Facile Syntheses of Precursors of 2-Alkyl-3-(trimethylsilyl)-1,3-butadienes and Their Diels-Alder Reactions

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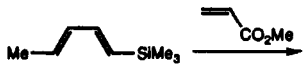
Organosilicon compounds are very useful in organic synthesis.[1] The silicon group can stabilize a β-carbocation.[2] In this respect, vinylsilanes and allylsilanes can readily undergo electrophilic substitution reactions.[3] The silicon group can also stabilize an α-carbanion.[4] In this way, the Peterson reaction can be used to synthesize functionalized alkenes.[5] Silyl-substituted dienes have been used in Diels-Alder reactions to prepare allyl- and vinylsilanes. For example, Fleming reported that 1-methyl-4-(trimethylsilyl)-1,3-butadiene (1) reacts with methyl acrylate to give the cyclization products 2 and 3 (eq 1).[6] The product



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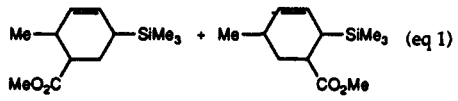
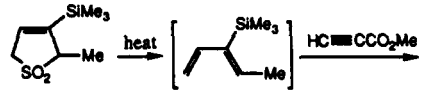


2 (44%) 3 (22%) (eq 1)

ratio revealed that the 4-(trimethylsilyl) substituent hampered the regioselectivity induced by the 1-methyl group. Substituted 3-sulfolenes are good precursors to the 1,3-dienes.[7] In this regard, 2-methyl-3-(trimethylsilyl)-3-sulfolene (4) has been used to generate 1-methyl-2-(trimethylsilyl)-1,3-butadiene (5) which can be trapped in the Diels-Alder reaction with methyl propynoate to give products 6 and 7 (eq 2).[8] The methyl group is also



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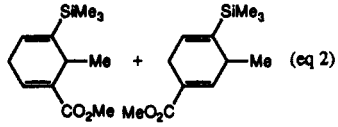
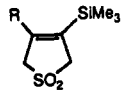


6 (38%) 7 (19%) (eq 2)

more dominant than the silyl group in determining the regiochemistry of the cycloaddition.

We have been interested in the synthetic applications of sulfur-substituted 3-sulfolenes.[9] We now report the first synthesis of 3-alkyl-4-(trimethylsilyl)-3-sulfolenes 8a-f, thermolysis to 2-alkyl-3-(trimethylsilyl)-1,3-butadienes 9, and the regiochemistry of the Diels-Alder reaction.



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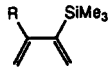

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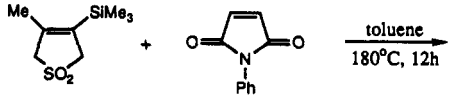
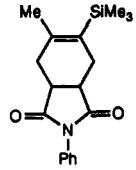
Results and Discussion

The preparation of 8 is shown in Scheme I. Oxidation of 3-(phenylthio)-4-(trimethylsilyl)-3-sulfolene (10)[9g] with *m*-CPBA (4 equiv) gave the corresponding sulfone 11 in 96% yield. Deprotonation of 11 with *n*-BuLi in THF at -78 °C in the presence of HMPA (8 equiv) followed by the addition of an alkyl halide gave the alkylation product 12. The yields were low for more hindered alkyl halides. Desulfonylation[9j] with Na/Hg and phosphoric acid in THF at reflux for 12-15 h led to the 3-sulfolenes 8 in excellent yield (Table I).

That the 3-sulfolenes 8 are convenient precursors of the dienes 9 was shown by carrying out the Diels-Alder reactions directly with 8. For example, heating of 8a with *N*-phenylmaleimide in toluene at 180 °C gave the cycloaddition product 13 in 81% yield (eq 3). The reaction



8a



13 (81%) (eq 3)

of 8a with methyl propynoate in DMA at 165 °C led to the cyclohexadienes 14 and 15 (2:1) in 54% yield (eq 4). The

