Two-Carbon Homologation of Aldehydes via Silyl Ketene Acetals: A New Stereoselective Approach to (*E*)-Alkenoic Acids

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Aldehydes are converted into (*E*)-α,*β*-unsaturated carboxylic acids using *C*,*O*,*O*-tris(trimethylsilyl)-ketene acetal **1**. This organosilicon reagent is easily generated from trimethylsilyl acetate, LDA, and chlorotrimethylsilane. The effectiveness of the reaction has been explored for a large variety of aldehydes with Lewis acids and fluorides as catalysts.

Introduction

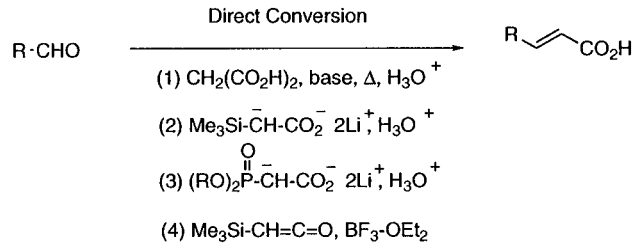
Direct conversion of aldehydes into their (*E*)-α,*β*-ethylenic carboxylic acids is an interesting and very useful reaction in organic synthesis. Beside the fact that alkenoic acids are versatile synthons which allow numerous transformations, this functionality is also widely present in natural products such as the queen substance of the honeybee[1] and caffeic acid.[2] Recently, products bearing this functionality have been tested as new enzymic browning inhibitors in replacement of sulfites.[3] Alkenoic acids have also found many applications in the total synthesis of biologically important subtances as, for example, tetrahydromyricoidine.[4]

To our knowledge, four general methods are available for the direct conversion of an aldehyde into an α,*β*-ethylenic carboxylic acid (Scheme 1): (1) the Knoevenagel reaction with malonic acid,[5] (2) the Peterson olefination with (trimethylsilyl)acetic acid dianion,[6] (3) the Wittig−Horner type reactions,[7] and lately (4) the cycloaddition of (trimethylsilyl)ketene.[8]

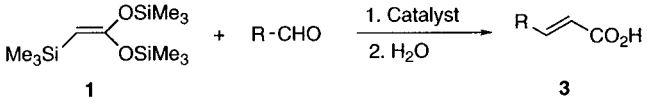
Nevertheless, these techniques are more or less effective. The Knoevenagel reaction (1) gives low yields with enolizable aldehydes,[9] the Peterson olefination (2) and the use of (trimethylsilyl)ketene (4) suffered from a lack of stereoselectivity and the Wittig−Horner type reactions (3) required fairly stringent conditions to isolate the α,*β*-unsaturated acids.[7b]

In a previous communication,[10] we have reported that *C*,*O*,*O*-tris(trimethylsilyl)ketene acetal **1** reacted with

Scheme 1



Scheme 2



1 **3**

aldehydes in the presence of a catalyst to give the corresponding (*E*)-α,*β*-ethylenic acids (Scheme 2). In this paper, we describe in detail our study on the preparation and the condensation reactions of the *C*,*O*,*O*-tris(trimethylsilyl)ketene acetal **1** with a large panel of aldehydes. Furthermore, our recent work,[11] concerning the use of the couple "CsF, DMSO" in the synthesis of polyenals by homologation of aldehydes and its efficacy, prompted us to investigate deeply our preliminary work.

Results and Discussion

Preparation of *C*,*O*,*O*-Tris(trimethylsilyl)ketene Acetal 1. To our knowledge, the preparation of trisilylated reagent **1** was described for the first time by Emde[12] starting from (trimethylsilyl)acetic ester and trimethylsilyl triflate. However, a mixture of three silylated products was obtained from which compound **1** had to be separated. We have now found that *C*,*O*,*O*-tris-(trimethylsilyl)ketene acetal **1** can be easily obtained in excellent yield from trimethylsilyl acetate (Scheme 3): deprotonation of the latter by 1 equiv of LDA at −70 °C overnight followed by trimethlysilyl chloride trapping affords the α-silylated (trimethylsilyl)acetic ester[13] **4** which is then subjected to a similar treatment to give the desired trisilylated reagent **1** in a 74% overall yield.

