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Reductive Coupling of Carbonyl Compounds with Zinc and Trimethylchlorosilane To Produce O-Silylated Pinacols. Effect of Ultrasonic Waves

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Trimethylchlorosilane reacts with carbonyl compounds in the presence of zinc to give O-silylated pinacols, vicinal bis(trimethylsiloxy)alkanes, in good yields via reductive dimerization. This is a very mild route to bis(siloxy)alkanes, which are easily converted to pinacols or pinacolones in excellent yields. Electron-donating groups accelerate coupling while electron-withdrawing groups have an inhibiting effect. Cross-coupling reactions yield a mixture of bis(siloxy)alkanes. Ultrasonic irradiation of these reactions increases the yields up to 50% compared to stirring at the same temperature.

Introduction

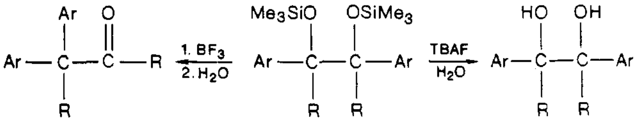
Reductive dimerization of carbonyl compounds is an important method for making carbon–carbon bonds. Alkali-metal-induced coupling of carboxylic acid derivatives, the acyloin condensation, is widely used; however, milder approaches have been developed.[1] For example, some carbonyl compounds are reductively dimerized to give pinacolic products in the presence of amalgamated aluminum.[2] This method is efficient for aliphatic and cyclic ketones but not for aryl-substituted ketones and benzaldehyde. Amalgamated magnesium–titanium tetrachloride,[3] cerium in the presence of iodine,[4] samarium iodide,[5] or ytterbium metal[6] have also been used for reductive coupling of aromatic and aliphatic carbonyl compounds to produce pinacols.

For acetophenone and benzaldehyde, good yields of reductive coupling have been observed in the presence of trimethylchlorosilane and magnesium turnings in hexamethylphosphoric triamide under vigorous conditions (95 °C, 22 h).[7] Under mild conditions, tetrahydrofuran (THF) or 1,4-dioxane as solvent at 40 °C for 24 h, no reaction is observed.[8] Chlorosilanes have also been used to transform ketones to alkenes,[9,10] organic sulfoxides to thioethers,[11] diols to alkenes,[12] aliphatic aldehydes to reductive coupling products,[13] and aryl-substituted carbonyl compounds to pinacolone products via carbenoid intermediates.[14]

Recently we reported that ultrasonic irradiation improved the reductive silylation of some dicarbonyl compounds in the presence of trimethylchlorosilane and zinc to give bis(trimethylsiloxy)alkenes.[15] This procedure is a convenient modification of the acyloin condensation with the benefit of being applicable to the preparation of unsymmetrical bis(siloxy)alkenes. We have extended our investigation to simple carbonyl compounds and report here a very mild method of producing vicinal bis(trimethylsiloxy)alkanes, which can be easily converted to pinacols or pinacolones.

Results and Discussion

Aryl- or vinyl-substituted carbonyl compounds are readily dimerized in the presence of trimethylchlorosilane and zinc (carbonyl:Me_3SiCl:Zn, 1:1:5 mole ratio)[16] in ether solvents to give O-silylated pinacols in good yields. These O-silylated pinacols are stable toward bases and can be purified by column chromatography. In the presence of a Lewis acid such as boron trifluoride etherate, however, they are readily hydrolyzed and rearranged to the pinacolone in excellent yields. Rearrangement can be avoided by hydrolyzing with tetrabutylammonium fluoride to give nearly quantitative yields of the pinacols. With aryl-substituted ketones, GC analysis of the reaction mixtures show mainly coupled products, a mixture of *d*, *l*, and *meso* stereoisomers. These stereoisomers were analysed by GC and ^1H NMR. The products and yields are summerized in Table I.



$$\mathrm{Ar_2C(R)\!-\!C(=O)\!-\!R} \xleftarrow[\text{2. } H_2O]{\text{1. } BF_3} \mathrm{Ar\!-\!C(R)(OSiMe_3)\!-\!C(R)(OSiMe_3)\!-\!Ar} \xrightarrow[H_2O]{TBAF} \mathrm{Ar\!-\!C(R)(OH)\!-\!C(R)(OH)\!-\!Ar}$$

Some α,β-unsaturated carbonyl compounds were converted efficiently to highly functionalized bis(trimethylsiloxy)alkanes. For example, acrolein, crotonaldehyde, and 2-cyclohexenone gave the coupled products in high yields

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(7) Chan, T. H.; Vinokur, E. *Tetrahedron Lett.* **1972**, 72–78.

(8) Trimethylchlorosilane (1.23 mL, 9.6 mmol) was added at room temperature with stirring to the mixture of acetophenone (1 mL, 8 mmol) and magnesium (0.236 g, 9.7 mmol) in 10 mL of THF or dioxane. The mixture was stirred for 24 h at 50 °C. Analysis of the reaction mixture by GC showed no decrease of reactant and no coupling products.

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(10) Hodge, P.; Khan, M. N. *J. Chem. Soc., Perkin Trans. 1* **1975**, 809–811.