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Scheme I

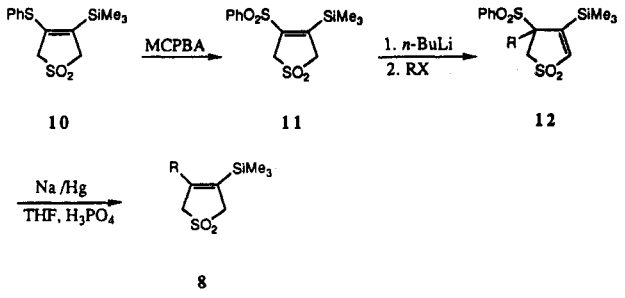
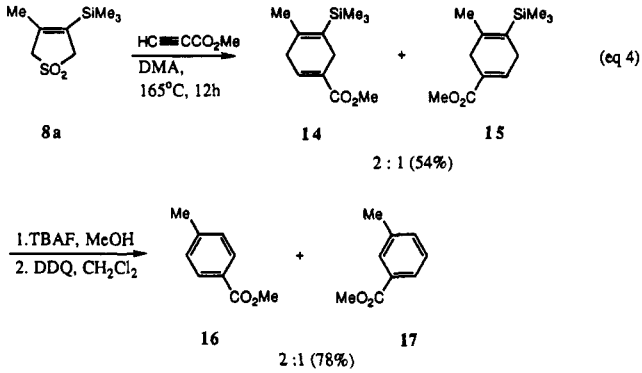


Table I. Alkylation of 11 and Desulfonylation of 12

entry	alkylating agent	12 (yield, %)	8 (yield, %)
1	CH_3I	**12a** (83)	**8a** (94)
2	C_2H_5I	**12b** (67)	**8b** (91)
3	$CH_2{=}CHCH_2Br$	**12c** (65)	**8c** (83)
4	$PhCH_2Br$	**12d** (61)	**8d** (89)
5	$CH_2{=}CH(CH_2)_3I$	**12e** (37)	**8e** (81)
6	$CH_2{=}CH(CH_2)_4I$	**12f** (33)	**8f** (85)

structures of 14 and 15 were determined by desilylation with tetra-*n*-butylammonium fluoride (TBAF) in methanol followed by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to give the corresponding methyl 4-toluenecarboxylate (**16**)[11] and methyl 3-toluenecarboxylate (**17**)[12] (eq 4). Thus, the regiochemistry of the Diels–



(eq 4)

Alder reaction of diene **9a** reflects the stronger directing effect of the methyl group, with little directing influence from the trimethylsilyl substituent.

In summary, we have developed a facile synthesis of 3-alkyl-4-(trimethylsilyl)-3-sulfolenes, which generates silyl-substituted dienes upon thermolysis. The regioselectivity observed in the subsequent Diels–Alder trapping of the silyl dienes supplements earlier findings that the trimethylsilyl substituent is weakly ortho,para-directing and only weakly opposes the directing effect of a methyl group.

Experimental Section

^1H and ^{13}C NMR spectra were measured in $CDCl_3$ at 300 and 75 MHz, respectively, with tetramethylsilane as the internal standard. HPLC was carried out with a LiChrosorb (Merck) column. The silica gel used for flash chromatography was made by Merck (60 H). All reagents were of reagent grade and were purified prior to use.[13]

3-(Phenylsulfonyl)-4-(trimethylsilyl)-3-sulfolene (11). To a solution of 3-(phenylthio)-4-(trimethylsilyl)-3-sulfolene (**10**)[9g] (6.0 g, 0.020 mol) in CH_2Cl_2 (50 mL) at 0 °C was added *m*-CPBA (13.8 g, 0.080 mol). The mixture was stirred at rt for 16 h and was washed sequentially with an aqueous $NaHCO_3$ solution and $Na_2S_2O_3$ solution. The solvent was removed by rotary evaporation, and pure product **11** (6.3 g, 96% yield) was obtained after recrystallization from ether: mp 186–187 °C; IR (KBr) 2950, 2150, 1380, 1300, 1200, 1180, 1120, 900, 850, 740, 730, 680, 650 cm^{-1}; ^1H NMR δ 0.40 (9 H, s), 3.82 (2 H, s), 4.09 (2 H, s), 7.56–7.85 (5 H, m); ^{13}C NMR δ 0.1, 55.9, 63.6, 128.0, 129.7, 134.5, 137.3, 142.4, 151.2; MS (relative intensity) *m/z* 330 (M^+, 1), 315 (20), 215 (100), 135 (50), 73 (73); exact mass calcd for $[C_{12}H_{15}O_4S_2Si]^+$ (M^+ – 15) *m/z* 315.0189, found 315.0179.