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(1) Callow, R. K.; Johnston, N. C. *Bee World* **1960**, *41*, 152.
(2) Cho, H.; Ueda, M.; Tamaoka, M.; Hamaguchi, M.; Aisaka, K.; Kiso, Y.; Inoue, T.; Ogino, R.; Tatsuoka, T.; Ishihara, T.; Noguchi, T.; Morita, I.; Murota, S. *J. Med. Chem.* **1991**, *34*, 1503.
(3) Walker, J. R. L.; Ferrar, P. H. *Chem. Ind.* **1995**, 836.
(4) Song, J.; Hesse, M. *Tetrahedron* **1993**, *49*, 6797.
(5) Jones, G. *Org. React.* **1967**, *15*, 204.
(6) Grieco, P. A.; Wang, C.-L. J.; Burke, S. D. *J. Chem. Soc., Chem. Commun.* **1975**, 537.
(7) (a) Koppel, G. A.; Kinnick, M. D. *Tetrahedron Lett.* **1974**, 711. (b) Coutrot, P.; Snoussi, M.; Savignac, P. *Synthesis* **1978**, 133. (c) Lombardo, L.; Taylor, R. J. K. *Synthesis* **1978**, 131.
(8) (a) Concepcion, A. B.; Maruoka, K.; Yamamoto, H. *Tetrahedron* **1995**, *51*, 4011. (b) Black, T. H.; Zhang, Y.; Huang, J.; Smith, D. C.; Yates, B. E. *Synth. Commun.* **1995**, *25*, 15.
(9) House, H. O. *Modern Synthetic Reactions*; W. A. Benjamin: Menlo Park, CA, 1972; p 649.
(10) Bellassoued, M.; Gaudemar, M. *Tetrahedron Lett.* **1988**, *29*, 4551.
(11) Bellassoued, M.; Salemkour, M. *Tetrahedron* **1996**, *52*, 4607.
(12) Emde, H.; Domsch, D.; Feger, H.; Frick, U.; Götz, A.; Hergott, H. H.; Hofmann, K.; Kober, W.; Krägeloh, K.; Oesterle, T.; Steppan, W.; West, W.; Simchen, G. *Synthesis* **1982**, 1.
(13) Bellassoued, M.; Gaudemar, M. *Tetrahedron Lett.* **1990**, *31*, 209.

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Scheme 3

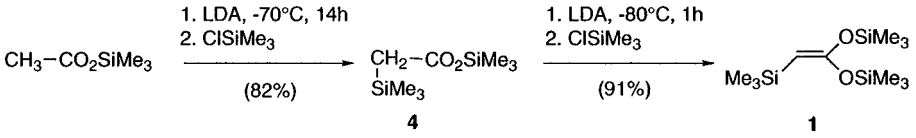
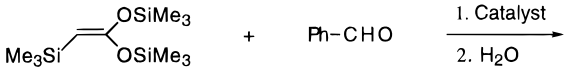


Table 1. Reaction of *C,O,O*-Tris(trimethylsilyl)ketene Acetal 1 with Benzaldehyde in the Presence of Various Catalysts[a]



1

2a **3a**

entry	cat. (10%)	solvent	temp (°C)	time (h)	yield (%) **2a**[b]	yield (%) **3a**[b,c]
1	$ZnBr_2$	THF	rt	24	0	95
2	$ZnBr_2$	THF	rt	3	0	85
3	$ZnBr_2$	toluene	rt	0.2	88	8
4	$ZnBr_2$	toluene	110	1	52	48
5	HgI_2	toluene	rt	1	96	0
6	HgI_2	toluene	50	1	59	47
7	HgI_2	toluene	50	2	0	100
8	$TiCl_4$	CH_2Cl_2	−70	1	100	0
9	$FeCl_3$	toluene	rt	0.5	65	35
10	$FeCl_3$	THF	rt	24	65	31
11	$MgBr_2$	toluene	110	2	0	20
12	$MgBr_2$	THF	80	24	0	0
13	CsF	CH_2Cl_2	rt	24	0	0
14	CsF	THF	rt	0.5	20	80
15	CsF	THF	rt	0.5	0	96
16	NaF	CH_2Cl_2	rt	24	0	0
17	NaF	THF	rt	24	0	0
18	NaF	DMSO	rt	1	6	94
19	NaF	DMF	rt	1	18	82
20	LiF	DMSO	rt	16	32	68
21	KF	DMSO	rt	1	7	93
22	TBAF	THF	rt	1.45	13	86
23	TBAF	THF	rt	1	10	90

[a] All reactions were conducted on a 1.7 mmol scale following the typical procedure described in the Experimental Section. [b] Estimated by ^1H NMR on the crude reaction mixture with respect to nonreacted aldehyde (molar percentage). [c] The cinnamic acid was fully characterized by spectrum comparison with authentic commercial sample.