(11) (a) Schmit, A. H.; Russ, M. *Chem. Ber.* **1981**, *114*, 822–824. (b) Olah, G. A.; Narang, S. C.; Gupta, B. G.; Malhotra, R. *Synthesis* **1979**, 61–62.

(12) (a) Barua, N. C.; Sharma, R. P. *Tetrahedron Lett.* **1982**, *23*, 1365–1366, (b) Sarma, J. C.; Barua, N. C.; Sharma, R. P.; Barua, J. N. *Tetrahedron* **1983**, *39*, 2843–2846.

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(16) The stoichiometry must be carefully controlled because excess Zn and Me_3SiCl leads to deoxysilylation. So, J.-H.; Park, M.-K.; Boudjouk, P., unpublished results.

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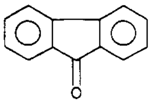
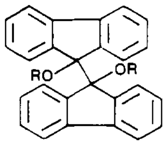
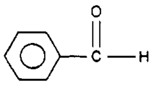
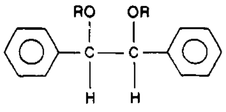
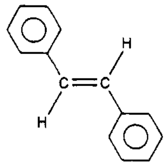
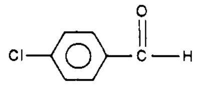
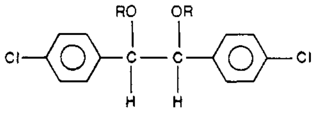
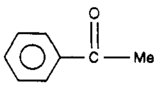
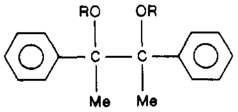
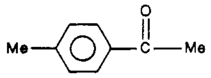
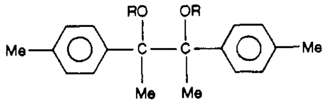
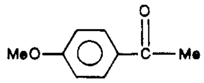
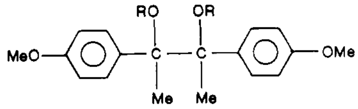
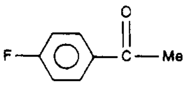
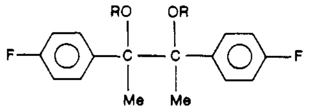
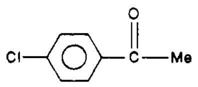
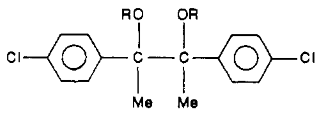
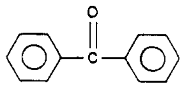
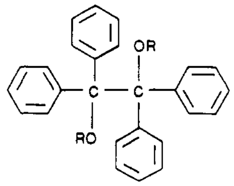
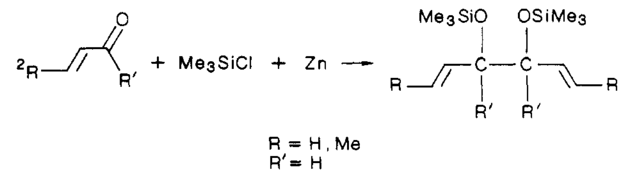
Table I. Reductive Coupling of Carbonyl Compounds in the Presence of Trimethylchlorosilane and Zinc (Ratio 1:1:5) for 2-h Reaction

entry	reactant	yields,[a] %; [stirring] sonication	products[b]
1		1A; [N.R.] 56	 **1A**
2		2A; [42] 56 2B; [trace] 15	 **2A**  **2B**
3		3A; [66] 67	 **3A**
4		4A; [54] 65	 **4A**
5		5A; [63] 76	 **5A**
6		6A; [50] 74	 **6A**
7		7A; [48] 62	 **7A**
8		8A; [81] 85	 **8A**
9		9A; [65] 84	 **9A**

[a] Dioxane solvent. No significant change observed in THF for runs 4 and 8. [b] R = Me_3Si, *d*, *l*, and *meso* stereoisomers were not separated.

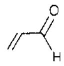
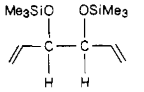
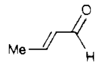
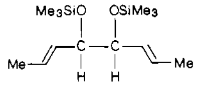
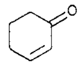
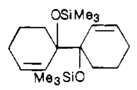
(Table II) but phenyl-substituted systems such as cinnamaldehyde and *trans*-4-phenyl-3-buten-2-one gave complex mixtures.



Reactions were monitored by GC by following the depletion of the reactant in the presence of an internal standard. The results are shown in Table III. Reactions times (t_{rxn}) were recorded at >99% completion and were usually <2 h. Both $t_{1/2}$ and t_{rxn} show that electron-donating groups on phenyl rings increase the reaction rate and electron-withdrawing groups have the opposite effect.