General Procedure for the Preparation of 12. To a solution of **11** (0.20 g, 0.60 mmol) and HMPA (0.80 mL) in THF (20 mL) at –78 °C was added *n*-BuLi/hexane (0.41 mL, 1.6 M, 0.66 mmol) dropwise. The mixture was stirred for another 10 min, and the alkyl halide (2.4 mmol) was added in one portion. The solution was slowly warmed to –10 °C. The solvent was removed under vacuum, and the crude product was purified by flash chromatography using hexane/ethyl acetate (3:1) as eluent. The products **12** were recrystallized from a mixture of hexane and ethyl acetate.

4-Methyl-4-(phenylsulfonyl)-3-(trimethylsilyl)-2-sulfolene (12a): yield 171 mg (83%); mp 163–164 °C; IR (KBr) 2960, 1460, 1380, 1300, 1210, 1150, 1120, 870, 780, 760, 680 cm^{-1}; ^1H NMR δ 0.45 (9 H, s), 1.71 (3 H, s), 2.75 (1 H, d, J = 13.4 Hz), 3.80 (1 H, d, J = 13.4 Hz), 6.84 (1 H, s), 7.56–7.85 (5 H, m); ^{13}C NMR δ 0.6, 23.2, 36.8, 73.7, 129.5, 130.3, 134.9, 135.3, 142.1, 154.3; MS (relative intensity) *m/z* 329 (M^+ – 15, 50), 315 (45), 203 (100), 139 (60), 73 (73); exact mass calcd for $[C_{13}H_{17}O_4S_2Si]^+$ (M^+ – 15) *m/z* 329.0338, found 329.0345.

4-Ethyl-4-(phenylsulfonyl)-3-(trimethylsilyl)-2-sulfolene (12b): yield 144 mg (67%); mp 152.5–153.5 °C; IR (KBr) 3060, 1400, 1330, 1240, 1150, 1120, 870, 780, 760, 680 cm^{-1}; ^1H NMR δ 0.45 (9 H, s), 0.89 (3 H, t, J = 7.5 Hz), 1.70–1.80 (1 H, m), 2.47–2.55 (1 H, m), 2.87 (1 H, d, J = 14.6 Hz), 3.62 (1 H, d, J = 14.6 Hz), 6.92 (1 H, s), 7.56–7.85 (5 H, m); ^{13}C NMR δ 0.4, 8.4, 12.2, 27.1, 53.3, 129.5, 130.5, 134.8, 135.2, 144.5, 152.3; MS (relative intensity) *m/z* 343 (M^+ – 15, 20), 315 (10), 279 (8), 217 (100), 73 (100); exact mass calcd for $[C_{14}H_{19}O_4S_2Si]^+$ (M^+ – 15) *m/z* 343.0494, found 343.0491.

4-(Phenylsulfonyl)-4-(2-propenyl)-3-(trimethylsilyl)-2-sulfolene (12c): yield 144 mg (65%); mp 144.5–145.5 °C; IR (KBr) 3010, 1390, 1330, 1240, 1180, 1100, 870, 780, 760, 680 cm^{-1}; ^1H NMR δ 0.45 (9 H, s), 2.50 (1 H, dd, J = 8.2, 6.1 Hz), 3.01 (1 H, d, J = 14.7 Hz), 3.26 (1 H, dd, J = 8.2, 6.1 Hz), 3.55 (1 H, d, J = 14.7 Hz), 5.18–5.55 (3 H, m), 6.88 (1 H, s), 7.60–7.85 (5 H, m); ^{13}C NMR δ 1.0, 38.0, 52.5, 76.5, 121.3, 129.0, 129.5, 130.6, 134.8, 135.0, 144.8, 152.1; MS (relative intensity) *m/z* 355 (M^+ – 15, 10), 291 (8), 229 (100), 73 (100); exact mass calcd for $[C_{15}H_{19}O_4S_2Si]^+$ (M^+ – 15) *m/z* 355.0494, found 355.0484.