Reaction with Benzaldehyde. Our goal was to study the condensation of *C,O,O*-tris(trimethylsilyl)-ketene acetal **1** with a large panel of aromatic, vinylic, and aliphatic aldehydes. To obtain the best yield and a total *E* stereoselectivity, a methodological study has been carried out. The choice of the catalyst and the solvent are important in stereochemical outcomes and yields. Thus, we first examined the reaction of **1** with benzaldehyde to determine the best reaction conditions for this Peterson-type reaction.

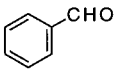
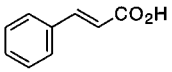
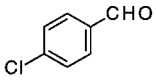
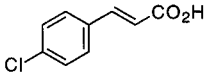
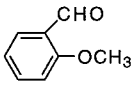
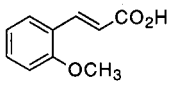
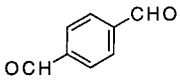
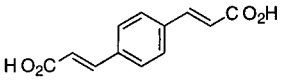
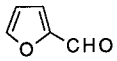
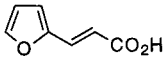
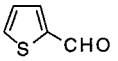
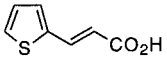
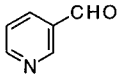
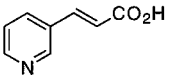
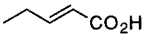
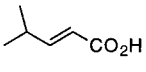
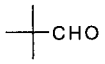
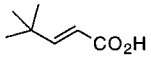
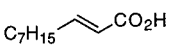
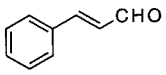
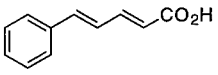
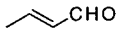
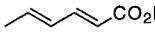
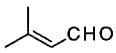
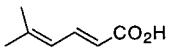
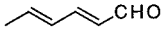
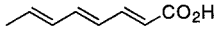
Lewis Acid Catalyst. As shown in Table 1, several Lewis acids were investigated in different solvents. First (entry 1), benzaldehyde was treated with **1** in the presence of a catalytic amount of zinc bromide in THF at room temperature for 24 h. The reaction proceeded to afford only the corresponding alkene **3a** in almost quantitative yield. The intermediate **2a** seems to eliminate hexamethyldisiloxane more easily in THF (entry 2) than in toluene (entry 4). However, this elimination could be suppressed completely using mercuric iodide (entry 5) or titanium tetrachloride (entry 8). One particular aspect of the reaction carried out with HgI_2 in toluene is the influence of the temperature on the nature of the adduct obtained (entries 5−7). Indeed, at room temperature for 1 h, siloxy acid **2a**, the single reaction product, was easily isolated. At higher temperature (50 °C), a gradual conversion of **2a** to the alkene **3a** was observed and found to be complete after 2 h. Ferric chloride seemed to be a good catalyst for this reaction but gave unfortunately a mixture of the two products **2a** and **3a** (entries 9, 10). Surprisingly, when $MgBr_2$ was used to carry out the condensation, a loss of chemical reactivity was observed with recovery of the starting benzaldehyde (entries 11, 12). On the basis of these results, $ZnBr_2$ and HgI_2 were found to be mild Lewis acid catalysts for the reaction of **1** with benzaldehyde.

Fluoride Ion Catalyst. Recently, our group at Paris VI has shown that a CsF−DMSO combination was very efficient for the conversion of aldehydes into (2*E*,4*E*) dienals using γ-trimethylsilyl crotonaldimine.[11] We have now found that fluoride ion was also efficient as catalyst for the reaction of **1** with benzaldehyde. Some of the results are reported in Table 1. Several sources of fluoride ion have been tested since a variety of alkali metal fluorides is commercially available. The correct choice of the solvent is very important because of the variable solubility shown by these ionic fluorides, and one must find which particular fluoride−solvent combination is the best for our condensation−olefination reaction. It is obvious from the results obtained in Table 1, that, as expected, the nature of the solvent is important. The reaction works faster and gives better yields when not only polar but also dissociating solvents are used with basic metal salts. Dichloromethane, which is a polar solvent (E_T (30) = 41.1)[14] but with a low dielectric constant (ϵ = 8.9) is totally ineffective (entries 13, 16). Tetrahydrofuran, which is also a polar, coordinating, but not really a dissociating, solvent (E_T (30) = 37.4, ϵ = 7.6), is more effective, but the overall result depends also on the nature of the catalyst (entries 14, 17, 22). These results prompted us to postulate that a dissociating solvent is essential for this reaction. Indeed, attempts at using dimethylformamide and dimethyl sulfoxide which are polar, dissociating, and coordinating solvents (E_T (30) = 43.8, ϵ = 37; E_T (30) = 45.0, ϵ = 47, respectively) were fruitful (entries 15, 18, 19, 20, 21, 23). From the reported examples of alkali metal fluoride-promoted reactions of **1** with benzaldehyde, CsF and NaF can be considered as the most active catalysts, the latter being, however, less hygroscopic and appreciably less expensive.

