Table I. 3-Alkyl-Substituted Isoprenylsilanes 4[a]

entry	NH_4^+ salt	RMgX	molar ratio of 3 to 2	product	yield, %
1	2a	BuMgBr (3a)	1.2	4a	11
2	2a	3a	4.1	4a	88
3	2a	3a[b]	4.1	4a	36
4	2a	3a[c]	4.1	4a	29
5	2a	3a[d]	4.1	4a	49
6	2b	3a	1.2	4a	38
7	2b	3a	2.5	4a	52
8	2c	3a	2.5	4a	92
9	2a	$PhCH_2MgCl$ (3b)	8.4	4b	91
10	2b	3b	3.5	4b	72
11	2c	3b	3.5	4b	92
12	2a	PhMgBr (3c)	8.4	4c	84
13	2b	3c	3.5	4c	65
14	2c	3c	3.5	4c	85
15	2a	Me_3SiCH_2MgCl (3d)	8.4	4d	87
16	2b	3d	3.5	4d	79
17	2c	3d	3.5	4d	89

[a] All reactions were carried out in tetrahydrofuran at −40 to −20 °C for 3 h and then −20 °C to room temperature for 3.5 h in the presence of dilithium tetrachlorocuprate, unless otherwise stated. [b] Cuprous chloride was used as a catalyst. [c] Cuprous bromide was used. [d] Cuprous iodide was used.

ticular, such as dilithium tetrachlorocuprate was effective[4] and the expected 3-pentyl-2-[(trimethylsilyl)methyl]-1,3-butadiene (**4a**) was obtained in excellent yield. However, use of cuprous chloride, cuprous bromide, and cuprous iodide as catalysts did not give satisfactory results. The yield of **4** depends on the ratio of **2** to **3**. Thus, a large excess of the Grignard reagent is required to attain improvement of the yield.

It is noteworthy that the butylammonium salt **2b** and the benzylammonium salt **2c** give more satisfactory results than **2a**, presumably due to the higher solubility of the ammonium salt in the reaction medium.

Thus, alkyl and aryl Grignard reagents react with **2** to afford the desired 3-substituted isoprenylsilanes **4**, which can be viewed as useful nucleophilic reagents for the introduction of a 1,3-diene skeleton and as highly reactive 1,3-dienes. The present reaction might be applicable to other functionalized Grignard reagents and open a way to a variety of functionalized isoprenylsilanes, useful in organic synthesis, that are otherwise inaccessible.

Experimental Section

3-Alkyl-Substituted Isoprenylsilanes 4. General Procedure. The ammonium salt **2** was prepared from **1** (116 mg, 0.59 mmol) and a small excess of the corresponding alkyl halide in dry THF (5 mL) at room temperature under argon. Without isolation of **2**, the Grignard reagent **3**, which was prepared from the halide (2.1–2.7 mmol) and an excess of magnesium in THF in a separate flask, was added to the solution of **2** in the presence of dilithium tetrachlorocuprate[5] (0.10 mmol, 2 mL of 0.05 M THF solution) at −40 °C. The resulting mixture was stirred magnetically for 3 h at −40 to −20 °C and for 3.5 h at −20 °C to room temperature. After hydrolysis with water (10 mL), extractive workup with ether (20 mL × 3), and drying over sodium sulfate, the solvent was evaporated and the residue was subjected to preparative TLC (silica gel) using hexane as an eluent to give pure **4**.

Because of the similarity of structures for **4**, spectral data are reported in the following tabulation.

3-Methylene-2-[(trimethylsilyl)methyl]-1-octene (**4a**): ^1H NMR (CCl_4) δ 0.07 (s, 9 H), 0.98 (t, J = 6.8 Hz, 3 H), 1.14–1.76 (m, 4 H), 1.84 (br s, 2 H), 2.17–2.42 (m, 2 H), 4.79 (br s, 1 H), 4.98 (br s, 1 H), 5.00–5.10 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.17 (q), 14.10 (q), 22.59 (t), 24.28 (t), 28.72 (t), 31.92 (t), 34.14 (t), 109.80 (t), 112.08 (t), 145.18 (s), 148.70 (s); IR (CCl_4) 2920 (s), 2860 (s), 1590 (w), 1460 (m), 1250 (m), 1165 (w), 910 (s), 880 (s), 855 (s) cm^{-1}; EIMS (70 eV), m/e (relative intensity) 210 (3, M^+), 118 (8), 93 (5), 82 (5), 75 (11), 74 (9), 73 (100), 59 (6), 44 (6), 44 (5); HRMS calcd for $C_{13}H_{26}Si$ 210.1804, found 210.1806.