4-Benzyl-4-(phenylsulfonyl)-3-(trimethylsilyl)-2-sulfolene (12d): yield 154 mg (61%); mp 187–188 °C; IR (KBr) 3010, 2980, 1360, 1320, 1240, 1180, 1100, 870, 780, 775, 760, 725, 680 cm^{-1}; ^1H NMR δ 0.56 (9 H, s), 3.02 (1 H, d, J = 14.6 Hz), 3.09 (1 H, d, J = 14.2 Hz), 3.54 (1 H, d, J = 14.6 Hz), 3.83 (1 H, d, J = 14.2 Hz), 6.86 (1 H, s), 6.96 (2 H, br s), 7.28 (3 H, br s), 7.64–7.95 (5 H, m); ^{13}C NMR δ 1.2, 38.8; 51.7, 78.6, 128.0, 128.8, 129.4, 130.2, 130.6, 132.5, 134.7, 134.9, 144.6, 155.5; MS (relative intensity) *m/z* 420 (M^+, 0.1), 405 (7), 279 (100), 263 (5), 73 (100); exact mass calcd for $C_{20}H_{24}O_4S_2Si$ *m/z* 420.0886, found 420.0889.

4-(4-Pentenyl)-4-(phenylsulfonyl)-3-(trimethylsilyl)-2-sulfolene (12e): yield 88 mg (37%); mp 149–150 °C; IR (KBr) 2950, 1610, 1570, 1550, 1475, 1300, 1250, 1040, 885, 760 cm^{-1}; ^1H NMR δ 0.42 (9 H, s), 1.03–1.20 (1 H, m), 1.30–1.50 (1 H, m), 1.60–1.80 (1 H, m), 1.95–2.15 (2 H, m), 2.40–2.52 (1 H, m), 2.87 (1 H, d, J = 14.7 Hz), 3.61 (1 H, d, J = 14.7 Hz), 4.90–5.10 (2 H, m), 5.60–5.80 (1 H, m), 6.88 (1 H, s), 7.58–7.87 (5 H, m); ^{13}C NMR δ 0.4, 22.0, 33.3, 33.4, 54.2, 78.0, 115.4, 130.6, 134.0, 134.5, 134.6, 137.1, 143.4, 152.2; MS (relative intensity) *m/z* 383 (M^+ – 15, 7), 319 (2), 257 (100), 135 (35), 73 (100); exact mass calcd for $[C_{17}H_{23}O_4S_2Si]^+$ (M^+ – 15) *m/z* 383.0808, found 383.0808.

4-(5-Hexenyl)-4-(phenylsulfonyl)-3-(trimethylsilyl)-2-sulfolene (12f): yield 82 mg (33%); mp 145–146 °C; IR (KBr) 3010, 1610, 1595, 1550, 1475, 1330, 1250, 1040, 885, 760 cm^{-1}; ^1H

(11) *Handbook of Proton NMR Spectra and Data*; Asahi Research Center, Ed.; Academic Press: New York, 1985; Vol. 3, p 314.

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(13) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd Ed.; Pergamon Press: New York, 1980.

NMR δ 0.42 (9 H, s), 1.10–1.41 (4 H, m), 1.50–1.65 (1 H, m), 1.95–2.10 (2 H, m), 2.40–2.55 (1 H, m), 2.89 (1 H, d, J = 14.7 Hz), 3.60 (1 H, d, J = 14.7 Hz), 4.91–5.02 (2 H, m), 5.65–5.82 (1 H, m), 6.88 (1 H, s), 7.58–7.87 (5 H, m); ^{13}C NMR δ 0.7, 23.4, 28.4, 33.1, 33.5, 53.5, 78.3, 115.2, 129.4, 130.4, 134.8, 134.9, 137.7, 144.1, 151.0; MS (relative intensity) m/z 412 (M^+, 0.1), 397 (7), 271 (100), 135 (20), 73 (100); exact mass calcd for $C_{19}H_{28}O_4S_2Si$ m/z 412.1200, found 412.1216.

General Procedure for Preparation of 8. A mixture of 12 (0.60 mmol), 6% sodium amalgam (1.10 g), and 3 drops of 85% H_3PO_4 in THF (25 mL) was refluxed under N_2 for 12–16 h. The mixture was cooled to rt, filtered with Celite, evaporated, and purified by flash chromatography using hexane/ethyl acetate (6:1) as eluent to give 8 as colorless liquids.

3-Methyl-4-(trimethylsilyl)-3-sulfolene (8a): yield 115 mg (94%); IR (neat) 2910, 1605, 1535, 1505, 1475, 1380, 1210, 1050 cm^{-1}; ^{1}H NMR δ 0.20 (9 H, s), 1.92 (3 H, s), 3.73 (2 H, s), 3.80 (2 H, s); MS (relative intensity) m/z 204 (M^+, 10), 185 (7), 140 (20), 125 (25), 73 (100); exact mass calcd for $C_8H_{16}O_2SSi$ m/z 204.0641, found 204.0633.

