Mercuric Iodide as an Exceptionally Mild Catalyst for the Condensations of Silyl Ketene Acetals with Electrophiles

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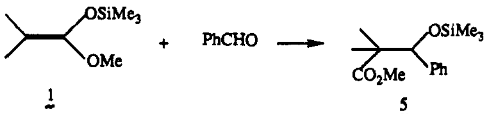
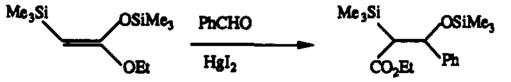
The condensation of silyl ketene acetals with electrophiles has been often exploited in organic synthesis.[1] Typically, such reactions have been catalyzed by Lewis acids such as $TiCl_4$[2] or $SnCl_4$ and, more recently, by anions such as fluoride[3] and bifluoride.[4] Unfortunately, these reactions often must be conducted at −78 °C and require an aqueous workup which hinders the ability to isolate products without concomitant desilylation. In our efforts to extend the utility of group transfer polymerization (GTP)[5] we found mercuric iodide to be a mild and useful catalyst[6] for the room temperature addition of silyl ketene acetals to acrylate esters. To our knowlege this was the first reported use of mercuric iodide for these purposes. We now report that mercuric iodide is also a catalyst for the condensation of silyl ketene acetals with other electrophiles. In the presence of catalytic amounts of HgI_2, silyl ketene acetals add to aldehydes and benzoyl fluoride at room temperature.[7] The addition to benzaldehyde is illustrated by eq 1. Typically, the silyl ketene acetal and 1-equiv of the desired aldehyde is added to a stirring suspension of HgI_2 in a nonprotic solvent such as toluene or hexane. Workup consists of diluting with hexane, filtering away the catalyst, and stripping off the solvent.



1 + PhCHO → 5 (1)

In this study, silyl ketene acetals 1–4 (Table I) were employed. Enriched isomers (*E* or *Z*) of **2** (88% *E*)[5], **3** (83% *E* or 97% *Z*)[8] and **4** (82% *E* or 80% *Z*)[9] were obtained by fractional distillation. Representative condensations are tabulated in Table I. Benzaldehyde (run 1) and terephthalaldehyde (run 2) reacted with silyl ketene acetal **1** to give adducts in >90% yield. Reaction of 88% *E*-**2** with benzaldehyde gave **7** in 87% yield with a small preference for the 2*R*,3*R* (erythro) isomer (run 3). Silyl ketene acetals **3** and **4** also showed a slight preference for formation of the 2*R*,3*R* isomers but the diastereomeric ratios[10] of the products appear to be relatively insensitive to the starting configuration of the silyl ketene acetal. It appears that the reaction is proceeding through an intermediate in which the geometry of the double bond has been lost, as in the reaction of α-mercurio ketones with aldehydes.[11] This is analogous to the nonspecificity reported for the reaction of α tin esters[12] with electrophiles.

The mildness of the aldol reaction permits the isolation of the sensitive adduct **8** (Table I) from the condensation of 83% *E*-**3** with benzaldehyde (run 4). Adduct **8** is known to eliminate hexamethyldisiloxane easily to give the olefin[13] (eq 2).



3 → 8 (2)

Interestingly, when starting from 97% *Z*-**3** (run 5), 11% *E*-olefin was obtained. Elimination from adduct **9** was also sensitive to the initial *E*/*Z* ratio in silyl ketene acetal **4**. Hence, 82% *E*-**4** gave a 55/45 mixture of 2*R*,3*R*/2*R*,3*S* isomers (run 7) whereas 80% *Z*-**4** gave 47% elimination to olefin but no detectable 2*R*,3*S* product (run 8). Elimination from the 2*R*,3*S* products might be expected to be preferred because the conformation required for syn-elimination[14] of hexamethyldisiloxane from 2*R*,3*S* leads to the thermodynamically more stable *E*-olefin. However, when already formed 2*R*,3*S* products were resubjected to condensation conditions (1.1 mmol of 2*R*,3*S*-**9**, 10 mol % of HgI_2, 5 mL of benzene, stirring at room temperature 22 h), no elimination was observed. This suggests that elimination occurs as a competing pathway, mainly through the *Z* reactants. In fact, elimination could be suppressed completely by dropping the catalyst level from 6% to 0.3 mol % (run 5).

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(3) Kuwajima, I.; Nakamura, E. *Acc. Chem. Res.* **1985**, *18*, 181.

