Unusual Transformation of Cyclobutenediones into Butenolides

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ABSTRACT. Butenolides are prepared from cyclobutenediones when cyclobutenediones are treated with lithium trimethylsilylacetylene, and quenched with water. A plausible mechanism, which contains an allene as an intermediate, is proposed. The usual diradical intermediate may not be formed because of the bulkiness of trimethylsilyl group, and the allenic intermediate may be stabilized by the \( \alpha \)-silyl group.

Keywords: Butenolides, Cyclobutenediones, Allene

INTRODUCTION

Quinone compounds can be prepared from by many different routes such as Diels-Alder reaction, oxidation, ring expansion from cyclobutenones, etc. The synthesis of quinones from 4-substituted cyclobutenones has been extensively studied by Moore and Liebeskind and their coworkers.¹ The starting cyclobutenediones are easily prepared from dialkyl squarates, which are prepared from commercially available squaric acid or halo-substituted cyclobutenones by coupling reaction with organostannane reagents.² The regioselective 1,2-addition of lithium reagents to cyclobutenediones would give unsymmetrical cyclobutenediones 1.³ Thermolysis of the resulting cyclobutenones in a variety of solvents results in electrocyclic ring opening to the conjugated ketene intermediate 3 which undergoes subsequent ring closure to ultimately form the product, quinones (Scheme 1). Of key importance in this process is the stereoselective ring opening to the conjugated ketene intermediates. The electrocyclic ring opening occurs with outward rotation of the hydroxy group. This transformation is governed by electronic effect as supported in calculations by Houk, and can be explained in terms of the frontier orbital theory.⁴ For \( R=\text{alkenyl or aryl} \), a 6-\( \pi \) electron electrocyclic ring closure of 3 gives cyclohexadienone 4, tautomerization of which gives hydroquinone 5. This leads to quinone 6 upon oxidation.
Alkynyllithium addition to the unsymmetrical diones followed by thermolysis leads to enynylketene intermediates 8. These ketenes undergo ring closure to form diradical species 9. 1,2-Migration of the

*Scheme 1.* Synthesis of quinones from alkenyl or aryl compounds with cyclobutenediones.

*Scheme 2.* Synthesis of quinones from alkynyl compounds with cyclobutenediones.
group on the oxygen (E) leads to the quinone products 11. Contrary to aryl and alkenyl cases, all studies on the alkynyl rearrangement support diradical intermediates 9 (Scheme 2).¹

Therefore, quinone compounds are expected from the coupling reaction of cyclobutenediones and lithium reagents upon thermolysis. However, when cyclobutenediones react with lithium trimethylsilylacetylene, an unusual transformation can take place. We report an unusual transformation of cyclobutenediones into butenolides in this article.

RESULTS AND DISCUSSION

An unexpected transformation took place when lithium trimethylsilylacetylene was treated with 3-methoxy-4-[(trimethylsilylethoxy)methoxy]methyl]-3-cyclobuten-1,2-dione (SEM dione) 15.⁴ The butenolides 16 and 17 were isolated in 26% yield instead of the expected quinones (Scheme 3). Compound 15 was prepared from a method developed by Fujita and Fuji.⁵

TLC analysis of the reaction revealed some interesting change. The single spot which formed upon addition of lithium trimethylsilylacetylene to 15 splits into two new spots upon quenching the reaction with water. It thus appears that a water molecule plays an important role in the above transformation. A plausible mechanism for this transformation is proposed in Scheme 4.

As expected, cyclobutenone 18 would be formed upon the addition of the lithium acetylide to the dione.⁶ This could then give the ketene intermediate 19 which would lead to allene 20 by the attack of a water molecule at the carbonyl carbon. And the allenic intermediate 20 might be stabilized by the α-silyl group and tautomerize easily to the stable silylenone 21. Subsequent ring closure would result in a stereoisomeric mixture of butenolides 16 and 17, which would be the two new spots in TLC. The cis isomer quantitatively isomerizes to the trans isomer at 81 °C. No other product was identified in this isomerization reaction. Same type of reactions with different alkynyls were performed to see if the reactions give the same results. However, comparison of these reactions with the reaction with trimethylsilylacetylen methyl group shows an interesting difference. No butenolide was isolated from the alkynyl derivatives having n-propyl, n-butyl and trimethylsilylmethyl groups (Scheme 5).