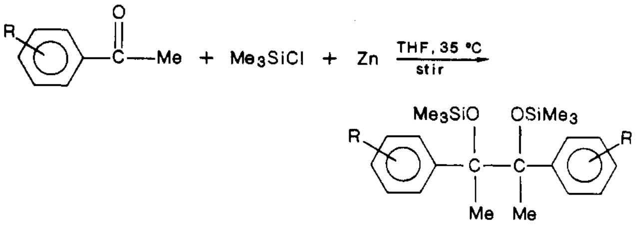
For examination of cross-coupling reactions, 1:1 mixtures of carbonyl compounds were treated with trimethyl-

Table II. Reductive Coupling of α,β-Unsaturated Carbonyl Compounds in the Presence of Trimethylchlorosilane and Zinc (Ratio = 1:1:5) after 2 h of Stirring at 35 °C in THF

entry	reactant	yield,[a] %	product[b]
10		81	
11		70	
12		80	

[a] Total yield of coupled products (90–95% of purity). (See Experimental Section). *d*, *l*, and *meso* isomers not separated.

Table III. Reaction Time of Carbonyl Compounds in the Presence of Trimethylchlorosilane and Zinc (Ratio = 1:1:5) To Produce Bis(trimethylsiloxy) Products in THF at 35 °C



R	$t_{1/2}$,[a] min	t_{rxn},[b] min	yields,[c] %
H	16 ± 2	85 ± 7	93
p-Me	13 ± 1	65 ± 5	91
p-MeO	9 ± 1	48 ± 5	95
p-Cl	17 ± 3	115 ± 10	91
m-MeO	18 ± 3	120 ± 10	84
m-Cl	18 ± 2	117 ± 10	90

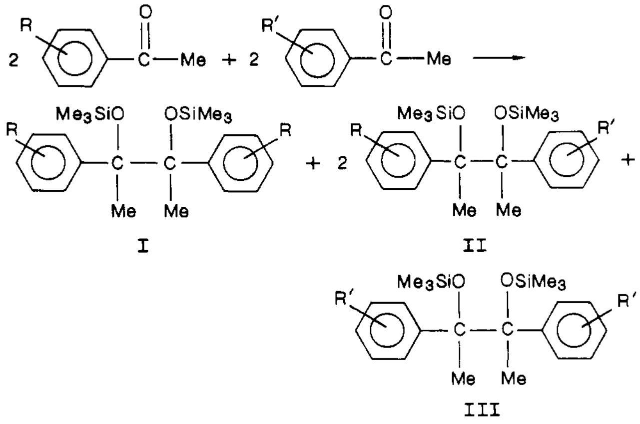
[a] All reactions are monitored with decreasing of carbonyls by GC. [b] t_{rxn} was taken when less than 1% of ketone remained. [c] Yields were estimated by GC analysis with internal standard.

chlorosilane under the same conditions. The results are given in Table IV and demonstrate that substituents on the phenyl ring have a significant effect on the yields. It is also shown that when the $t_{1/2}$ values of two carbonyl compounds are close, a high yield of the cross-coupling product is obtained. However, differences in electronic effects were not sufficient to lead to a single dominant product for any pair of acetophenones, reducing the synthetic utility of the reaction.

In a separate experiment, trimethylchlorosilane was refluxed and sonicated for 24 h in the presence of zinc, but no reaction was observed. However, when carbonyl compounds were refluxed for 24 h with zinc in the absence of trimethylchlorosilane, 3% of pinacol was obtained.[17] Even with trimethylchlorosilane, small amounts of pinacols were detected by GC. These observations lead us to suggest the mechanism in Scheme I.

For the formation of pinacolic products from carbonyl compounds in the presence of metals, radical intermediates have been suggested.[3,18] Thus we propose that zinc re-

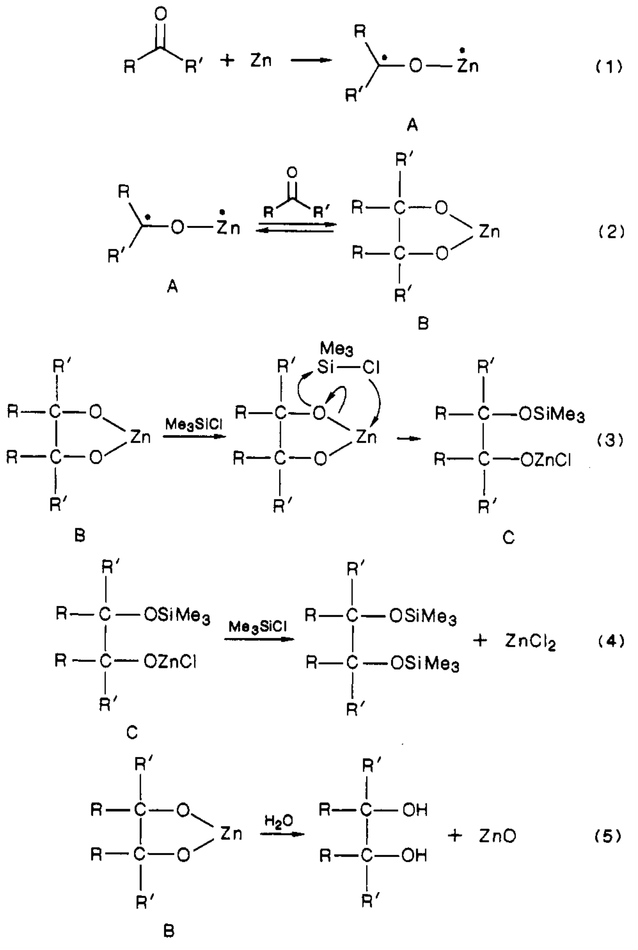
Table IV. Cross-Coupling Reaction of Aryl Methyl Ketones in the Presence of Trimethylchlorosilane and Zinc in THF at 35 °C