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(5) Dicker, I. B., Cohen, G. M., Farnham, W. B., Hertler, W. H., Laganis, E. D., Sogah, D. Y. *Macromolecules*, **1990** *23*(18), 4034–4041. Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473.

(6) Dicker, I. B. U.S. Pat. 4,732,955. Group Transfer Polymerization catalyzed by mercury compounds. Dicker, I. B. U.S. Pat. 4,866,145. Catalyst For Group Transfer Polymerization. Dicker, I. B. U.S. Pat. 4,943,648. Initiators For Group Transfer Polymerization.

(7) Electrophiles such as acetals (Makin, S. M.; Kruglikova, R. I.; Kharitonva, O. V. *Zhur. Org. Khim.* **1985** *21*(7), 1408) and orthoesters also react with silyl ketene acetals in the presence of 10 mol % mercuric iodide at room temperature within 2 h. For example, the cyclic acetal 1,3-dioxolane and THP-protected methacrylic acid (Kearns, J. E.; McLean, C. D.; Solomon, D. H.; *J. Macromol. Sci.* **1974** *A8*(4), 673) condensed with **1** to give only the expected products ($Me_2(CO_2Me)CCH_2OCH_2OSiMe_3$ and $Me_2(CO_2Me)CCH(CH_2)_3CH_2$) as judged by small-scale reactions conducted in an NMR tube in benzene-d_6 with 10 mol % mercuric iodide. Dithioacetals, however, did not react under these conditions. Orthoesters appear to give only the product of monoaddition as in the trimethylsilyl triflate-catalyzed condensation of silyl enol ethers with ortho esters (Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248). For example, reaction with trimethyl orthoformate appeared to give only the dimethyl acetal ester ($Me_2(CO_2Me)CCHC(OMe)_2$. The reaction with orthoesters is sensitive to steric effects: trimethyl orthoacetate and trimethyl orthobenzoate failed to react overnight at room temperature.

(8) Matsuda, I.; Murata, S., Izumi, Y. *J. Org. Chem.* **1980**, *45*, 237.

(9) Prepared in two steps by methylation of ethyl trimethylsilylacetate at −78° (THF/LDA/MeI), purification by distillation and silylation of ethyl 2-(trimethylsilyl)propionate (THF/LDA/TMSCl) to give 82/18 (*E*/*Z*) 1-ethoxy-1-(trimethylsiloxy)-2-methyl-2-(trimethylsilyl)ethylene, bp 45 °C (0.7 mm): ^1H (*E*-isomer, 360 MHz, $CDCl_3$) 0.045 (s, 9 H, $CSiMe_3$) 0.19 (s, 9 H, OSiMe), 1.23 (t, 3 H, Me of ethyl), 1.51 (s, 3 H, vinyl Me), 3.80 (q, 2 H, OCH_2). Anal. Calcd for C, 53.59; H, 10.63; Si, 22.79. Found: C, 53.77; H, 10.64; Si, 23.07.

(10) The configurational assignments are based on consideration of the observed coupling constants using the *J*(threo) > *J*(erythro) relationship: House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310. Assignments for **9** and **10** were deduced from the geometry (*E*) of the alkenes which were formed by elimination of hexamethyldisiloxane.

(11) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1982**, *104*, 2323.

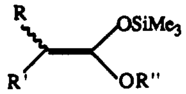
(12) Noltes, J. G.; Verbeek, F.; Creemers, J. C. *Organomet. Chem. Synth.* **1970–71**, *1*, 57.

(13) Matsuda, I.; Izumi, Y. *Tetrahedron Lett.* **1981**, *22*(19), 1805.

(14) Hudlrick, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464.

0022-3263/93/1958-2324$04.00/0

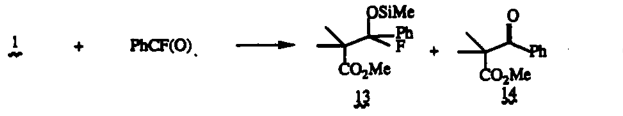
Table I. Condensations of Silyl Ketene Acetals Catalyzed by HgI_2[a]