3-Ethyl-4-(trimethylsilyl)-3-sulfolene (8b): yield 119 mg (91%); IR (neat) 3010, 1625, 1535, 1485, 1410, 1375, 1310, 1210, 1050 cm^{-1}; ^{1}H NMR δ 0.19 (9 H, s), 0.91 (3 H, t, J = 9.1 Hz), 2.83 (2 H, q, J = 9.1 Hz), 3.73 (2 H, s), 3.80 (2 H, s); MS (relative intensity) m/z 218 (M^+, 12), 203 (25), 155 (11), 123 (9), 73 (100); exact mass calcd for $C_9H_{18}O_2SSi$ m/z 218.0800, found 218.0812.

3-(2-Propenyl)-4-(trimethylsilyl)-3-sulfolene (8c): yield 115 mg (83%); IR (neat) 3010, 1625, 1535, 1485, 1410, 1375, 1310, 1210, 1050 cm^{-1}; ^{1}H NMR δ 0.19 (9 H, s), 2.95–3.05 (2 H, m), 3.71 (2 H, s), 3.82 (2 H, s), 5.05–5.20 (2 H, m), 5.60–5.80 (1 H, m); ^{13}C NMR δ −0.40, 37.8, 59.5, 61.8, 118.0, 133.6, 133.8, 143.9; MS (relative intensity) m/z 230 (M^+, 5), 215 (7), 205 (10), 151 (15), 123 (11), 73 (100); exact mass calcd for $C_{10}H_{18}O_2SSi$ 230.0800, found 230.0803.

3-Benzyl-4-(trimethylsilyl)-3-sulfolene (8d): yield 150 mg (89%); IR (neat) 3110, 1615, 1535, 1505, 1475, 1380, 1210, 1050, 890, 775 cm^{-1}; ^{1}H NMR δ 0.25 (9 H, s), 3.55 (2 H, s), 3.63 (2 H, s), 3.89 (2 H, s), 7.10–7.38 (5 H, m); ^{13}C NMR δ −0.40, 39.5, 58.8, 61.3, 127.4, 128.8, 129.3, 133.1, 136.9, 144.4; MS (relative intensity) m/z 280 (M^+, 8), 265 (10), 215 (20), 142 (25), 91 (17), 73 (100); exact mass calcd for $C_{14}H_{19}O_2SSi$ m/z 280.0954, found 280.0950.

3-(4-Pentenyl)-4-(trimethylsilyl)-3-sulfolene (8e): yield 125 mg (81%); IR (neat) 2950, 1605, 1575, 1505, 1475, 1440, 1350, 1210, 1050 cm^{-1}; ^{1}H NMR δ 0.12 (9 H, s), 1.42–1.53 (2 H, m), 2.00–2.10 (2 H, m), 2.20–2.30 (2 H, m), 3.79 (2 H, s), 3.82 (2 H, s), 4.96–5.06 (2 H, m), 5.70–5.82 (1 H, m); ^{13}C NMR δ −0.40, 27.5, 33.2, 33.4, 58.8, 61.2, 122.3, 127.0, 137.5, 146.0; MS (relative intensity) m/z 258 (M^+, 2), 204 (6), 179 (8), 137 (13), 121 (33), 73 (100); exact mass calcd for $C_{12}H_{21}O_2SSi$ m/z 258.1107, found 258.1110.

3-(5-Hexenyl)-4-(trimethylsilyl)-3-sulfolene (8f): yield 139 mg (85%); IR (neat) 2970, 1625, 1565, 1505, 1475, 1440, 1350, 1210, 1050 cm^{-1}; ^{1}H NMR δ 0.19 (9 H, s), 1.30–1.42 (4 H, m), 2.00–2.10 (2 H, m), 2.20–2.30 (2 H, m), 3.71 (2 H, s), 3.78 (2 H, s), 4.92–5.05 (2 H, m), 5.70–5.90 (1 H, m); ^{13}C NMR δ −0.40, 27.8, 28.8, 33.7, 33.8, 59.0, 61.2, 115.0, 131.7, 138.5, 146.5; MS (relative intensity) m/z 272 (M^+, 0.1), 250 (2), 135 (10), 93 (17), 73 (100); exact mass calcd for $C_{13}H_{23}O_2SSi$ m/z 272.1260, found 272.1267.