Stereoselective Synthesis of (*E*)-Alkenoic Acids. To determine the scope and limitations of this new method, the reaction has been performed on a variety of structurally different aldehydes. The alkenoic acids obtained are listed in Table 2. As can be seen from the

(14) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 98.

Table 2. Synthesis of Alkenoic Acids 3 Using Reagent 1

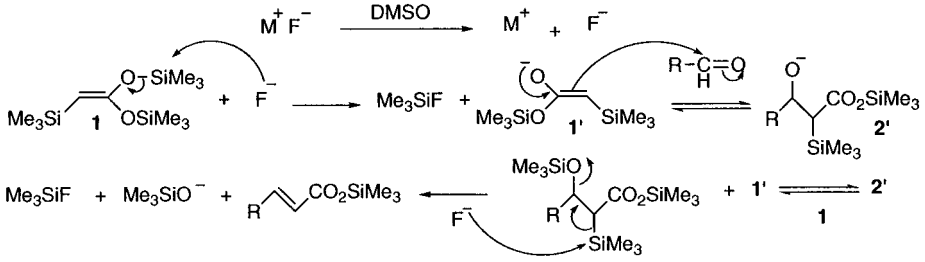
Entry	Starting Aldehydes	Catalyst	Solvent	Time (h)	Unsaturated Acids 3[a]	Yields[b] (%)	ref.
a		CsF	DMF	0.5		96	7a
b		NaF	DMF	5.5		73	16
c		NaF	DMSO	2.5		60	17
d		NaF	DMF	2		68	18
e		NaF	DMSO	1		77	19
f		$ZnBr_2$	THF	32		81	20
g		NaF	DMF	2		50	16b 21
h		CsF	DMSO	1.3		73	22
i		CsF	DMSO	1.5		84	23
j		CsF	DMSO	0.5		82	24
k	C_7H_{15}-CHO	CsF	DMSO	3		80	4
l		CsF	DMSO	3		90	25
m		$ZnBr_2$	THF	3		85	26
n		CsF	DMSO	1		90	27
o		$ZnBr_2$	THF	2.5		95	28

[a] The *E* stereoselectivity of each compound is confirmed by the ^1H NMR spectrum of the crude product.
[b] Isolated yield.

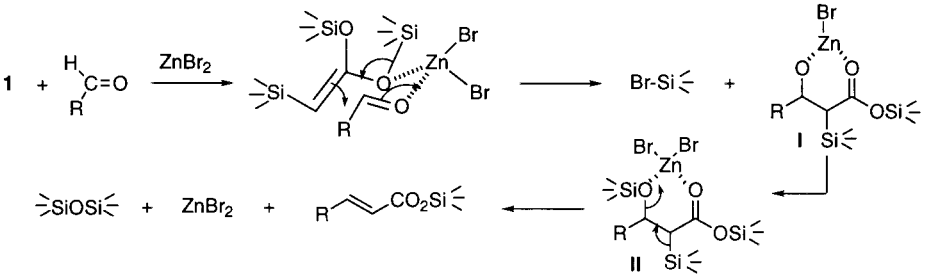
data, the reaction was exceptionally effective for a large class of aldehydes. Nonenolizable aromatic aldehydes with electroattracting or electrodonor groups were tested and gave the corresponding α,β-ethylenic carboxylic acids in good yield and with a total *E* stereoselectivity (entries a−d). Heteroaromatic aldehydes were also tested and gave the desired products (entries e−g). With saturated aldehydes, the reaction was also very efficient (entries h−k). This methodology was thus successfully applied to the synthesis of (*E*)-2-decenoic acid (entry k), an intermediate in the total synthesis of tetrahydromyricoidine.[4] The reaction has also been performed on a number of α,β-ethylenic aldehydes (entries l−o). Conjugated alkenoic acids, resulting from 1,2 addition were exclusively formed in high yields and with a total *E* stereoselectivity.