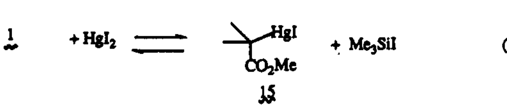
entry	silyl ketene acetal no.	E/Z ratio	R	R′	R″	aldehyde	adduct	(2*R*,3*R*)/(2*R*,3*S*)	% yield[b]	% alkene
1	**1**	–	Me	Me	Me	PhCHO	**5**	–	92	0
2	**1**	–	Me	Me	Me	OHCPhCHO	**6**[c]	–	99	0
3	**2**	88/12	Me	H	Me	PhCHO	**7**	61/39	87	0
4	**3**	83/17	$SiMe_3$	H	Et	PhCHO	**8**	59/41	97	0
5	**3**	3/97	$SiMe_3$	H	Et	PhCHO	**8**	56/32	89	11[d]
6	**3**	3/97[e]	$SiMe_3$	H	Et	PhCHO	**8**	57/43[d]	81	0
7	**4**	82/18	$SiMe_3$	Me	Et	PhCHO	**9**	55/45	90	0
8	**4**	20/80	$SiMe_3$	Me	Et	PhCHO	**9**	100/0	53	47[d]

[a] Six mole percent based on silyl ketene acetal. [b] Isolated yield. [c] 1:1 meso:*d*,*l* mixture. [d] *E*-isomer only. [e] A 0.3 mole percent HgI_2 based on **3**.

Benzoyl fluoride was found to react with **1** (17 h, room temperature in benzene) giving the unstable α-fluorosiloxy ester **13**. Product **13** is the tetrahedral adduct of direct addition, analogous to the product formed from the addition of trimethylsilyl cyanide to ketones[15] and the reversible adduct formed from the addition of trimethylsilyl iodide to aldehydes.[16] The addition of a trace of trifluoroacetic acid to **13** in an NMR tube resulted in its quantitative transformation to **14** within minutes.



The mechanism by which mercuric iodide catalyzes these reactions is unclear but the reaction is formally analogous to the Lewis acid-catalyzed addition of silyl enol ethers[1] and allyl silanes[1] to various electrophiles. In this sense, HgI_2 may be considered to be functioning as a mild Lewis acid which catalyzes the reaction of silyl enol ethers by coordinating to the incoming electrophile.[17] However, Hg(II) is not oxophilic as is evidenced by its low Lewis acidity[18] and the predominance of the keto form[19] of mercury bis(acetylacetonate). In contrast, the association of Hg(II) with double bonds is facile and well known.[20] For this reason, the reaction may proceed via the prior formation of a small equilibrium amount of an α-iodomercury ester **15**[21] (eq 4), which reacts with the electrophile to give the observed products. Such an intermediate has been postulated in the *E*/*Z* isomerization of silyl ketene acetals catalyzed by $HgBr_2$/TMSBr[22] and HgI_2,[23,24] the HgI_2-catalyzed rearrangement of α-silyl ketones to enol silyl ethers[25] and the HgI_2-catalyzed rearrangement of certain silyl ketene acetals to α-silyl esters.[26]



α-Iodomercury ester **15** was synthesized[27] but did not itself undergo an aldol condensation with benzaldehyde under HgI_2 catalysis. This lack of reactivity is consistent with the report that α-iodomercurio ketones enter into aldol condensations only under the influence of strong Lewis acids[10] and suggests that TMSI, known to behave as a Lewis acid,[28] might be an essential participant in the reaction, though apparently not as a Lewis acid catalyzing the addition of an intermediate α-mercurio ester to the aldehyde. This latter mechanism is unlikely considering the relatively slow isomerization of *E*-**2** in the presence of HgI_2 ([*E*-**2**] = 0.2 M, [HgI_2] = 0.49 mM, 27 °C in benzene-d_6, apparent first-order rate constant = 672 s^{-}[29]) as compared to the instantaneous reaction of benzaldehyde with *E*-**2** under the same conditions. If *E*-**2** were reacting with benzaldehyde through an α-mercurio intermediate, one would expect isomerization to be at least as fast as electrophilic addition, which it is not. Alternatively, it is also unlikely that TMSI is the actual Lewis acid catalyst in these condensations because competitive NMR studies show that the rate of the aldol reaction of **1** with benzaldehyde catalyzed by mercuric iodide is considerably faster than that catalyzed by equimolar amounts of TMSI ([HgI_2] or [TMSI] = 2.5 mM, [**1**] = 0.42 mM, benzene-d_6, 25 °C, 30 min). Furthermore, the product distribution for the condensation of **3** with benzaldehyde is different for the two catalysts under the same conditions, i.e., with HgI_2 there is no elimination under conditions in which TMSI gives significant amounts of olefin. Finally, the condensation of **1** with benzoyl fluoride is not catalyzed by TMSI.

We favor the alternate possibility that HgI_2 forms a

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(16) Jung, M. E.; Mossman, A. B.; Lyster, M. A. *J. Org. Chem.* **1978**, *43*, 3698.