3-Methylene-5-phenyl-2-[(trimethylsilyl)methyl]-1-pentene (**4b**): ^1H NMR (CCl_4) δ 0.00 (s, 9 H), 1.78 (br s, 2 H), 2.37–2.88 (m, 4 H), 4.76 (br s, 1 H), 4.90 (br s, 1 H), 5.02 (br s, 2 H), 7.11 (br s, 5 H); ^{13}NMR ($CDCl_3$) δ −1.17 (q), 24.15 (t), 35.51 (t), 36.10 (t), 109.99 (t), 112.67 (t), 125.66 (t), 128.21 (d), 142.17 (s), 144.79 (s), 147.72 (s); IR (CCl_4) 3020 (w), 2920 (s), 2840 (m), 1585 (w), 1450 (m), 1245 (m), 890 (m), 875 (s), 850 (s) cm^{-1}; EIMS (70 eV) m/e (relative intensity) 244 (5, M^+), 170 (4), 121 (4), 91 (19), 75 (5), 74 (9), 73 (100), 59 (5), 45 (6), 44 (5); HRMS calcd for $C_{16}H_{24}Si$ 244.1645, found 244.1622.

3-Methylene-4-phenyl-2-[(trimethylsilyl)methyl]-1-butene (**4c**): ^1H NMR (CCl_4) δ −0.01 (s, 9 H), 1.76 (br s, 2 H), 3.50 (br s, 2 H), 4.70 (br s, 1 H), 4.83 (br s, 1 H), 4.99 (br s, 1 H), 5.15 (br s, 1 H), 7.13 (br s, 5 H); ^{13}C NMR ($CDCl_3$) δ −1.17 (q), 24.22 (t), 40.54 (t), 111.03 (t), 114.95 (t), 125.79 (d), 128.07 (d), 128.73 (d), 140.15 (s), 144.46 (s), 146.94 (s); IR (CCl_4) 3020 (m), 2950 (s), 2850 (m), 1590 (m), 1450 (m), 1250 (s), 905 (s), 880 (s), 850 (s), 700 (s) cm^{-1}; EIMS (70 eV), m/e (relative intensity) 230 (28, M^+), 187 (8), 182 (13), 156 (14), 143 (14), 135 (14), 91 (66), 74 (9), 73 (100), 59 (17); HRMS calcd for $C_{15}H_{22}Si$ 230.1490, found 230.1470.

3-Methylene-2-[(trimethylsilyl)methyl]-5-(trimethylsilyl)-1-pentene (**4d**): ^1H NMR (CCl_4) δ 0.11 (s, 9 H), 0.12 (s, 9 H), 0.71–0.95 (m, 2 H), 1.22–1.49 (m, 2 H), 1.88 (br s, 2 H), 4.82 (br s, 1 H), 5.03–5.14 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ −1.11 (q), −1.76 (q), 16.25 (t), 24.41 (t), 28.26 (t), 109.67 (t), 111.10 (t), 145.11 (s), 151.18 (s); IR (CCl_4) 3080 (m), 2910 (s), 2850 (m), 1410 (m), 1250 (s), 1160 (w), 910 (s), 855 (s), 835 (s), 690 (m) cm^{-1}; EIMS (70 eV), m/e (relative intensity) 240 (8, M^+), 137 (11), 135 (6), 124 (6), 121 (9), 74 (9), 73 (100), 59 (5), 45 (7), 44 (11); HRMS calcd for $C_{13}H_{28}Si_2$ 240.1729, found 240.1731.