Reaction Mechanism. A tentative reaction mechanism with fluoride ion is shown in Scheme 4. It is very reasonable to assume that the reaction is initiated by fluoride ion to generate the enolate **1′** which then reacts with the aldehyde to give the alkoxide **2′**. The reaction of the latter with **1** affords the corresponding β-siloxy ester and the enolate **1′** generated in the reaction media. Further elimination of (trimethylsilyl)alkoxide gives the corresponding alkene. Alternatively, the reaction could also be catalyzed by the in situ formed (trimethylsilyl)-alkoxide. In fact, when this reaction was tested using potassium *tert*-butoxide as catalyst, the cinnamoester was

Scheme 4



Scheme 5



obtained with almost quantitative yield. This result clearly supports the postulated mechanism.

The mechanism by which Lewis acids catalyze this reaction is not very clear at present, but we presume that the mechanism is formally analogous to the Lewis acid-catalyzed addition of silyl enol ethers to carbonyl compounds. Indeed, the reaction may proceed via the prior complexation of the C=O with the Lewis acid ($ZnBr_2$ in Scheme 5). Subsequent reaction of **1** with the aldehyde according to the well-established Zimmerman−Traxler chairlike transition-state model affords the corresponding silyl zinc chelate **I**. Further Peterson-type elimination of **II** gives the unsaturated trimethylsilyl ester with regeneration of the catalyst.

Concerning the stereoselectivity of the reaction, in all cases only *E* isomers of **3** are formed. This result is very likely due to a thermodynamical control of the reaction. However, a mixture of the diastereoisomers **2** is formed. The study of the correlation between the elimination mechanism and the product's stereochemistry is under investigation.

Conclusion

In conclusion and from the results reported here, it is clear that this new method is a straightforward process for direct homologation of aldehydes into α,*β*-ethylenic carboxylic acids. *C,O,O*-Tris(trimethylsilyl)ketene acetal **1** reacts with aldehydes in the presence of a catalytic amount of catalyst at room temperature to give the desired α,*β*-ethylenic carboxylic acids with a good yield and a total *E* stereoselectivity. The mildness of the reaction conditions (room temperature), the good yields of the products obtained, and the simple workup procedure show the usefulness of the trisilylated reagent **1**.

Experimental Section

General. All experiments are carried out under a nitrogen atmosphere. Unless otherwise noted, starting materials are obtained from commercial suppliers and are used without further purification. Tetrahydrofuran and diethyl ether are distilled over sodium and benzophenone prior to use. Trimethylchlorosilane is distilled over magnesium. Diisopropylamine is distilled from CaH_2 and stored over molecular sieves. LDA is prepared in situ according to the method of Gaudemar.[15]

Chemical shifts are given in ppm (*J* in MHz) relative to tetramethylsilane. Flash column chromatography is done on Merck grade 60 silica gel (230−400 mesh) with a mixture of cyclohexane/ethyl acetate as eluent.

Preparation of Trimethylsilyl α-Trimethylsilylated Acetate (4). LDA is prepared as described in reference[15] from phenanthrene (2.3 g, 12.5 mmol), diisopropylamine (10.6 g, 110 mmol), and hammered lithium (0.7 g, 100 mmol) in ether (20 mL)−THF (20 mL). To this solution, trimethylsilyl acetate (10.56 g, 80 mmol) in 10 mL of THF is added at −70 °C over 30 min, and the solution is stirred at the same temperature overnight. Chlorotrimethylsilane (13 mL, 100 mmol) is added over 5 min at −70 °C, and the reaction mixture is then allowed to reach room temperature. The precipitate is filtered off on Celite, the solvent evaporated, and the product distilled in vacuo; bp: 61 °C (10 mmHg); yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9 H, $Si(CH_3)_3$), 0.26 (s, 9 H, $OSi(CH_3)_3$), 1.89