reactants		ratio[a]			
R	R′	I	II	III	yields,[b] %
p-Me	*p*-MeO	0.73	1	0.76	95
p-Me	*p*-MeO	0.87	1	0.73	96[c]
H	*p*-Cl	0.61	1	0.45	94
H	*m*-Cl	0.79	1	0.78	97
H	*p*-Me	0.72	1	0.73	76
H	*p*-MeO	1.74	1	1.56	84
p-Me	*p*-Cl	0.78	1	0.90	93
p-MeO	*p*-Cl	1.54	1	2.04	82

[a] Ratios were calculated from GC analysis of the mixture. [b] All yields were calculated from GC with internal standard. [c] This reaction was run at 10 °C for 5 h to check the temperature effect on the distribution of products.

Scheme I



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[17] The mixture of acetophenone (1 mL, 8 mmol) and zinc (5.3 g, 80 mmol) and 10 mL of THF was sonicated for 24 h. The unreacted zinc powder was filtered out and the solution was hydrolysed with 10% HCl solution. The mixture then was extracted with benzene and dried over anhydrous magnesium sulfate. GC showed 3% of pinacol, which was identified by GC-MS.

[18] Clerich, A.; Porta, O. *Tetrahedron* **1983**, *39*, 1239–1246.

ductions of carbonyl compounds lead to the dimer B via A (eq 1 and 2). Since alkoxides react efficiently with chlorosilanes, eq 3 should be facile. Since there is essentially no reaction in the absence of trimethylchlorosilane, an equilibrium between A and B seems reasonable. Small quantities of pinacols are observed in all reactions. We suspect hydrolysis of B by adventitious water as the primary source. Hydrolysis of the O-silylated pinacols by zinc chloride was ruled out by a control experiment.[21]

Experimental Section

General Method. Proton NMR spectra were obtained at 90 MHz on a Varian EM 390 spectrometer. ^{13}C NMR spectra were taken on a JEOL FX 90 spectrometer and are reported in ppm downfield from TMS (δ). Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were obtained on a Perkin-Elmer 137 and/or Cygnus 25 FT-IR (Mattson Instrument Inc.) spectrophotometer. Gas chromatography-mass spectra were taken on a Hewlett-Packard 5992B instrument and mass spectra were taken on a MAT CH-5DF or CH7 mass spectrometer at 70 eV. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

All reactions were monitored by IR spectroscopy and products were analyzed by GLC on a Hewlett-Packard Model 5880A gas chromatograph equipped with a flame ionization detecter and a Hewlett-Packard cross-linked methylsilicon capillary column (0.2 mm × 12 m). The products were separated and purified by column chromatography. Aldrich Florisil (60–100 mesh) or silica gel (70 μm) was used for column chromatography (2.5 × 25 cm) with hexane, petroleum ether, and/or chloroform as eluents.

Petroleum ether (50–70 °C) and hexane were stirred with sulfuric acid for 3–4 days and distilled before use. Chloroform and dioxane were purified by standard methods.[19] Trimethylchlorosilane was distilled from calcium hydride. Commercial zinc dust was used without further activation. Liquid ketones were distilled before use but solid ketones were used without purification. Sonication was performed on a Branson Model 220 (100–120 V, 50–60 Hz, 125 W) ultrasound cleaner filled with distilled water stabilized at 35 °C. The reaction flask was positioned at the point that gave maximum cavitation. All sonication reactions required mechanical stirring during sonication because the zinc dust was not dispersed through the reaction flask. Comparison reactions were run at 35 °C with magnetic stirring only. All reactions were carried out under a nitrogen atmosphere.

9-Fluorenone. General Procedure. With Sonication. Dioxane (10 mL) and 3.27 g of zinc dust (0.05 mol) were placed in a 100-mL three-neck flask. With stirring and sonication, 1.3 mL of trimethylchlorosilane (0.01 mol) was added followed by the addition of a solution of 1.802 g of 9-fluorenone (0.01 mol) in 10 mL of dioxane through a dropping funnel and the funnel was washed with 5 mL of dioxane. After 2 h of reaction, a standard workup procedure was used: The reaction mixture was filtered and the filtrate washed with petroleum ether. Solvents were evaporated under reduced pressure and the residue was mixed with hexane and filtered again. Evaporation of hexane gave crude product. Purification of the product by column chromatography on Florisil (2.5 × 20 cm) using petroleum ether as eluent gave 1.41 g (56% yield) of **1A**.

With Stirring. A reaction mixture of the same composition was stirred at 35 °C for 2 h. No reaction was observed. When the ratio of the reagents was changed (0.1 mol of zinc, 0.05 mol of trimethylchlorosilane, and 0.01 mol of 9-fluorenone), **1A** was obtained in 65% yield.