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Convenient Preparation of 1,3-Bis(2,3,4,5-tetramethylcyclopentadienyl)-propane: Use of 2,3,4,5-Tetramethylcyclopent-2-enone Enolate as a Synthetic Equivalent for the Tetramethylcyclopentadienyl Anion

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The preparation and reactivity of organometallic complexes containing bridged tetramethylcyclopentadienyl ligands is of considerable current interest.[1-5] Unfortu-

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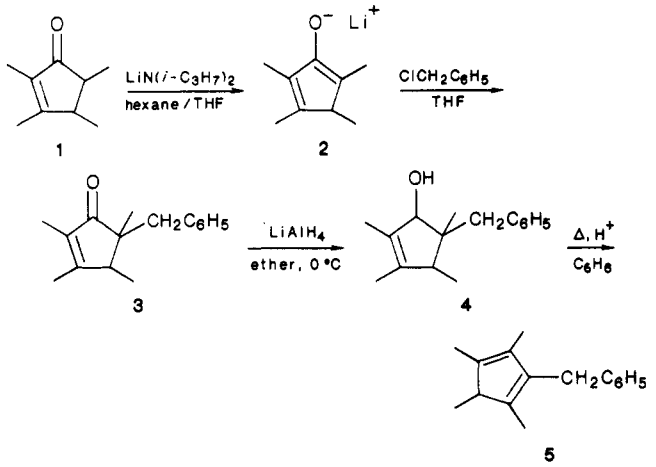
0022-3263/87/1952-2948$01.50/0

Scheme I



nately, this work has been limited by the lack of general, high-yield, synthetic routes to prepare the desired ligands.[6]

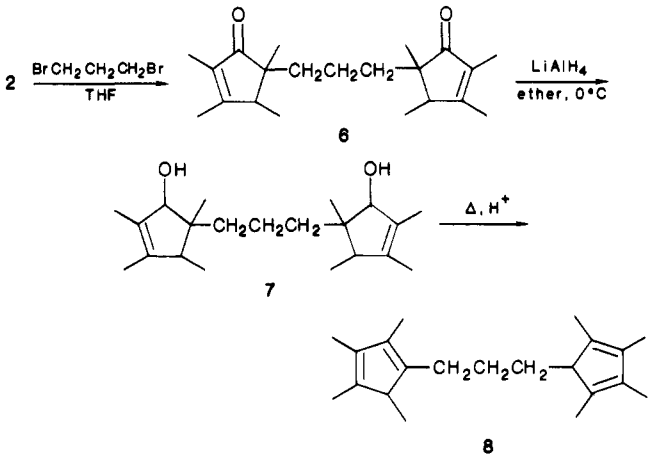
We report here the use of 2,3,4,5-tetramethylcyclopent-2-enone (**1**)[7] as a convenient starting material for high-yield preparation of bridged tetramethylcyclopentadienyl ligands. The use of **1** as a tetramethylcyclopentadienyl anion synthetic equivalent is exemplified by the preparation of benzyl-2,3,4,5-tetramethylcyclopentadiene (**5**). Treatment of **1** with $LiN(i\text{-}C_3H_7)_2$ followed by alkylation with benzyl chloride produces the benzyl ketone **3** in high yield (Scheme I). Reduction of **3** with $LiAlH_4$ produces the corresponding alcohol **4** which upon treatment with *p*-toluenesulfonic acid in refluxing benzene undergoes dehydration and Wagner–Meerwein rearrangement to give benzyl-2,3,4,5-tetramethylcyclopentadiene (**5**) in 64% overall yield based on enone **1**. In an analogous manner, treatment of 1,3-dibromopropane with 2 equiv of **2** followed by reduction with $LiAlH_4$ and acid-catalyzed dehydration produces 1,3-bis(2,3,4,5-tetramethylcyclopentadienyl)propane (**8**) as a mixture of six possible tautomers in 71% overall yield based on **1**. The identification of this material by ^1H and ^{13}C NMR spectroscopy was complicated by the numerous tautomers present (Scheme II).