Based on the experimental results, it appears that the α-silyl group may stabilize the allenic intermediate 20 from 18, or diradical intermediates may not be formed because of the bulkiness of TMS group. Further mechanistic study will be required to elucidate the mechanism. And this process can be used for the synthesis of butenolides, which are found abundantly in nature,⁷ ⁹ even
though the yields need to be improved.

**EXPERIMENTAL**

**General procedure.** Commercial reagents were used without further purification excepts as indicated below. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone ketyl immediately before use. All air or water sensitive reactions were carried out in flame dried glassware under a positive pressure of argon or nitrogen. Air sensitive solutions were transferred via cannula and were transferred via cannula and were

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*Scheme 4. Proposed mechanism for the unexpected transformation.*

*Scheme 5. Products from various alkynyl derivatives.*

<table>
<thead>
<tr>
<th>Entry</th>
<th>$R_1$</th>
<th>$R_2$</th>
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<td>a</td>
<td>CH$_3$</td>
<td>$n$-C$_4$H$_9$</td>
<td>40</td>
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<tr>
<td>b</td>
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<td>16</td>
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<td>d</td>
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<td>$n$-C$_6$H$_7$</td>
<td>18</td>
</tr>
<tr>
<td>e</td>
<td>$t$-Bu</td>
<td>CH$_3$Si(CH$_3$)$_3$</td>
<td>15</td>
</tr>
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</table>

*Yields from cyclobutenediones*

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introduced into the reaction vessel through rubber septa. Butyllithiums were introduced to the reaction vessels via syringe. The reaction solutions were concentrated by a Buchi rotary evaporator at 15-30 mmHg. Column chromatography was performed by using E. Merck silica gel (230-400 mesh) mostly with hexanes and ethyl acetate as eluents.

**Instruments.** Proton and $^{13}$C carbon NMR were recorded on a General Electric $\Omega$ 500 NMR or a General Electric GN 500 NMR spectrometer. Infrared spectra were recorded on a Perkin-Elmer FT IR spectrophotometer. Low-resolution mass spectra (MS) were recorded on a Finigan 4000 spectrometer and high-resolution mass spectra (HRMS) were measured with a VG Analytic 7070E spectrometer.

-$^{[\text{Trimethylsilylethoxymethoxy}]}$tributyllstannane (14). The solution of 13 (0.57 g, 2.0 mmol) in 10 mL of dry CH$_2$Cl$_2$ were added $i$-Pr$_2$NEt (2.74 mL, 10 mmol) and SEMCl (0.38 mL, 2.4 mmol) and warmed up to 40 $^\circ$C. The reaction mixture was stirred for 3 hrs (color of the reaction solution changed from colorless to orange) at 40$^\circ$C, cooled to room temperature, and poured into a separatory funnel containing 100 mL of petroleum ether. The organic layer was washed with water (2 × 20 mL), and brine (10 mL), and dried over magnesium sulfate and finally concentrated in vacuo. The resulting residue was purified by flash column chromatography (20/1 petroleum ether/ethyl acetate) and gave 850 mg (94%) of the desired product 14 as a colorless liquid: IR (CHCl$_3$) 2956, 2923, 1717, 1464, 1376, 1249, 1100, 1032 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 4.55 (s, 2H), 3.78 (s, 2H), 3.56 (t, $J$=8.5 Hz, 2H), 1.50 (m, 6H), 1.30 (m, 6H), 0.90 (m, 17H); $^{13}$C NMR (CDCl$_3$) $\delta$ 97.9, 64.7, 57.5, 29.1, 27.3, 18.2, 13.7, 8.9, -1.4; MS (CI), m/z 279, 103, 91, 73; MS (EI), m/z (rel. intensity) 395(1), 179(8), 177(9), 121(9), 119(8), 101(11), 89(12), 73(100), 57(5); HRMS, m/z calculated for C$_{19}$H$_{44}$SiSnO$_2$, 452.1232; found, 452.2127.