9,9′-Bis(trimethylsiloxy)-9,9′-bi-9*H*-fluorene (1A): ^{1}H NMR –0.27 (s, 18 H), 6.88–7.45 (m, 16 H); ^{13}C NMR 1.23 (CH$_3$), 118.6 (CH), 126.2 (CH), 128.5 (CH), 88.3 (C), 140.7 (C), 145.9 (C); IR 3073 (w), 3019 (m), 2960 (m), 1685 (w), 1254 (s), 1077 (m); MS, *m/e* (relative intensity) 491 (M^+ – 15, 0.7), 253 (M^+/2, 75), 139 (100), 73 (64). Anal. Found: C, 75.98 (calcd 75.86); H, 6.70 (calcd 6.76).

Benzaldehyde. Products were isolated by column chromatography (silica gel/petroleum ether). Sonication: **2A** (1.00 g, 56%), **2B** (0.137 g, 15%). Stirring: **2A** (0.75 g, 42%).

1,2-Bis(trimethylsiloxy)-1,2-diphenylethane (2A): ^{1}H NMR (I) –0.22 (s, 18 H), 4.4 (s, 2 H), 7.2–7.5 (m, 16 H); (II) 0.06 (s, 18 H), 4.65 (s, 2 H), 7.1–7.3 (m, 16 H) (I:II = 52:48); IR 3025 (m), 2950 (w), 1453 (w), 1253 (s), 1102 (s), 1069 (m), 871 (s), 845 (s); MS, *m/e* (relative intensity) 343 (M^+ – 15, 3.8), 179 (M^+/2, 98), 73 (Me$_3$Si, 100). Anal. Found: C, 66.85 (calcd 67.00); H, 8.47 (calcd 8.43).

***trans*-Stilbene (2B):** ^{1}H NMR 7.13 (s, 2 H), 7.21–7.65 (m, 8 H); IR 3083 (w) 3063 (w), 3016 (w), 1709 (w), 1601 (m), 1497 (s), 1453 (s), 963 (s), 695 (s); MS, *m/e* (relative intensity) 180 (M^+, 100), 179 (M^+ – 1, 98), 178 (M^+ – 2, 66), 89 ((M^+ – 2)/2, 27), 102 (M – 78, 13).

4-Chlorobenzaldehyde. Products were separated by column chromatography (Florisil/petroleum ether). Sonication: **3A** (1.55 g, 66%). Stirring: **3A** (1.56 g, 67%).

1,2-Bis(trimethylsiloxy)-1,2-bis(4′-chlorophenyl)ethane (3A): ^{1}H NMR (I) –0.15 (s, 18 H), 4.4 (s, 2 H), 7.3 (s, 8 H); (II) 0.05 (s, 18 H), 4.6 (s, 2 H), 6.9–7.2 (m, 10 H) (I:II = 50:50); MS, *m/e* (relative intensity) 411 (M^+ – 15, 3.27), 213 (M^+/2, 100), 215 (37.73), 163 (11), 73 (90.96).

Acetophenone. Products were separated by column chromatography (silica gel/hexane). Sonication: **4A** (1.26 g, 65%). Stirring: 4A (1.05 g, 54%).

1,2-Bis(trimethylsiloxy)-1,2-diphenylbutane (4A): ^{1}H NMR (I) –0.1 (s, 18 H), 1.4 (s, 6 H), 7.2–7.65 (m, 10 H); (II) 0.1 (s, 18 H), 1.78 (s, 6 H), 6.8–7.1 (m, 10 H) (I:II = 54:46); IR 3623 (w), 3012 (w), 2975 (m), 2361 (w), 1252 (s), 1148 (s), 857 (s); MS, *m/e* (relative intensity) 371 (M^+ – 15, 0.7), 193 (M^+/2, 100), 74 (91). Anal. Found: C, 68.07 (calcd 68.34); H, 8.70 (calcd 8.86).

4-Methylacetophenone. Product was isolated by column chromatography (silica gel/petroleum ether). Sonication: **5A** (1.58 g, 76%). Stirring: **5A** (1.30 g, 63%).

2,3-Bis(trimethylsiloxy)-2,3-bis(4′-methylphenyl)butane (5A): ^{1}H NMR (I) – 0.12 (s, 18 H), 1.35 (s, 6 H), 2.35 (s, 6 H), 7.07–7.53 (m, 8 H); (II) 0.1 (s, 18 H), 1.7 (s, 6 H), 2.26 (s, 6 H), 6.83 (s, 8 H) (I:II = 51:49); IR 3621 (m), 3013 (w), 2977 (s), 1252 (s), 1050 (s); MS, *m/e* (relative intensity) 207 (M^+/2, 100), 73 (39). Anal. Found: C, 69.55 (calcd 69.51); H, 9.35 (calcd 9.23).

4-Methoxyacetophenone. Product was purified by column chromatography (Florisil/petroleum ether). Sonication: **6A** (1.65 g, 74%). Stirring: **6A** (1.12 g 50%).