***N*-Phenyl-4-methyl-5-(trimethylsilyl)-1,2,3,6-tetrahydrophthalimide (13).** A mixture of 8a (0.20 g, 0.98 mmol), *N*-phenylmaleimide (0.59 g, 3.92 mmol), and hydroquinone (10 mg) in toluene (17 mL) was heated in a sealed tube at 165 °C for 12 h. The solvent was then removed under vacuum, and the crude product was purified by flash chromatography using hexane/ethyl acetate (10:1) as eluent to give 13 (0.25 g, 81% yield): IR (neat) 2980, 1780, 1445, 1380, 1210, 1180, 880, 760 cm^{-1}; ^{1}H NMR δ 0.10 (9 H, s), 1.91 (3 H, s), 2.10–2.20 (1 H, m), 2.25–2.35 (1 H, m), 2.55–2.70 (2 H, m), 3.15–3.25 (2 H, m), 7.16–7.44 (5 H, m); MS (relative intensity) m/z 313 (M^+, 14), 299 (41), 298 (100), 73 (32); exact mass calcd for $C_{18}H_{23}NO_2Si$ m/z 313.1499, found 313.1496.

Methyl 4-Methyl-5-(trimethylsilyl)-1,4-cyclohexadienecarboxylate (14) and Methyl 5-Methyl-4-(trimethylsilyl)-1,4-cyclohexadienecarboxylate (15). A mixture of 8a (0.20 g, 0.98 mmol), methyl propynoate (0.33 g, 3.9 mmol), and hydroquinone (10 mg) in *N*,*N*-dimethylaniline (7 mL) was heated in a sealed tube at 165 °C for 12 h. The solvent was removed by rotary evaporation, and the crude product was purified by flash chromatography using hexane/ethyl acetate (10:1) as eluent to give a mixture of 14 and 15 (2:1, 54% yield). These two compounds could not be separated by HPLC. The following data were measured for the mixture: IR (neat) 2930, 1750, 1560, 1480, 1430, 1380, 1230, 1165, 1010 cm^{-1}; ^{1}H NMR δ 0.15 (s), 1.78 (s), 1.90 (s), 2.70–2.95 (m), 3.72 (s), 6.86–6.98 (m); the two isomers have distinct ^{1}NMR absorptions at δ 1.78 and 1.90, respectively. The structures of 14 and 15 were proven by conversion to 16 and 17 (see below). The mass spectra of 14 and 15 showed that they were aromatized to $C_{12}H_{18}O_2Si$ by dehydrogenation during the measurement; MS (relative intensity) m/z 222 (M^+, 26), 207 (100), 110 (38), 73 (17); exact mass calcd for $C_{12}H_{18}O_2Si$ m/z 222.1076, found 222.1069.

Conversion of 14 and 15 to Methyl 4-Toluenecarboxylate (16) and Methyl 3-Toluenecarboxylate (17). To a mixture of 14 and 15 (50 mg) in methanol (5 mL) was added tetra-*n*-butylammonium fluoride (200 mg). The mixture was stirred at rt for 16 h. The solvent was then removed under vacuum, and the residue was partitioned between CH_2Cl_2 and water. The organic layer was dried and evaporated, and the crude product was purified by flash chromatography using hexane/ethyl acetate (20:1) to give a colorless liquid (29 mg) which was treated with DDQ (200 mg, 0.88 mmol) and CH_2Cl_2 (3 mL) at rt for 8 h. The solvent was evaporated under vacuum, and the crude product was purified by flash chromatography using hexane as eluent to give a 2:1 mixture of 16 and 17 (27 mg, 78% yield). The structures and ratio of 16 and 17 were determined from the ^{1}H NMR spectrum, and the data match well with the literature values.[11,12] The ^{1}H NMR spectrum of the mixture of 16 and 17 indicates that both of the benzylic methyl groups appear at δ 2.40 and the two carbomethoxy groups are almost inseparable at δ 3.897 and 3.906. However, 16 has two doublets (J = 9.0 Hz) at δ 7.23 and 7.92, whereas 17 has two multiplets at δ 7.30–7.45 and 7.82–7.90.

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Supplementary Material Available: ^{1}H NMR spectra of all compounds (16 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.