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(19) Flatau, K.; Musso, H. *Angew. Chem. Int. Ed. Engl.* **1980**, *9*(5), 379. Meyer, R.; Gorrichon-Guigon, L.; Maroni, P. *J. Organomet. Chem.* **1980**, *188* 11.

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(24) Brittain, W. J.; Dicker, I. B. *Polymer International* **1993**, *30*, 101.

(25) Litvinova, O. V.; Baukov, Yu., I.; Lutsenko, I., F. *Dokl. Akad. Nauk. SSSR* **1967**, *173*, 578.

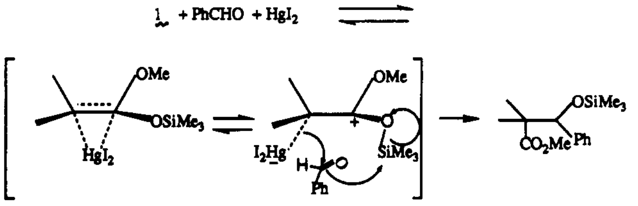
(26) Baukov, Yu. I., Burlachenko, G. S., Lutsenko, I. F., *Dokl. Akad. Nauk. SSSR* **1964**, *157*(1), 119.

(27) 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene was converted to bis[1-methoxycarbonyl)-1-methylethyl)mercury by reaction with 0.5 equiv of mercuric acetate (in THF at reflux, 82% yield, mp 119–122°). Metathesis to the α-mecurio ester **16**, performed according to the method of Lutsenko (*Dokl. Akad. Nauk SSSR* **1961**, *141*(5), 1107) with 1 equiv of HgI_2 in refluxing methanol gave **16**, mp 83.5–85; mass spectrum *m*/*e* 429.9356. Anal. Calcd C, 14.01; H, 2.10. Found: C, 13.84; H, 2.21.

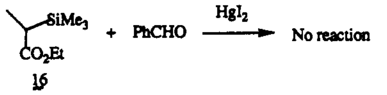
(28) Sakurai, H.; Sasaki, K.; Hosumi, A. *Tetrahedron. Lett.* **1981**, *745*.

(29) Dicker, I. B. *Abstracts of Papers*, American Chemical Society; Miami Beach, FL, Spring 1985; American Chemical Society: Washington, DC, 1985; abstract no. 238.

Scheme I



π-complex with the silyl ketene acetal in which the polarized electropositive trimethylsilyl group coordinates to the incoming electrophile thereby facilitating the condensation (Scheme I). The lack of diastereospecificity in the aldol reaction of unsymmetrical silyl ketene acetals suggests the intermediate π complex is free to undergo single bond rotation about the carbon–Hg bond. Prior rearrangement of the silyl ketene acetals to α-silyl esters[22,25] can be ruled out since **16** failed to undergo condensation with benzaldehyde under HgI_2 catalysis (eq 5). In either case, there are similarities with the reported intramolecular cyclization of acetyleneic silyl enol ethers with mercuric chloride in which a transient α-chloromercury ketone adds intramolecularly across a triple bond.[30]



(5)

Summary and Conclusion

In summary, mercuric iodide catalyzes the addition of silyl ketene acetals to aldehydes and benzoyl fluoride at room temperature. Formally, the reaction is analogous to the Lewis acid-catalyzed addition of silyl ketene acetals, silyl enol ethers, and allyl silanes to various electrophiles and, in this sence, HgI_2 may be considered to be functioning as a mild Lewis acid though the reaction may be driven by prior reaction or complexation of the HgI_2 with the silyl ketene acetal. Typically, the silyl ketene acetal is added to a stirring mixture of the catalyst containing 1 equiv of the desired electrophile at room temperature. Workup consists of diluting with hexane, filtering away the catalyst and stripping off the solvent. The usefulness of this catalyst is due to its ease of use (room temperature), good yields (greater than 80%), simple workup (dilution and filtration), and mildness of reaction conditions. These conditions permit the isolation of sensitive adducts, such as bis-silylated adducts **8** and **9** with little elimination of hexamethyldisiloxane to give olefin.

Experimental Section

General Procedures. All experiments were run under a positive pressure of dry argon. THF and toluene were distilled from sodium prior to use. ^1H and ^{19}F spectra were obtained at 360 and 100 MHz, respectively. All products gave satisfactory elemental analysis and NMR spectra.

