}H NMR ($CDCl_3$) δ=0.16 and 0.18 (s, 9H, CH_3Si), 1.01 (d, J=6.3 Hz, 3H, $C\underline{H}_3CH$), 1.04 (t, J=7.0 Hz, 3H, $C\underline{H}_3CH_2$), 1.4—2.6 (m, 6H, aliphatic CH), 2.44 (q, J=7.0 Hz, 2H, $C\underline{H}_2CH_3$), 2.5 (m, 2H, C$\underline{H}$C$\underline{H}$CO), and 4.60 and 4.79 (two br, 62 : 38 ratio, 1H, C=CH); IR (CCl_4) 1657 (C=C) and 1706 (C=O) cm^{-1}.

4-Methyl-5-phenyl-7-trimethylsiloxy-6-octen-3-one (40a) (Table 4, Entry 5). Bp 155 °C (bath temp)/0.6 Torr; ^{1}H NMR ($CDCl_3$) δ=0.11 and 0.13 (two s, 1 : 2 ratio, 9H, CH_3Si), 0.78 (t, J=7.3 Hz, 3H, $C\underline{H}_3CH_2$), 0.88 and 1.08 (two d, 1 : 2 ratio, J=6.7 and 6.7 Hz, 3H, $C\underline{H}_3CH$), 1.73 and 1.79 (two s, 1 : 2 ratio, 3H, $C\underline{H}_3C$=CH), 2.0—2.5 (m, 2H, $CH_3C\underline{H}_2$), 2.7—3.1 (m, 1H, $CH_3C\underline{H}$), 3.92 (t, J=9.3 Hz, 1H, PhCH), 4.55—4.80 (m ,1H, CH=C), and 7.17 (s, 5H, C_6H_5); IR (CCl_4) 1665 (C=C) and 1708 (C=O) cm^{-1}.

5-Methyl-4-phenyl-2,6-octanedione (40b). Obtained from **40a** by hydrolysis. A mixture of diastereomers (syn : anti=31 : 69). ^{1}H NMR ($CDCl_3$) δ=0.82 (t, J=7.0 Hz, 3H, $C\underline{H}_3CH_2$), 1.09 (d, J=7.0 Hz, 3H, $C\underline{H}_3CH$), 1.97 and 2.00 (two s, 1 : 2.2 ratio, 3H, CH_3CO), 2.1—2.4 (m, 2H, $CH_3C\underline{H}_2$), 2.4—3.1 (m, 3H, $C\underline{H}_2CHC\underline{H}CH_3$), 3.3—3.8 (m, 1H, PhC$\underline{H}$), and 7.20 (s, 5H, C_6H_5); IR (CCl_4) 1710 (C=O) cm^{-1}; GC (OV-1, 160 °C) t_R 9.1 min (syn), 9.6 min (anti). The authentic sample of **39b** was prepared by means of the $Ph_3C^+ClO_4^-$-mediated reaction of **9** with **22**.[9b]

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