-$^{5}$Hydroxy-4-methoxy-3-(trimethylsilylethoxymethoxy)methyl-5-trimethylsilvinyl-2-furanone (16, 17). To a solution of trimethylsilylacetylene (0.08 mL, 0.6 mmol) in dry THF (20 mL) was added $n$-BuLi (1.6 M in hexanes, 0.4 mL, 0.6 mmol) slowly for 20 min at −78 $^\circ$C. The reaction mixture was stirred for 30 min at −78 $^\circ$C. The resulting solution was transferred to the solution of dimethyl squarate (0.93 g, 6.5 mmol) in dry THF (150 mL) in 50 mL round bottom flask via cannula at −78 $^\circ$C and stirred for an additional 30 min. Trifluoroacetic anhydride (TFAA) (1.3 mL, 7.85 mmol) was added to the reaction mixture slowly at −78 $^\circ$C and stirred for 30 min and quenched with 5% NH$_4$Cl solution (5 mL). The reaction mixture was then warmed to room temperature. The organic solution was washed with water (2 × 20 mL), and brine (10 mL), and dried over magnesium sulfate, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (3/1 hexanes/ethyl acetate) and gave 1.35 g (69%) of the desired product 15a as a pale yellow liquid: IR (CHCl$_3$) 2955, 2896, 1806, 1766, 1607, 1460, 1393, 1337, 1250, 1161, 1108, 1061 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 4.72 (s, 2H), 4.62 (s, 2H), 4.44 (s, 3H), 3.64 (t, $J$=8.5 Hz, 2H), 0.93 (t, $J$=8.5 Hz, 2H), 0.01 (s, 9H); $^{13}$C NMR (CDCl$_3$) $\delta$ 197.9, 193.1, 192.5, 177.9, 94.9, 65.7, 59.1, 18.0, -1.5; MS (CI), m/z 273 (MH$^+$); MS (EI), m/z (rel. intensity) 214(3), 199(8), 171(4), 103(4), 97(4), 89(4), 87(4), 78(4), 73(100), 69(15); HRMS, m/z calculated for C$_{12}$H$_{20}$SiO$_5$, 272.1080; found, 272.0883.

-$^{3}$-Methoxy-4-[(trimethylsilylethoxymethoxy)methyl]-3-cyclobutene-1,2-dione (15a). To a solution of Bu$_3$SnCH$_2$OSEM (3.25 g, 7.2 mmol) in dry THF (30 mL) was added $n$-BuLi (1.6 M in hexanes, 0.4 mL, 0.6 mmol) slowly for 20 min at −78 $^\circ$C. The reaction mixture was stirred for 30 min at −78 $^\circ$C. The resulting solution was transferred to the solution of trimethyl squarate (0.93 g, 6.5 mmol) in dry THF (150 mL) in 50 mL round bottom flask via cannula at −78 $^\circ$C and stirred for an additional 30 min. Trifluoroacetic anhydride (TFAA) (1.3 mL, 7.85 mmol) was added to the reaction mixture slowly at −78 $^\circ$C and stirred for 30 min and quenched with 5% NH$_4$Cl solution (5 mL). The reaction mixture was then warmed to room temperature. The organic solution was washed with water (2 × 20 mL), and brine (10 mL), and dried over magnesium sulfate, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (3/1 hexanes/ethyl acetate) and gave 1.35 g (69%) of the desired product 15a as a pale yellow liquid: IR (CHCl$_3$) 2955, 2896, 1806, 1766, 1607, 1460, 1393, 1337, 1250, 1161, 1108, 1061 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 4.72 (s, 2H), 4.62 (s, 2H), 4.44 (s, 3H), 3.64 (t, $J$=8.5 Hz, 2H), 0.93 (t, $J$=8.5 Hz, 2H), 0.01 (s, 9H); $^{13}$C NMR (CDCl$_3$) $\delta$ 197.9, 193.1, 192.5, 177.9, 94.9, 65.7, 59.1, 18.0, -1.5; MS (CI), m/z 273 (MH$^+$); MS (EI), m/z (rel. intensity) 214(3), 199(8), 171(4), 103(4), 97(4), 89(4), 87(4), 78(4), 73(100), 69(15); HRMS, m/z calculated for C$_{12}$H$_{20}$SiO$_5$, 272.1080; found, 272.0883.