General Procedure for the Preparation of Aldols by Reaction of Silyl Ketene Acetals with Aldehydes Catalyzed by HgI_2. Methyl 2,2-Dimethyl-3-phenyl-3-(trimethylsiloxy)-propionate (5). To a vigorously stirring suspension of 0.07 g (0.15 mmol) HgI_2 in 5 mL of toluene under argon was added 1.0 mL (5.0 mmol) of 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene 1)[5] and 0.51 mL (5.0 mmol) of benzaldehyde in 5 mL of toluene. After 40 min, the mixture was placed under high vacuum to remove toluene. The residue was dissolved with 20 mL of hexane, filtered through Celite, and removed under reduced pressure. Evaporation of excess benzaldehyde under high vacuum gave 1.29 g (92%) of **5** as an oil: ^1H NMR ($CDCl_3$) −0.067 (s, $OSiMe_3$), 0.967 (s, CMe), 1.098 (s, CMe), 3.646 (s, OMe), 4.945 (s, $CHOSiMe_3$), 7.240 (s, ArH). Anal. Calcd for C, 64.24; H, 8.63. Found: C, 64.47; H, 8.56.

1,4-Bis[2-(Methoxycarbonyl)-2-methyl-1-(trimethylsiloxy)propyl]benzene (6). Similarly, but with 0.05 g (0.11 mol) of HgI_2, 1.0 mL (5.0 mmol) of 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (**1**), and 0.33 g (2.5 mmol) of terephthalaldehyde. After 60 min, the mixture was redissolved in a small amount of CH_2Cl_2 before dilution with 40 mL of hexane. An amount of 1.2 g (99%) of a 1:1 mixture of meso and *d,l* forms of **6** as a solid, pure by NMR and C and H analysis, after recrystallization from petroleum ether/diethyl ether: ^1H NMR ($CDCl_3$) 0.009 (s, $OSiMe_3$, 18 H), 1.059/1.063 (s/s, CMe_2, 6 H, one of two diastereomers), 1.194/1.202 (s, CMe_2, 6 H, one of two diastereomers), 3.731 (s, OMe, 3 H), 3.735 (s, OMe, 3 H), 5.010 (s, $CHOSiMe_3$, 2 H), 7.342 (s, AH, 8 H). Anal. Calcd for C, 59.71; H, 8.77. Found: C, 59.58; H, 8.76.

Methyl 2-Methyl-3-phenyl-3-(trimethylsiloxy)propionate (7). Similarly, but with 0.5 mL (2.7 mmol) of 1-methoxy-1-(trimethylsiloxy)-1-propene (**1**) and 0.28 mL (2.7 mmol) of benzaldehyde gave 87% of **7** (oil) as a 61/39 mixture of 2*R*,3*R*/2*R*,3*S* isomers: ^1H NMR ($CDCl_3$) 2*R*,3*R*, −0.047 (s, $OSiMe_3$, 9 H), 0.864 (d, CH*Me*, 3 H, *J* = 7.2 Hz), 2.695–2.778 (m, $CHCO_2Me$, 1 H), 3.718 (s, OMe, 3 H), 4.702 (d, CHOSiMe, 1 H, *J* = 9.4 Hz), 7.215–7.313 (m, ArH, 5 H); 2*R*,3*S*, 0.014 (s, $OSiMe_3$, 9 H), 1.130 (d, CH*Me*, 3 H, *J* = 6.8 Hz), 2.695–2.778 (m, $CHCO_2Me$, 1 H), 3.554 (s, OMe, 3 H), 5.015 (d, CHOSiMe, 1 H, *J* = 5.8 Hz), 7.215–7.313 (m, ArH, 5 H). Anal. Calcd for C, 63.15; H, 8.27. Found: C, 63.11; H, 8.35.