Treatment of enolate **2** with 1,2-dibromopropane in an attempt to prepare the two-carbon-chain analogue of **6**, not unexpectedly, failed to produce the corresponding two-carbon analogue.[8] We are currently exploring alternate routes for the preparation of the two-carbon-chain analogue of **8** as well as using **8** to prepare novel new bimetallic complexes.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen. Solvents were purified by distillation from Na/K alloy under nitrogen. Diisopropylamine (Aldrich) was distilled from barium oxide prior to use. Benzyl chloride (Aldrich) and 1,3-dibromopropane (Aldrich) were freshly distilled prior to use. Methyllithium (Aldrich), *n*-butyllithium (Aldrich), $LiAlH_4$ (Aldrich), *p*-toluenesulfonic acid (Aldrich), and alumina were used as purchased. 2,3,4,5-Tetramethylcyclopent-2-enone was prepared by published procedures.[7]

Scheme II



^1H NMR spectra were recorded at 270 MHz on a JEOL GX 270 NMR spectrometer. ^{13}C NMR spectra were recorded at 67.5 MHz on a JEOL GX 270 NMR spectrometer. Spectra were measured at ambient temperature in $CDCl_3$ with residual solvent peaks or tetramethylsilane as an internal standard. Elemental analyses were performed by Microlytics, South Deerfield, MA.

Preparation of 5-Benzyl-2,3,4,5-tetramethylcyclopent-2-enone (3). To a solution of 12.2 mL of diisopropylamine (86.3 mmol) in 30 mL of THF was added 53.4 mL of 1.6 M *n*-BuLi (85.5 mmol) in hexane. This solution was stirred for 0.5 h at 0 °C until the evolution of methane was complete. To this solution was added 10.0 g of 2,3,4,5-tetramethylcyclopent-2-enone (71.9 mmol) at 0 °C; the reaction mixture was then refluxed for 12 h. The diisopropylamine and THF were then removed under vacuum, leaving a viscous orange residue. THF (50 mL) was added, the solution was cooled to 0 °C, and 8.3 mL of benzyl chloride (71.9 mmol) in 10 mL of THF added slowly. The resulting solution was allowed to warm to room temperature and refluxed for 12 h. The THF was removed under vacuum, and the resulting residue was dissolved in 50 mL of ether. The ether solution was washed with 25 mL of 6 M HCl and then twice with 25 mL of H_2O. The aqueous layers were combined and back-extracted with 50 mL of ether. The combined ether layers were dried over $MgSO_4$. Removal of the solvent afforded 12.2 g of **3** (74% yield): ^1H NMR (270 MHz, $CDCl_3$) δ 0.91 (3 H, d, CH_3), 1.05 (3 H, s, CH_3), 1.59 (3 H, s, CH_3), 1.79 (3 H, s, CH_3), 2.61 (1 H, m, CH), 2.62–2.82 (2 H, AB pattern δ 2.64, 2.82, J = 13.19 Hz), 7.21–7.05 (5 H, m, Ar); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$), δ 7.96 (CH_3), 13.42 (CH_3), 14.48 (CH), 20.03 (CH_2), 44.25 (CH_3), 45.00 (CH_3), 50.50 (q, C), 126.16 (Ar-*p*), 127.80 (Ar-*m*), 129.97 (Ar-*o*), 133.36 (vinyl, C), 137.94 (Ar-*i*), 171.40 (vinyl, C), 212.63 (C=O). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.56, H, 8.97.

Reduction of 5-Benzyl-2,3,4,5-tetramethylcyclopent-2-enone (3). A suspension of 5.2 g of **3** (22.8 mmol) in 30 mL of ether was added to a suspension of 0.46 g of $LiAlH_4$ (12.1 mmol) in 50 mL of ether at 0 °C over 10 min. The solution was maintained at 0 °C for 3 h, warmed to room temperature, and stirred for 6 h. The reaction was quenched with methanol until the evolution of gas was complete. Dilute HCl (6 M) was added until the aqueous layer no longer contained solids. The aqueous and ethereal layers were separated, and the aqueous layer was extracted with three successive 20-mL portions of ether. The ether layers were combined and dried over $MgSO_4$. Removal of the solvent afforded 5.09 g of **4** (97% yield) as a colorless oil. Compound **4** tended to eliminate to **5** upon workup and was used without further purification.