(15) Gaudemar-Bardone, F.; Gaudemar, M. *Synthesis* **1979**, 463.
(16) (a) Balakrishnan, P.; Baumstark A. L.; Boykin, D. W. *Org. Magn. Reson.* **1984**, *22*, 753. (b) Jovanovic, B.; Misic-Vukovic, M.; Drmanic, S.; Csanadi, J. *Heterocycles* **1994**, *37*, 1495.
(17) (a) Royer, R.; Bodo, B.; Demerseman, P.; Clavel, J.-M. *Bull. Soc. Chim. Fr.* **1971**, 2929. (b) Copinga, S.; Tepper, P. G.; Grol, C. J.; Horn, A. S.; Dubocovich, M. L. *J. Med. Chem.* **1993**, *36*, 2891.
(18) Koepp, E.; Vögtle, F. *Synthesis* **1987**, 177.
(19) Mori, A.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3037.
(20) (a) Taniguchi, Y.; Katô, H. *Chem. Pharm. Bull.* **1973**, *21*, 2070. (b) Freeman, F.; Chang, L. Y.; Kappos, J. C.; Sumarta, L. *J. Org. Chem.* **1987**, *52*, 1460.
(21) Wenkert, E.; Halls, T. D. J.; Kunesch, G.; Orito, K.; Stephens, R. L.; Temple, W. A.; Yadav, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 5370.
(22) Mori, K.; Brevet, J.-L. *Synthesis* **1991**, 1125.
(23) (a) Royer, J.; Beugelmans-Verrier, M. *Tetrahedron* **1979**, *35*, 2369. (b) Pirrung, M. C.; Han, H.; Ludwig, R. T. *J. Org. Chem.* **1994**, *59*, 2430.
(24) (a) Beckwith, A. L. J.; Cross, R. T.; Gream, G. E. *Aust. J. Chem.* **1974**, *27*, 1693. (b) Freeman, F.; Kappos, J. C. *J. Org. Chem.* **1986**, *51*, 1654.
(25) Saljoughian, M.; Williams, P. G. *J. Org. Chem.* **1987**, *52*, 3481.
(26) (a) Ressler, C.; Goodman, F. J.; Tsutsui, R.; Tsutsumi, M. *J. Org. Chem.* **1979**, *44*, 2027. (b) Crombie, L.; Crombie, W. M. L. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1267.
(27) (a) Murali, D.; Rao, G. S. K. *Synthesis* **1987**, 254. (b) Veith, M.; Lorenz, M.; Boland, W.; Simon, H.; Dettner, K. *Tetrahedron* **1994**, *50*, 6859. (c) Abarbri, M.; Parrain, J.-L.; Cintrat, J.-C.; Duchêne, A. *Synthesis* **1996**, 82.
(28) Kamal, A.; Haider, Y.; Akhtar, R.; Qureshi, A. A. *Pak. J. Sci. Ind. Res.* **1971**, *14*, 63.

(s, 2 H, CH_2); MS: $M^{\bullet+}$ = 204. Anal. Calcd for $C_8H_{20}O_2Si_2$: C, 47.00; H, 9.86. Found: C, 47.02; H, 9.81.

Preparation of *C,O,O*-Tris(trimethylsilyl)ketene Acetal (1). To a cooled (−80 °C) solution of LDA prepared as above is added a solution of trimethylsilyl α-trimethylsilylated acetate **4** (14.28 g, 70 mmol) in THF (10 mL) during 30 min. The resulting mixture is stirred at the same temperature for 1 h and then quenched with chlorotrimethylsilane (13 mL, 100 mmol) at −80 °C. After being stirred at the same temperature for 30 min, the solution is gradually warmed to room temperature and filtered through a pad of Celite. The solvent is removed under reduced pressure and the residue distilled; bp: 86 °C (10 mmHg); yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 0.17 (s, 9 H, $OSi(CH_3)_3$), 0.23 (s, 9 H, $OSi(CH_3)_3$), 2.95 (s, 1 H, CH═); MS: $M^{\bullet+}$ = 276. Anal. Calcd for $C_{11}H_{28}O_2Si_3$: C, 47.76; H, 10.20. Found: C, 47.70; H, 10.15.

Preparation of 3-Hydroxy-3-phenyl-2-(trimethylsilyoxy)propionic Acid (2a). Procedure A. To a cooled (−70 °C) dichloromethane (10 mL) solution of benzaldehyde (0.40 g, 1.7 mmol) is added via syringe $TiCl_4$ (10%). Reagent **1** (0.55 g, 2 mmol) in dichloromethane (3 mL) is added dropwise and the resulting mixture stirred at −70 °C for 1 h. After quenching with H_2O (20 mL) at the same temperature, the solution is raised to room temperature. The aqueous layer is extracted with ether (3 × 20 mL), and the combined organic phases are dried over $MgSO_4$. The solvent is evaporated in vacuo. Purification by recrystallization in pentane gives pure product **2a** (yield: 95%).