Ethyl 2-(trimethylsilyl)-3-phenyl-3-(trimethylsiloxy)-propionate (8). Similarly, but with 0.50 mL (1.9 mmol) of 83/17 *E*/*Z* 1-ethoxy-1-(trimethylsiloxy)-2-(trimethylsilyl)ethene (**3**) and 0.19 mL (1.9 mmol) of benzaldehyde in 5 mL of toluene. A 59/41 mixture of 2*R*,3*R*/2*R*,3*S* isomers of **8** (94%) was obtained: ^1H ($CDCl_3$) 2*R*,3*R* isomer, −0.087 (s, $OSiMe_3$, 9 H), 0.176 (s, $CSiMe_3$, 9 H), 1.041 (t, OCH_2CH_3, 3 H, *J* = 7.2 Hz), 2.606 (d, $CHCO_2Et$, 1 H, *J* = 10 Hz), 3.843 (q, OCH_2, 4 H, *J* = 7.2 Hz), 5.097 (d, $CHOSiMe_3$, 1 H, *J* = 10 Hz), 7.197–7.328 (m, ArH, 5 H); 2*R*,3*S* isomer, −0.257 (s, $OSiMe_3$, 9 H), −0.087 (s, $CSiMe_3$ 9 H), 0.181 (t, OCH_2CH_3, 3 H, *J* = 7.1 Hz), 2.646 (d, $CHCO_2Et$, 1 H, *J* = 11 Hz), 4.057–4.257 (m, OCH_2, 2 H), 5.066 (d, $CHOSiMe_3$, 1 H, *J* = 11 Hz), 7.201–7.328 (m, ArH) ppm. Anal. Calcd for C, 60.30; H, 8.93. Found: C, 60.24; H, 9.00.

Ethyl 2-Methyl-2-(trimethylsilyl)-3-phenyl-3-(trimethylsiloxy)propionate (9). Similarly, but with 0.50 mL of 82/18 *E*/*Z* 1-ethoxy-1-(trimethylsiloxy)-2-(trimethylsilyl)-1-propene (1.9 mmol) (**4**) and 0.19 mL (1.9 mmol) of benzaldehyde in 5 mL of toluene. A 55/45 2*R*,3*R*/2*R*,3*S* mixture of **9** (90%) was obtained: ^1H NMR ($CDCl_3$) 2*R*,3*S* isomer, −0.174 (s, $CSiMe_3$, 9 H), −0.105 (s, $OSiMe_3$, 9 H), 1.251 (s, $MeC(SiMe)_3$, 3 H), 1.306 (t, OCH_2CH_3, 3 H), 4.061–4.033 and 4.214–4.234 (m, OCH_2, 2 H), 5.477 (s, $HC(OSiMe)_3$, 1 H), 7.1–7.4 (m, ArH, 5 H); 2*R*,3*R* isomers, −0.020 (s, $CSiMe_3$, 9 H), 0.142 (s, $OSiMe_3$, 9 H), 1.069 (s, $MeC(SiMe)_3$, 3 H), 1.215 (t, OCH_2CH_3, 3 H, *J* = 7.0Hz), 4.95–4.15 (m, OCH_2, 2 H), 5.510 (s, $HC(OSiMe)_3$, 1 H), 7.151–7.335 (m, ArH, 5 H) ppm. Anal. Calcd for C, 61.35; H, 9.09. Found: C, 61.42; H, 9.00.

Methyl 2,2-Dimethyl-3-fluoro-3-phenyl-3-(trimethylsiloxy)propionate (13) and Methyl 2,2-Dimethyl-3-phenyl-3-oxopropionate (14). A volume of 0.28 mL (2.5 mmol) of benzoyl fluoride was added to a stirring mixture of **1** (0.5 mL, 2.5 mmol) and 0.11 g (0.15 mol) of HgI_2 in 5 mL of toluene. After stirring 2.2 h, the mixture was placed under high vacuum to remove toluene. Proton and fluorine NMR indicated that no starting materials remained; only resonances consistent with the structure of **13** were observed: ^1H NMR ($CDCl_3$) −0.007 (s, $OSiMe_3$, 3 H), 0.427 (s, $OSiMe_3$, 3 H), 1.200 (s, C*Me*, 3 H), 1.233 (s, C*Me*, 3 H), 3.611 (s, OMe, 3 H) ppm; ^{19}F NMR ($CDCl_3$ referenced to $CFCl_3$) −101.7 ppm. A trace of trifluoroacetic acid was added to the adduct in $CDCl_3$. Within 5 min **14** was formed quantitatively as determined by ^1H NMR: ($CDCl_3$) 1.570 (s, C*Me*2, 6 H), 3.679 (s, OMe, 3 H), 7.446 (t, *m*-ArH, 2 H, *J* = 7.6 Hz), 7.560 (t, *p*-ArH,

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1 H, $J = 7.5$ Hz), 7.808 (d of d, *o*-ArH, 2 H, $J_{ortho} = 8.3$ Hz, $J_{meta} = 1.5$ Hz) ppm. Pure **14** was isolated by removing solvent under reduced pressure and chromatography over silica gel and further characterized by mass spectra (M^+ 206) and chemical analysis. Anal. Calcd for C, 69.86; H, 6.80. Found: C, 69.78; H, 6.85.

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