Preparation of 1-Benzyl-2,3,4,5-tetramethylcyclopentadiene (5). Alcohol **4** (5.00 g, 21.7 mmol) was dissolved in 150 mL of benzene in a round-bottomed flask fitted with a Dean–Stark trap and condenser. To this was added 0.42 g of *p*-toluenesulfonic acid (2.2 mmol) after which the solution turned deep purple. This mixture was refluxed with the removal of H_2O for 12 h. The benzene was washed with 50 mL of saturated Na_2CO_3 solution followed by two successive 25-mL washings with H_2O. The aqueous washings were then back-extracted with 25 mL of ether. The benzene and ether layers were combined and

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dried over $MgSO_4$. Removal of the solvents under vacuum yielded 4.1 g of benzyl-2,3,4,5-tetramethylcyclopentadiene as a mixture of tautomers as a clear yellow oil, in 90% yield. Compound **5** was purified by column chromatography on alumina and eluted with hexane: ^1H NMR (270 MHz, $CDCl_3$) δ 1.4 (3 H, s, CH_3), 1.62 (3 H, s, CH_3), 1.64 (3 H, d, CH_3), 1.71 (3 H, s, CH_3), 1.95 (1 H, q, CH), 2.82 (2 H, s, CH_2), 7.21–7.08 (5 H, m, Ar); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 9.27 (CH_3), 9.64 (CH_3), 19.29 (CH_3), 23.82 (CH_2), 37.98 (CH_2), 44.30 (CH), 48.04 (CH), 53.91 (CH_2), 122.17 (CH, Ar), 124.50 (CH, Ar), 125.67 (CH, Ar), 127.61 (CH, Ar), 129.89 (CH, Ar), 133.74 (C), 136.45 (C), 141.81 (C), 145.43 (C). Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.24; H, 9.60.

Preparation of 1,3-Bis(2,3,4,5-tetramethyl-1-oxocyclopent-2-en-5-yl)propane (6). In a manner similar to that outlined above 20.0 g of 2,3,4,5-tetramethylcyclopent-2-enone (145 mmol) in 20 mL of THF was added dropwise to a solution of LDA at 0 °C, prepared from 21 mL of diisopropylamine (150 mmol) and 92.5 mL of *n*-BuLi (1.6 M in hexanes, 148 mmol) in 50 mL of THF at 0 °C. This yellow solution was then refluxed for 12 h. The reaction mixture was cooled to room temperature, and the diisopropylamine and THF were removed under vacuum. The residue was taken up in 50 mL of THF, and the solution was cooled to 0 °C. A solution of 7.34 mL of 1,3-dibromopropane (72 mmol) in 20 mL of THF was then added dropwise over 1 h, and the reaction mixture refluxed for 48 h. The reaction was then cooled to room temperature, the solvent removed under vacuum, and the residue taken up in 50 mL of ether. The ether solution was then washed with two 20-mL portions of water and one 20-mL portion of saturated NH_4Cl solution. The aqueous layers were back-extracted with two 20-mL portions of ether. The ether layers were combined and dried over $MgSO_4$. Removal of the solvent under vacuum yielded a thick orange-yellow liquid. Unreacted enone **1** was removed by distillation between 25 and 60 °C (0.1 mmHg) to give 16.3 g (72% yield) of **6**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.71 (6 H, s, CH_3), 0.81 (2 H, m, CH_2), 0.82 (6 H, d, CH_3), 1.18 (4 H, m, CH_2), 1.48 (6 H, s, CH_3), 1.80 (6 H, s, CH_3), 2.3 (2 H, m, CH); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 8.17 (CH_3), 14.19 (CH_3), 14.92 (CH_3), 19.40 (CH_2), 46.20 (CH), 49.55 (q, C), 133.48 (C), 171.52 (C), 213.38 (CO). Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.74; H, 10.24.