-$^{5}$-Hydroxy-4-methoxy-3-(trimethylsilylethoxymethoxy)methyl-5-trimethylsilvinyl-2-furanone (16, 17). To a solution of trimethylsilylacetylene (0.08 mL, 0.6 mmol) in dry THF (20 mL) was added $n$-BuLi (1.6 M in hexanes, 0.4 mL, 0.6 mmol) slowly at −78 $^\circ$C via syringe. After stirring for 20 min at −78 $^\circ$C, the resulting solution was transferred to a solution of SEM-dione 15 (136 mg, 0.5 mmol) in dry THF (30 mL) at −78 $^\circ$C via cannula. Immediately after the completion of transfer, the reaction mixture was quenched with 5% NH$_4$Cl solution (3 mL) and poured into a separatory funnel containing 50 mL of diethyl ether and 10 mL of water. The organic solution was washed with water (2 × 20 mL) and brine (10 mL), and dried over magnesium sulfate, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (3/1 hexanes/ethyl acetate) and gave 29 mg (16%) of cis
isomer 17 and 18 mg (10%) of trans isomer 16 as colorless liquids with heavy base line compounds: IR (CHCl₃) 3600, 3019, 2400, 1761, 1734, 1670, 1521, 1422, 1210, 1046 cm⁻¹ on the mixture of cis and trans; ¹H NMR (CDCl₃, 500 MHz) δ 6.23 (d, J=14.9 Hz, 1H), 6.03 (d, J=14.9 Hz, 1H), 4.72 (s, 2H), 4.35 (dd, J=4.7 and 6 Hz, 2H), 4.21 (s, 3H), 3.64 (t, J=8.5 Hz, 2H), 0.97 (t, J=7.3 Hz, 2H), 0.18 (s, 9H), 0.02 (s, 9H); ¹³C NMR (CDCl₃) δ 78 o C. After stirring for 20 min at that temperature, 57.5, 18.0, 0.6, -1.5 for cis isomer 17. ¹H NMR (CDCl₃, 500 MHz) δ 6.42 (d, J=19.7 Hz, 1H), 4.72 (s, 2H), 4.34 (dd, J=4.7 and 6 Hz, 2H), 4.21 (s, 3H), 3.64 (t, J=8.4 Hz, 2H), 0.9 (t, J=8.4 Hz, 2H), 0.10 (s, 9H), 0.02 (s, 9H); ¹³C NMR (CDCl₃) δ 174.2, 171.2, 138.4, 136.2, 99.9, 98.9, 94.4, 65.6, 59.5, 57.5, 18.0, 0.6, -1.5 for cis isomer 17. ¹H NMR (CDCl₃, 500 MHz) δ 6.24 (d, J=19.7 Hz, 1H), 6.02 (d, J=19.7 Hz, 1H), 4.72 (s, 2H), 4.34 (dd, J=4.7 and 6 Hz, 2H), 4.21 (s, 3H), 3.64 (t, J=8.4 Hz, 2H), 0.9 (t, J=8.4 Hz, 2H), 0.10 (s, 9H), 0.02 (s, 9H); ¹³C NMR (CDCl₃) δ 174.2, 171.2, 138.4, 136.2, 99.9, 98.9, 94.4, 65.6, 59.5, 57.5, 18.0, 0.6, -1.5 for trans isomer 16; MS (CI), m/z 389 (MH⁺); MS, (EI), m/z (rel. intensity) 242(9), 241(4), 225(5), 151(6), 101(3), 99(5), 89(14), 75(35), 73(100), 59(10); HRMS, m/z calculated for C₁₅H₂₆SiO₅, 388.1737; found, 388.1745.