2,3-Bis(trimethylsiloxy)-2,3-bis(4′-methoxyphenyl)butane (6A): ^{1}H NMR (I) –0.1 (s, 18 H), 1.37 (s, 6 H), 3.85 (s, 6 H), 6.83–6.95 (d, 4 H), 7.45–7.55 (d, 4 H); (II) 0.13 (s, 18 H), 1.43 (s, 6 H), 3.87 (s, 6 H), 6.56–6.90 (m, 8 H), (I:II = 47:53); IR 3006 (w), 2962 (m), 2838 (w), 1611 (w), 1509 (s), 1253 (s), 1144 (m), 844 (s); MS, *m/e* (relative intensity) 431 (M^+ – 15, 7), 223 (M^+/2, 100), 73 (92). Anal. Found: C, 64.27 (calcd 64.53); H, 8.62 (calcd 8.57).

4-Fluoroacetophenone. Product was separated by column chromatography (Florisil/petroleum ether). Sonication: **7A** (1.32 g, 62%). Stirring: **7A** (1.02 g, 48%).

2,3-Bis(trimethylsiloxy)-2,3-bis(4′-fluorophenyl)butane (7A): ^{1}H NMR (I) –0.09 (s, 18 H), 1.40 (s, 6 H), 6.85–7.15 (m, 4 H), 7.35–7.60 (m, 4 H); (II) 0.09 (s, 18 H), 1.75 (s, 6 H), 6.65–6.85 (m, 8 H) (I:II = 55:45); IR 2960 (w), 1601 (w), 1507 (s), 1254 (s), 1144 (s), 845 (s); MS, *m/e* (relative intensity) 407 (M^+ – 15, 1.7), 211 (M^+/2, 98), 73 (100). Anal. Found: C, 62.39 (calcd 62.52); H, 7.80 (calcd 7.63).

4-Chloroacetophenone. Product was separated by column chromatography (Florisil/hexane). Sonication: **8A** (2.10 g, 85%). Stirring: **8A** (2.01 g, 81%).

2,3-Bis(trimethylsiloxy)-2,3-(4′-chlorophenyl)butane (8A): ^{1}H NMR (I) –0.1 (s, 18 H), 1.35 (s, 6 H), 7.15–7.5 (m, 10 H); (II) 0.1 (s, 18 H), 1.75 (s, 6 H), 6.8–7.2 (m, 10 H) (I:II = 34:66); MS, *m/e* (relative intensity) 439 (M^+ – 15, 1), 227 (M^+/2, 100), 212 (M^+/2 – 15, 1), 73 (40).

Benzophenone. Product was isolated by column chromatography (silica gel/hexane). Sonication: **9A** (2.14 g, 84%). Stirring: **9A** (1.66 g, 65%).

1,2-Bis(trimethylsiloxy)-1,1,2,2-tetraphenylethane (9A): ^{1}H NMR 0.02 (s, 18 H), 7.17 (s, 20 H); MS, *m/e* (relative intensity) 495 (M^+ – 15, 0.23), 255 (M^+/2, 100), 239 (84), 240 (60), 73 (94). Anal. Found: C, 74.87 (calcd 75.24); H, 7.67 (calcd 7.50%).

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(19) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*, 1st ed.; John Wiley & Sons Inc: New York, 1972; pp 430–436.

Acrolein. After standard workup procedures, 1.05 g (81%) of a *d*, *l*, and *meso* mixture was obtained (95% purity by GC). Attempts to further purify the product by vacuum distillation failed, and column chromatography (Florisil/hexane) or preparative GC led to partial decomposition and/or polymerization. No further attempt of purification was made. Stirring: **10A** (1.05 g, 81%).

3,4-Bis(trimethylsiloxy)-1,5-hexadiene (10A): ^{1}H NMR (I) 0.04 (s, 18 H), 3.9 (d, 2 H), 4.95–5.3 (m, 4 H), 5.6–6.2 (m, 2 H); (II) 0.05 (s, 18 H), 3.9 (d, 2 H), 4.95–5.3 (m, 4 H), 5.6–6.2 (m, 2 H); MS, *m/e* (relative intensity) 129 (M$^+$/2, 56.33), 113 (23), 73 (100); IR 3000 (s), 2920 (s), 1450 (m), 1250 (s), 1100 (s), 965 (s), 850 (s), 755 (m).

***trans*-Crotonaldehyde.** After standard workup procedures, 1.08 g (70%) of a *d*, *l*, and *meso* mixture was obtained (95% purity by GC). Attempts to further purify the product by vacuum distillation failed, and column chromatography (Florisil/hexane) or preparative GC led to partial decomposition and/or polymerization. No further attempt of purification was made. Stirring: **11A** (1.08 g, 70%).

4,5-Bis(trimethylsiloxy)-2,6-*trans*,*trans*-octadiene (11A): ^{1}H NMR (I) –0.05 (s, 18 H), 1.55 (s, 6 H), 3.75 (d, 2 H), 5.3–5.7 (m, 2 H); (II) 0.05 (s, 18 H), 1.50 (s, 6 H), 3.75 (d, 2 H), 5.3–5.75 (m, 2 H); MS, *m/e* (relative intensity) 271 (M$^+$ – 15, 0.3), 143 (M$^+$/2, 64), 73 (100); IR 3000 (m), 2990 (s), 1460 (m), 1450 (m), 1260 (s), 1100 (s), 960 (s), 860 (s), 750 (s).