Preparation of 1,3-Bis(2,3,4,5-tetramethylcyclopentadienyl)propane (8). To a suspension of 2.0 g of $LiAlH_4$ (53 mmol) in 50 mL of ether at 0 °C was added 16.3 g of 1,3-bis(2,3,4,5-tetramethyl-1-oxocyclopenta-2-en-5-yl)propane (51.6 mmol) dissolved in 30 mL of ether over 30 min. The solution was stirred at 0 °C for 6 h, after which it was allowed to warm to room temperature and stirred an additional 3 h. The resulting reaction mixture was worked up as described above for the reduction of **3**. Upon removal of the solvent, the product was dissolved in 250 mL of benzene and 1.1 g of *p*-toluenesulfonic acid (5.76 mmol) was added. This solution was then fitted with a Dean–Stark trap and refluxed, with the removal of water, for 24 h. The product was then worked up as described above for **5** to afford 10.6 g (72%) as a light orange oil. Further purification was achieved on an alumina column eluted with hexane: ^1H NMR (270 MHz, $CDCl_3$) δ 0.89 (3 H, d, CH_3, J = 7.02 Hz), 1.04 (3 H, d, CH_3, J = 6.78 Hz), 1.35 (3 H, s, CH_3), 1.36 (3 H, s, CH_3), 1.71 (3 H, s, CH_3), 1.74 (3 H, brs, CH_3), 1.80 (3 H, s, CH_3), 1.20–1.85 (multiple signals representing CH_2 groups), 2.16 (2 H, m, CH); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 9.81 (CH_3), 10.96 (CH_3), 11.23 (CH_3), 12.02 (CH_3), 12.58 (CH_3), 17.16 (CH_3), 19.08 (CH_3), 20.36 (CH_3), 21.83 (CH_3), 39.87 (CH_2), 46.74 (CH), 49.33 (CH), 50.58 (CH_2), 55.67 (CH_2), 131.14 (olefinic), 134.27 (olefinic), 137.73 (olefinic), 140.45 (olefinic), 143.21 (olefinic), 144.81 (olefinic). Anal. Calcd for $C_{21}H_{32}$: C, 88.66; H, 11.34. Found: C, 88.47; H, 11.34.

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Registry No. **1**, 54458-61-6; **2**, 108344-82-7; **3**, 108344-69-0; **4**, 108344-70-3; **5**, 108344-81-6; **6**, 108344-71-4; **6**(two-carbon chain analogue), 108344-72-5; **7**, 108344-73-6; **8**(isomer 1), 108344-74-7; **8**(isomer 2), 108344-75-8; **8**(isomer 3), 108344-76-9.

Selective Addition of Methanol to 1,2-Epoxy-1-vinylcyclopentane

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The chemical properties of simple oxiranes (epoxides) are well established. Such investigations have been prompted not only by the versatility of oxiranes as synthetic intermediates[1] but also by an interest in their biological activities.[2] However, the reactions of vinyloxiranes, which present four contiguous carbon atoms[3] for potential reactions, have not been studied as thoroughly.[1] Reactions of vinyloxiranes with carbanions can afford primarily products of either δ addition (via copper species)[4] or α,β addition (via alkyl- or aryllithiums).[5] Regiochemistry of Grignard reagent addition is a function of the reagent, substrate or conditions used.[6] Amines or some oxygen nucleophiles, in the presence of certain aluminum species,[7] and thiols[8] give α,β addition products, although the latter also can undergo conjugate addition. We have probed the reactivity of vinyloxiranes with methanol in the presence of mercuric salts using 1,2-epoxy-1-vinylcyclopentane (**1**) as a model compound. The addition of methanol occurs regioselectively and is stereospecific.

In these studies, solutions of **1** in methanol were reacted first with either mercuric acetate (**2**) or mercuric nitrate (**3**) and then with sodium borohydride. Although **2** and **3** are standard reagents for routine solvomercurations of olefins,[9] they differ considerably in their reactivity with some substrates. For example, oxymercuration of conjugated dienes affords the α,β- or α,δ-addition products with **2** or **3**, respectively.[10] Furthermore, the ratio of syn/anti ring openings of substituted phenylcyclopropanes is greater when mercuric nitrate (**3**) is substituted for mercuric acetate (**2**).[11] We thought that such differences, which are attributed to the greater ionic character of **3**,[12] might also be manifested upon reaction of these salts with **1**.

Gas chromatography–mass spectrometry (GC/MS) was used for an initial analysis of the reaction products. The molecular ion and fragmentation pattern of each compound were determined and compared with those of their deuteriated analogues obtained from reactions utilizing deuteriomethanol and reactions utilizing sodium borodeuteride. Additionally, products with acidic protons were

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