3-ter-Butoxy-4-[(trimethylsilylethoxymethoxy)methyl]-3-cyclobutene-1,2-dione (15b). To the solution of Bu₃SnCH₂OSEM (5.40 g, 12 mmol) in dry THF (30 mL) was added n-BuLi (2.5 M in hexanes, 5.0 mL, 13 mmol) slowly via cannula at −78 °C. After stirring for 20 min at that temperature, the reaction mixture was transferred to the solution of di-ter-butyl squarate (2.26 g, 10 mmol) in dry THF (50 mL) via cannula at −78 °C. After stirring for an additional 20 min, TFAA (1.77 mL, 13 mmol) was added slowly. After stirring for 20 min, the reaction mixture was quenched with 5% NH₄Cl solution (5 mL) and poured into a separatory funnel containing 100 mL of ether. The organic solution was washed with water (30 mL), and brine (10 mL), and dried over magnesium sulfate, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (1/1 hexanes/ethyl acetate) and gave 4-hexynyl-4-hydroxy-3-methoxy-[15b] as a pale yellow liquid: 1H NMR (CDCl₃, 500 MHz) δ 4.65 (s, 2H), 4.10 (s, 2H), 3.60 (t, J=7.3 Hz, 2H), 2.24 (t, J=7.2 Hz, 2H), 1.47 (m, 1H), 1.44 (m, 1H), 0.96 (m, 5H); ¹³C NMR (CDCl₃) δ 186.1, 182.2, 124.3, 94.3, 91.8, 83.1, 73.9, 65.4, 60.3, 56.2, 30.2, 21.9, 18.6, 18.0, 13.5, -1.5; MS (CI), m/z (rel. intensity) 355(5, MH⁺), 347(5), 297(38), 209(100), 207(50), 91(39). The resulting hydroxycyclobutenone (36 mg, 0.10 mmol) was heated at reflux in acetonitrile for 1 hr. After cooling the reaction, the solution was concentrated in vacuo at 50 °C. The resulting residue was purified by flash column chromatography (3/1 hexanes/ethyl acetate) and gave 11 mg of (33%) of benzoinone compound 23a as a pale yellow liquid. 2) Without purification of the hydroxycyclobutenone. To a solution of 1-hexyne (0.069 mL, 0.6 mmol) in dry THF (20 mL) was added n-BuLi (1.6 M in hexanes, 0.38 mL, 0.6 mmol) slowly at −78 °C via syringe. After stirring for 20 min, the resulting solution was transferred to the solution of SEM-dione (136 mg, 0.5 mmol) in dry THF (30 mL) via cannula. Right after the completion of transfer, the reaction mixture was quenched with 5% NH₄Cl solution (5 mL) and poured into a separatory funnel containing 100 mL of ether. The organic solution was washed with water (30 mL), and brine (10 mL), and dried over magnesium sulfate, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (1/1 hexanes/ethyl acetate) and gave 103 mg (58%) of 4-hexynyl-4-hydroxy-3-methoxy-2-[(trimethylsilylethoxymethoxy)methyl]-2-cyclobuten-1-one (22a) as a pale yellow liquid: ¹H NMR (CDCl₃, 500 MHz) δ 4.65 (s, 2H), 4.30 (s, 3H), 4.10 (s, 2H), 3.60 (t, J=7.3 Hz, 2H), 2.24 (t, J=7.2 Hz, 2H), 1.47 (m, 1H), 1.44 (m, 1H), 0.96 (m, 5H); ¹³C NMR (CDCl₃) δ 186.1, 182.2, 124.3, 94.3, 91.8, 83.1, 73.9, 65.4, 60.3, 56.2, 30.2, 21.9, 18.6, 18.0, 13.5, -1.5; MS (CI), m/z (rel. intensity) 355(5, MH⁺), 297(15), 237(38), 209(100), 207(50), 91(39). The resulting hydroxycyclobutenone (36 mg, 0.10 mmol) was heated at reflux in acetonitrile for 1 hr. After cooling the reaction, the solution was concentrated in vacuo at 50 °C. The resulting residue was purified by flash column chromatography (3/1 hexanes/ethyl acetate) and gave 11 mg of (33%) of benzoinone compound 23a as a pale yellow liquid.
resulting solution was transferred to the solution of SEM-dione 15a (136 mg, 0.5 mmol) in dry THF (30 mL) via cannula. Immediately after the completion of transfer, the reaction mixture was quenched with 5% NH₄Cl solution (5 mL) and poured into a separatory funnel containing 100 mL of ether. The resulting organic solution was washed with water (10 mL), and brine (10 mL), and dried over magnesium sulfate, and concentrated in vacuo. The crude product was heated at reflux in acetonitrile (30 mL) for 2 hrs. After cooling the reaction, the solution was concentrated in vacuo at 50 °C. The resulting residue was purified by flash column chromatography (3/1 hexanes/ethyl acetate) and gave 70 mg (40%) of the desired benzoquinone 23a as a pale yellow liquid: IR (CHCl₃) 2955, 2874, 1654, 1608, 1460, 1323, 1249, 1059 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 6.4 (s, 1H), 4.72 (s, 2H), 4.45 (s, 2H), 4.11 (s, 3H), 3.63 (t, J=8.5 Hz, 2H), 2.42 (t, J=7.3 Hz, 2H), 1.36 (m, 2H), 0.93 (m, 5H); ¹³C NMR (CDCl₃) δ 186.8, 184.8, 156.7, 149.9, 130.7, 125.9, 94.9, 65.1, 61.5, 57.6, 30.0, 28.7, 22.4, 18.1, 13.8, -1.5; MS (EI), m/z (rel. intensity) 281(1), 208(16), 207(16), 165(14), 137(50), 101(6), 73(100), 58(6); HRMS, m/z calculated for C₁₅H₁₀SiO₃, 354.1832; found, 354.1837.