2-Cyclohexenone. After standard workup procedures, 1.09 g (80%) of a *d*, *l* and *meso* mixture was obtained (90% purity by NMR). Attempts to further purify the product by vacuum distillation failed, and column chromatography (Florisil/hexane) or preparative GC led to partial decomposition and/or polymerization. No further attempt of purification was made. Stirring: **13A** (1.09 g, 80%).

1,1′-Bis(trimethylsiloxy)-1,1′-bi-2-cyclohexene (12A): ^{1}H NMR (I) 0.18 (s, 18 H), 1.4–2.3 (m, 12 H), 4.73 (d, 1 H), 5.6–6.2 (m, 1 H); (II) 0.3 (s, 18 H), 1.4–2.3 (m, 12 H), 4.73 (d, 1 H), 5.6–6.2 (m, 1 H) (I:II = 28:72); IR 3005 (m), 2940 (s), 2850 (s), 1650 (w), 1460 (m), 1360 (m), 1250 (s), 1200 (s), 1050 (s), 860 (s); MS, *m/e* (relative intensity) 323 (M$^+$ – 15, 0.38), 169 (M$^+$/2, 100), 154 (0.89), 75 (13.89), 73 (96.28).

Hydrolysis of Bis(trimethylsiloxy)alkanes. (A) With Lewis Acid. **6A** (0.223 g, 0.5 mmol) and 10 mL of CCl$_4$ were placed in a 50-mL flask. Then 113 mg of a trifluoroborane etherate solution (47%, 53 mg of trifluoroborane; 0.375 mmol) was added and the resulting solution was stirred for 10 min. The volume of mixture was decreased with reduced pressure to 5 mL, then 20 mL of methylene chloride and 10 mL of water were added, and the mixture was stirred for 30 min. The organic layer was separated and washed with 5 mL of water twice and dried over sodium sulfate anhydride. Solvent was removed under reduced pressure to give 3,3-bis(4′-methoxyphenyl)-2-butanone (0.135 g, 95% yield).

3,3-Bis(4′-methoxyphenyl)-2-butanone: ^{1}H NMR 1.78 (s, 3 H), 2.07 (s, 3 H), 3.90 (s, 6 H), 6.7–7.3 (m, 8 H); IR 3021 (s), 2840 (w), 1710 (s), 1609 (w), 1513 (s), 1255 (s), 1183 (m); MS, *m/e* (relative intensity) 241 (M$^+$ – 43, 100), 193 (60), 105 (5.2).

(B) With Tetrabutylammonium Fluoride.[20] **4A** (0.55 g, 14 mmol), 5 mL of THF, and 2.8 mL of a 1 M solution of tetrabutylammonium fluoride in THF (contains 5% of water) were placed in a 50-mL flask. The mixture was refluxed for 4 h with stirring. The solvent was evaporated at reduced pressure, and the mixture was washed with water, extracted with ether, and dried over magnesium sulfate anhydrous. Solvent was evaporated at reduced pressure to give a colorless solid. Recrystallization from ether gave 2,3-diphenylbutane-2,3-diol (320 mg, 91% yield).

2,3-Diphenylbutane-2,3-diol: mp 110–112 C; ^{1}H NMR (I) 1.53 (s, 6 H), 2.3 (br, 1 H), 7.25 (s, 10 H); (II) 1.6 (s, 6 H), 1.3 (br, 1 H), 7.25 (s, 10 H) (I:II = 49:51); MS, *m/e* (relative intensity) 165 (M$^+$ – 77, 1.3), 121 (M$^+$/2, 100), 105 (15), 77 (34).

Rate Study. Zinc powder (20 mmol), 50 μL of decane as internal standard, and 10 mL of THF were placed in a 100-mL flask. Under nitrogen, trimethylchlorosilane (4.8 mmol) was added to the flask, followed by addition of carbonyl compound (4 mmol) at 35 °C. Reaction samples were taken from the flask every 5 min and stored with dry ice after being diluted with hexane until analyzed by GC. Reaction rates were measured by the depletion of the reactant, reaction was stopped when there was less than 1% of unreacted carbonyl compound, and the mixture was worked up as usual.

2,3-Bis(trimethylsiloxy)-2,3-bis(3′-methoxyphenyl)butane: ^{1}H NMR (I) –0.05 (s, 18 H), 1.4 (s, 6 H), 3.83 (s, 6 H), 7.0–7.4 (m, 8 H); (II) 0.15 (s, 18 H), 1.8 (s, 6 H), 3.6 (s, 6 H), 6.4–7.0 (m, 8 H); MS, *m/e* (relative intensity) 431 (M$^+$ – 15, 0.76), 223 (M$^+$/2, 100), 208 (6.4), 73 (100).

2,3-Bis(trimethylsiloxy)-2,3-bis(3′-chlorophenyl)butane: ^{1}H NMR (I) –0.01 (s, 18 H), 1.4 (s, 6 H), 6.6–7.6 (m, 8 H); (II) 0.11 (s, 18 H), 1.8 (s, 6 H), 6.6–7.6 (m, 8 H); MS, *m/e* (relative intensity) 229 (20.8), 227 (M$^+$/2, 56.32), 211 (5.34), 73 (100).