Procedure B. To a toluene (10 mL) solution of benzaldehyde (1.7 mmol) and **1** (2 mmol) is added HgI_2 (10%) at room temperature. After being heated at 50 °C for 2 h, the mixture is placed under high vacuum to remove toluene, and then 20 mL of hexane is added and the solid is eliminated by filtration through Celite. The product is quenched with H_2O (20 mL) and extracted with ether (3 × 20 mL). The organic layers are washed with H_2O (20 mL) and dried over $MgSO_4$, and the solvent is evaporated under reduced pressure affording **2a** which is purified by recrystallization in pentane (yield: 96%); mp: 120−122 °C;^{1}H NMR (250 MHz, $CDCl_3$) δ 0.11 (s, 9 H, $Si(CH_3)_3$), 2.62 (d, 1 H, J = 7.78 Hz, H-2), 5.20 (d, 1 H, J = 7.78 Hz, H-3), 7.19−7.42 (m, 5 H, ArH), 11.0 (s, 1 H, COOH); ^{13}C NMR ($CDCl_3$) δ 0.00, 48.15, 74.35, 128.58, 128.84, 129.50, 144.07, 181.41; IR (KBr): 3500−2500 (OH), 1681 (C═O); MS: $M^{\bullet+}$ = 238. Anal. Calcd for $C_{12}H_{18}O_3Si$: C, 60.46; H, 7.61. Found: C, 60.44; H, 7.59.

Preparation of α,β-Unsaturated Acids (3a−o). General Procedure. A detailed procedure for the reaction of **1** with carbonyl compounds is given below. All reactions are carried out in similar manner under nitrogen at room temperature. Solvents, catalysts, reaction times, and yields are reported in Table 2. Physical, spectral, and analytical data for typical compounds (**3c, 3d, 3f, 3g, 3j, 3k, 3l, 3o**) follow. Full spectral data for closely related compounds (**3b, 3e, 3h, 3i, 3m, 3n**) are given in Supporting Information.

Procedure Using Zinc Bromide. To a stirred solution of the corresponding aldehyde (1.7 mmol) and zinc bromide (0.17 mmol) in THF (5 mL), is added **1** (2 mmol) dropwise at room temperature. After being stirred at the same temperature, the mixture is hydrolyzed with a saturated solution of NH_4Cl (20 mL). Acid−base workup, to remove any remaining nonacidic organic material, gives acids **3** which are purified by recrystallization or flash chromatography (silica gel, cyclohexane/ethyl acetate, 30:70).

Procedure Using Fluoride Ion. To a stirred solution of aldehyde (1.7 mmol) and reagent **1** (2 mmol) in solvent (5 mL) is added the metal fluoride (0.2 mmol). The reaction mixture is then hydrolyzed with water (20 mL). Acid−base workup, to remove any remaining nonacidic organic material, gives acids **3** which are purified by recrystallization or flash chromatography (silica gel, cyclohexane/ethyl acetate, 30:70).

***(E)*-3-(2-Methoxyphenyl)-2-propenoic acid (3c):** recrystallized in ethanol; mp = 183−186 °C; ^{1}H NMR (250 MHz, $CDCl_3$), δ 3.95 (s, 3 H, Me), 6.58 (d, 1 H, J = 16 Hz, H-2), 7.02 (td, 1 H, J = 7.53, 7.4 Hz, H-5 Ar), 7.15 (d, 1 H, J = 8 Hz, H-3 Ar), 7.47 (td, 1 H, J = 8, 7.4 Hz, H-4 Ar), 7.75 (d, 1 H, J = 7.53 Hz, H-6 Ar), 7.92 (d, J = 16 Hz, 1 H, H-3), 12.4 (s, 1 H, COOH); ^{13}C NMR δ 54.4, 110.5, 116.7, 119.7, 122.0, 128.2, 130.9, 141.4, 157.5, 171.7; IR (KBr): 3500−2500 (OH), 1685 (C═O). MS: $M^{\bullet+}$ = 178. Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.65. Found: C, 67.39; H, 5.63.

***(E,E)*-3,3′-(1,4-Phenylene)bis-2-propenoic acid (3d):** recrystallized in H_2O; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.60 (d, 2 H, J = 16.0 Hz, H-2), 7.59 (d, 2 H, J = 16.0 Hz, H-3), 7.70 (s, 4 H, Ar), 12.45 (s, 1 H, COOH); ^{13}C NMR δ 121.0, 128.6, 136.7, 140.8, 160.3; IR (KBr): 3500−2500 (OH), 1682 (C═O). MS: $M^{\bullet+}$ = 218. Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.61. Found: C, 66.02; H, 4.63.

***(E)*-3-(2-Thienyl)-2-propenoic acid (3f):** recrystallized in ethanol; mp = 146−148 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.22 (d, 1 H, J = 15.7 Hz, H-2), 7.20 (dd, 1 H, J = 3.3 Hz, H-4 Ar), 7.50 (d, 1 H, J = 3.3 Hz, H-3 Ar), 7.70 (m, 1 H, H-5 Ar), 7.75 (d, 1 H, J = 15.7 Hz, H-3); ^{13}C NMR δ 117.9, 129.0, 129.9, 132.1, 137.2, 139.4, 167.7; IR (KBr): 3500−2500 (OH), 1672 (C═O). MS: $M^{\bullet+}$ = 154. Anal. Calcd for $C_7H_6O_2S$: C, 54.53; H, 3.92. Found: C, 54.54; H, 3.93.