3-Methoxy-6-n-propyl-2-[(trimethylsilylethoxy)methy]benzoquinone (23b). Compound 23b was prepared from 1-pentyne (0.06 mL, 0.6 mmol) by the similar procedure for the synthesis of 23a in 13 mg (16%) overall yield as a yellow liquid: IR (CHCl₃) 2952, 2893, 1740, 1657, 1612, 1596, 1461, 1331, 1267, 1248, 1103, 1038, 860, 836 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 6.43 (s, 1H), 4.72 (s, 2H), 4.45 (s, 2H), 4.12 (s, 3H), 3.63 (t, J=8.5 Hz, 2H), 2.4 (t, J=7.3 Hz, 2H), 1.55 (m, 2H), 0.95 (m, 6H), 0.02 (s, 9H); ¹³C NMR (CDCl₃) δ 186.9, 184.2, 157.5, 149.6, 130.8, 125.9, 95.0, 65.1, 61.5, 57.6, 31.0, 29.7, 21.1, 18.1, 18.0, 13.8, -1.4; MS (EI), m/z (rel. intensity) 279, 267; MS (EI), m/z (rel. intensity) 340(0.1), 267(2), 193(4), 103(13), 101(7), 75(20), 73(100), 59(4); HRMS, m/z calculated for C₁₅H₁₀SiO₃, 340.1706; found, 340.1888.