Cross-Coupling Reaction of Acetophenone and 4-Chloroacetophenone. General Procedure. Zinc powder (20 mmol), 20 μL of decane as internal standard, and 10 mL of THF were placed in a 100-mL flask. At 35 °C, 4.8 mmol of trimethylchlorosilane and a mixture of 2 mmol of acetophenone and 2 mmol of 4-chloroacetophenone were added to the flask with stirring. After 2 h of stirring, GC analysis of the reaction mixture showed no carbonyls but three major products. Products were analysed by GC with an authentic sample as well as with GC-MS and ^{1}H NMR. Products separation involved Florisil column chromatography with hexane as eluent.

2,3-Bis(trimethylsiloxy)-2-(4′-chlorophenyl)-3-phenylbutane: ^{1}H NMR (I) –0.1 (s, 18 H), 1.4 (s, 6 H), 6.7–7.6 (m, 9 H); (II) 0.1 (s, 18 H), 1.8 (s, 6 H), 6.7–7.6 (m, 9 H); MS, *m/e* (relative intensity) 407 (1.15), 405 (M$^+$ – 15, 2.74), 229 (12.27), 227 (34.22), 193 (100), 73 (100).

2,3-Bis(trimethylsiloxy)-2-(4′-methoxyphenyl)-3-(4′-methylphenyl)butane: ^{1}H NMR (I)- –0.05 (s, 18 H), 1.45 (s, 6 H), 2.45 (s, 3 H), 3.85 (s, 3 H), 6.6–7.6 (m, 8 H); (II) 0.15 (s, 18 H), 1.8 (s, 6 H), 2.38 (s, 3 H), 3.9 (s, 3 H), 6.6–7.6 (m, 8 H); MS, *m/e* (relative intensity) 415 (M$^+$ – 15, 1.1), 223 (100), 207 (17.63), 73 (36.3).

2,3-Bis(trimethylsiloxy)-2-(3′-chlorophenyl)-3-phenylbutane: ^{1}H NMR (I) 0.01 (s, 1 H), 1.45 (s, 6 H), 6.6–7.7 (m, 9 H); (II) 0.15 (s, 18 H), 1.8 (s, 6 H), 6.6–7.7 (m, 9 H); MS, *m/e* (relative intensity) 407 (1.25), 4.5 (M$^+$ – 15, 2.96), 229 (6.32), 227 (16, 88), 193 (100), 177 (22.37), 73 (100).

2,3-Bis(trimethylsiloxy)-2-(4′-chlorophenyl)-3-(4′-methoxyphenyl)butane: ^{1}H NMR (I) –0.07 (s, 18 H), 1.4 (s, 3 H), 3.78 (s, 3 H), 6.5–7.6 (m, 8 H); (II) 0.07 (s, 18 H), 1.8 (s, 6 H), 2.35 (s, 3 H), 6.8–7.7 (m, 8 H); MS, *m/e* (relative intensity) 437 (1.19), 435 (M$^+$ – 15, 2.11), 229 (2.15), 227 (5.37), 223 (100), 73 (73.44).

2,3-Bis(trimethylsiloxy)-2-(4′-chlorophenyl)-3-(4′-methylphenyl)butane: ^{1}H NMR (I) –0.05 (s, 18 H), 1.4 (s, 6 H), 2.4 (s, 3 H), 6.7–7.6 (m, 8 H); (II) 0.11 (s, 1, H), 1.78 (s, 6 H), 2.35 (s, 3 H), 6.7–7.6 (m, 8 H); MS, *m/e* (relative intensity) 421 (0.9), 419 (M$^+$ – 15, 1.2), 229 (2.2), 227 (5.6), 207 (100), 73 (89).

2,3-Bis(trimethylsiloxy)-2-(4′-methoxyphenyl)-3-phenylbutane: ^{1}H NMR (I) –0.1 (s, 18 H), 1.43 (s, 3 H), 1.45 (s, 3 H), 3.85 (s, 3 H), 6.5–7.7 (m, 9 H); (II) 0.1 (s, 18 H), 1.75 (s, 3 H), 1.79 (s, 3 H), 3.8 (s, 3 H), 6.5–7.7 (m, 9 H); MS, *m/e* (relative intensity) 401 (M$^+$ – 15, 1.77), 223 (100), 193 (5.93), 73 (28.32).

2,3-Bis(trimethylsiloxy)-2-(4′-methylphenyl)-3-phenylbutane: ^{1}H NMR (I) –0.1 (s, 18 H), 1.43 (s, 6 H), 2.43 (s, 3 H), 6.8–7.7 (m, 9 H); (II) 0.07 (s, 18 H), 1.8 (s, 6 H), 2.35 (s, 3 H), 6.8–7.7 (m, 9 H); MS, *m/e* (relative intensity) 385 (M$^+$ – 15, 0.5), 2.7 (100), 193 (24.93), 73 (32.68).

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[20] Corey, E. J.; Snider, B. B. *J. Am. Chem. Soc.* **1972**, *94*, 2549–2550.

[21] The mixture of **5A** (0.5 mmol) and ZnCl$_2$·2H$_2$O (2.9 mmol) in 10 mL of THF was stirred at room temperature for 12 h. GC analysis of the mixture showed no decrease of **5A** or new product.