***(E)*-3-(3-Pyridinyl)-2-propenoic acid (3g):** recrystallized in H_2O; mp = 232−234 °C; ^{1}H NMR (250 MHz, DMSO) δ 6.58 (d, 1 H, J = 16 Hz, H-2), 7.30 (dd, 1 H, J = 8.2, 5.2 Hz, H-5 Ar), 7.50 (d, 1 H, J = 16 Hz, H-3), 8.00 (dt, 1 H, J = 8.5, 2 Hz, H-4 Ar), 8.48 (dd, 1 H, H-6 Ar), 8.75 (d, 1 H, J = 2 Hz, H-2 Ar); ^{13}C NMR δ 121.7, 123.9, 130.2, 134.6, 140.4, 149.7, 150.7, 167.3; IR (Nujol mull): 3500−2500 (OH), 1700 (C═O). MS: $M^{\bullet+}$ = 149. Anal. Calcd for $C_8H_7O_2N$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.45; H, 4.69; N, 9.35.

***(E)*-4,4-Dimethyl-2-pentenoic acid (3j):** recrystallized in hexane; mp = 79 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.01 (s, 9 H, Me), 5.60 (d, 1 H, J = 15.9 Hz, H-2), 6.90 (d, 1 H, J = 15.9 Hz, H-3), 11.3 (s, 1 H, COOH); ^{13}C NMR δ 29.11, 34.53, 116.65, 162.00, 173.22; IR (KBr): 3500−2500 (OH), 1689 (C═O). MS: $M^{\bullet+}$ = 128. Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.43. Found: C, 65.60; H, 9.39.

***(E)*-2-Decenoic acid (3k):** oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 7.2 Hz, Me), 1.20−1.40 (m, 8 H, H-6−9), 1.47 (m, 2 H, J = 7.3 Hz, H-5), 2.23 (dt, 2 H, J = 1.5, 7.0 Hz, H-4), 5.70 (td, 1 H, J = 15.6, 1.5 Hz, H-2), 6.95 (td, 1 H, J = 15.6, 7.0 Hz, H-3), 10.6 (s, 1 H, COOH); ^{13}C NMR δ 14.36, 22.98, 29.41, 29.48, 32.14, 32.66, 121.10, 152.70, 172.73; IR ($CHCl_3$): 3500−2500 (OH), 1697 (C═O). MS: $M^{\bullet+}$ = 170. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.65. Found: C, 70.50; H, 10.61.

***(E,E)*-5-Phenyl-2,4-pentadienoic acid (3l):** recrystallized in ether; mp = 163−164 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.90 (d, 1 H, J = 15.0 Hz, H-2), 6.70−6.80 (m, 2 H, H-4−5), 7.10−7.30 (m, 3 H, Ar), 7.40 (d, 2 H, J = 7.9 Hz, Ar), 7.49 (dd, 1 H, J = 15.0, H-3); ^{13}C NMR δ 123.30, 124.63, 128.39, 128.80, 131.00, 136.15, 141.88, 146.34, 169.88; IR (KBr): 3500−2600 (OH), 1682 (C═O). MS: $M^{\bullet+}$ = 174. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.78. Found: C, 75.88; H, 5.76.

***(E,E,E)*-2,4,6-Octatrienoic acid (3o):** recrystallized in hexane; mp = 185−187 °C; ^{1}H NMR (400 MHz, DMSO) δ 1.71 (d, 3 H, J = 6.6 Hz, Me), 5.75 (d, 1 H, J = 15.2 Hz, H-2), 5.86 (m, 1 H, H-7), 6.06 (dd, 1 H, J = 14.8, 10.8 Hz, H-6), 6.20 (dd, 1 H, J = 14.8, 11.3 Hz, H-4), 6.45 (dd, 1 H, J = 14.8, 11.3 Hz, H-5), 7.10 (dd, 1 H, J = 15.2, 11.2 Hz, H-3); ^{13}C NMR δ 19.17, 121.77, 128.66, 132.15, 135.71, 141.63, 145.28, 169.48; IR (KBr): 3400−2500 (OH), 1682 (C═O); MS: $M^{\bullet+}$ = 138. Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.29. Found: C, 69.50; H, 7.25.

Supporting Information Available: Spectral and analytical data for **3b**, **3e**, **3h**, **3i**, **3m**, and **3n** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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