3-t-Butoxy-6-n-butyl-2-[(trimethylsilylethoxy)methy]benzoquinone (23c). Compound 23c was prepared with 65% yield from 1-hexyne (0.07 mL, 0.6 mmol) and a cyclobutenedione (157 mg, 0.5 mmol), 15b, by the similar process for the synthesis of 23a as a yellow oil: IR (CHCl₃) 2930, 2875, 1670, 1656, 1605, 1465, 1394, 1366, 1248, 1139, 1104, 1059, 1028 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 6.45 (s, 1H), 4.74 (s, 2H), 4.43 (s, 2H), 3.67 (t, J=7.3 Hz, 2H), 2.41 (m, 2H), 1.5 (m, 4H), 1.4 (s, 9H), 0.96 (m, 5H), 0.01 (s, 9H); ¹³C NMR (CDCl₃) δ 187.4, 185.7, 156.0, 150.0, 132.4, 131.1, 95.2, 85.3, 65.2, 58.7, 29.8, 29.2, 28.6, 22.4, 18.0, 13.7, -1.5; MS (EI), m/z (rel. intensity) 282(3), 267(6), 223(3), 194(11), 193(13), 151(4), 122(4), 103(8), 101(5), 94(4), 79(4), 75(100), 73(94), 67(8), 57(64), 56(22); HRMS, m/z calculated for C₁₄H₁₆O₂SiO, 396.2332; found, 396.2305.

3-t-Butoxy-6-n-propyl-2-[(trimethylsilylethoxy)methyl]benzoquinone (23d). Compound 23d was prepared (32 mg, 50%) from 1-pentyne (0.06 mL, 0.6 mmol) by the similar process for the synthesis of 23c as a yellow oil: IR (CHCl₃) 2959, 2937, 2877, 1669, 1655, 1459, 1395, 1370, 1319, 1250, 1137, 1058, 1021, 862, 838 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 6.45 (s, 1H), 4.74 (s, 2H), 4.44 (s, 2H), 3.66 (t, J=7.2 Hz, 2H), 2.41 (t, J=6.5 Hz, 2H), 1.55 (m, 2H), 1.43 (s, 9H), 0.97 (m, 5H), 0.03 (s, 9H); ¹³C NMR (CDCl₃) δ 187.5, 187.8, 156.0, 149.6, 132.5, 131.1, 95.2, 85.3, 65.2, 58.7, 30.9, 29.2, 21.0, 18.1, 13.8, -1.4; MS (EI), m/z (rel. intensity) 385 (MH⁺); MS (EI), m/z (rel. intensity) 253(17), 180(46), 179(28), 103(11), 75(30), 73(100), 57(60); HRMS, m/z calculated for C₁₆H₁₄O₃SiO, 384.3232; found, 384.3215.

3-t-Butoxy-6-n-trimethylsilylmethyl-2-[(trimethylsilylethoxy)methyl]benzoquinone (23e). Compound 23e was prepared (32 mg, 50%) from 3-trimethylsilylepropyne (0.06 mL, 0.6 mmol) by the similar process for the synthesis of 23e as a yellow oil: IR (CHCl₃) 2956, 2898, 1565, 1597, 1464, 1370, 1251, 1135, 1059 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 6.33 (s, 1H), 4.73 (s, 2H), 4.43 (s, 2H), 3.67 (t, J=8.5 Hz, 2H), 2.00 (s, 2H), 1.43 (s, 9H), 0.96 (t, J=8.5 Hz, 2H), 0.03 (s, 9H), 0.02 (s, 9H); ¹³C NMR (CDCl₃, 500) δ 187.3, 185.2, 156.2, 150.3, 132.1, 128.2, 95.2, 85.2, 65.2, 58.7, 29.2, 21.2,
18.1, -1.4, -1.5; MS (EI), m/z (rel. intensity) 281(1), 224(2), 207(3), 103(2), 73(100), 57(30); HRMS, m/z calculated for C₂₁H₃₈Si₂O₅, 426.2258; found, 426.2286.

REFERENCES