Journal of the Korean Chemical Society
2003, *Vol. 47, No. 3*
Printed in the Republic of Korea

Cyclobutenediones 에서 Butenolides로의 이색적인 반응

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(2003. 4. 25 접수)

Unusual Transformation of Cyclobutenediones into Butenolides

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(Received April 25, 2003)

요 약. Cyclobutenedions을 lithium trimethylsilylacetylene과 반응시키고 물로 반응을 정지시키면 butenolides가 생성된다. 이 색다른 반응을 위해 allene을 intermediate로 하는 기전을 제안하였다. 이는 trimethylsilyl group이 너무 크기 때문에 보통의 diradical intermediate는 형성이 어렵고, allene이 α-silyl group에 의해 안정화되기 때문이라고 사료된다.

주제어: 뷰티놀라이드, 사이클로 뷰틴다이온, 알렌

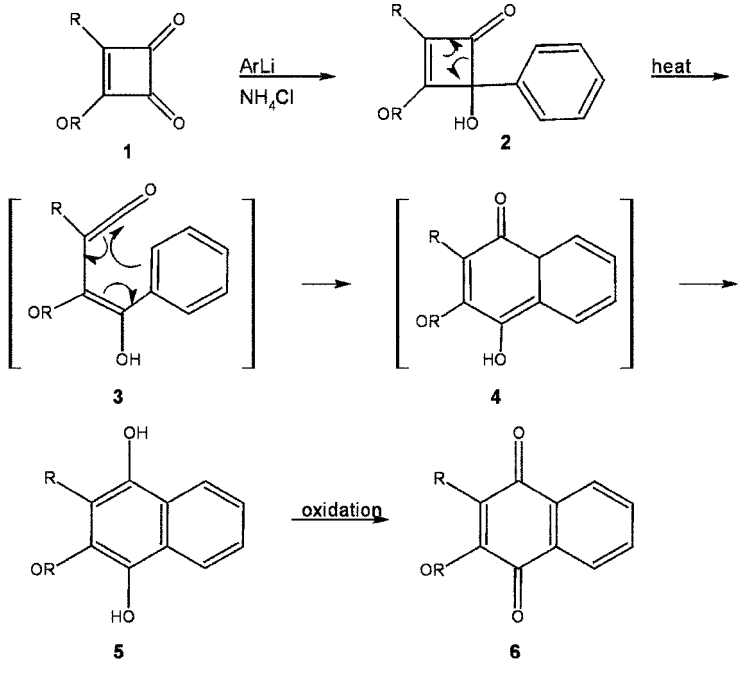
ABSTRACT. Butenolides are prepared from cyclobutenediones when cyclobutenediones are treated with lithium trimethylsilylacetylene, and quenched with water. A plausible mechanism, which contains an allene as an intermediate, is proposed. The usual diradical intermediate may not be formed because of the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

Keywords: Butenolides, Cyclobutendiones, Allene

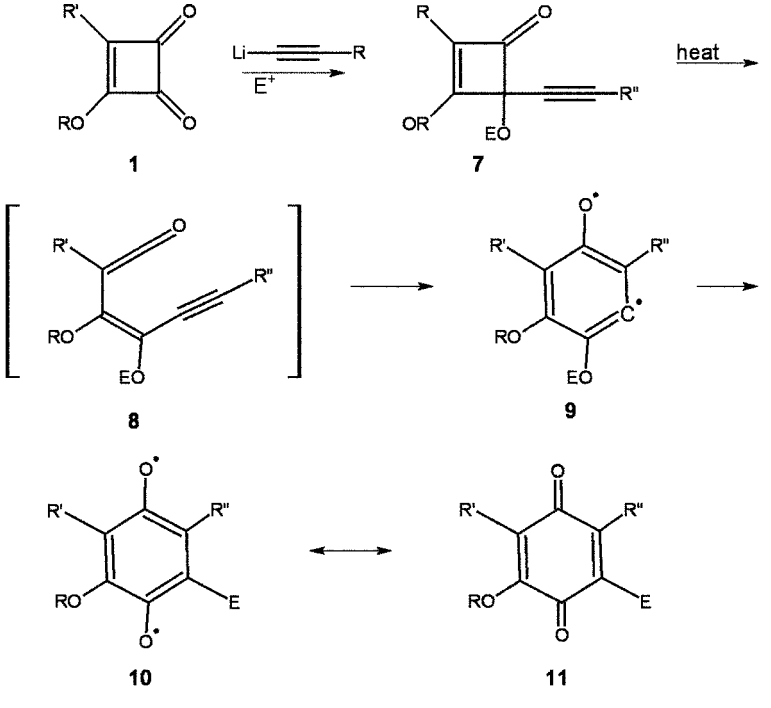
INTRODUCTION

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**.[1] 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.[3]

For R=alkenyl or aryl, a 6-π electron electrocyclic ring closure of **3** gives cyclohexadienone **4**, tautomerization of which gives hydroquinone **5**. This leads to quinone **6** upon oxidation.

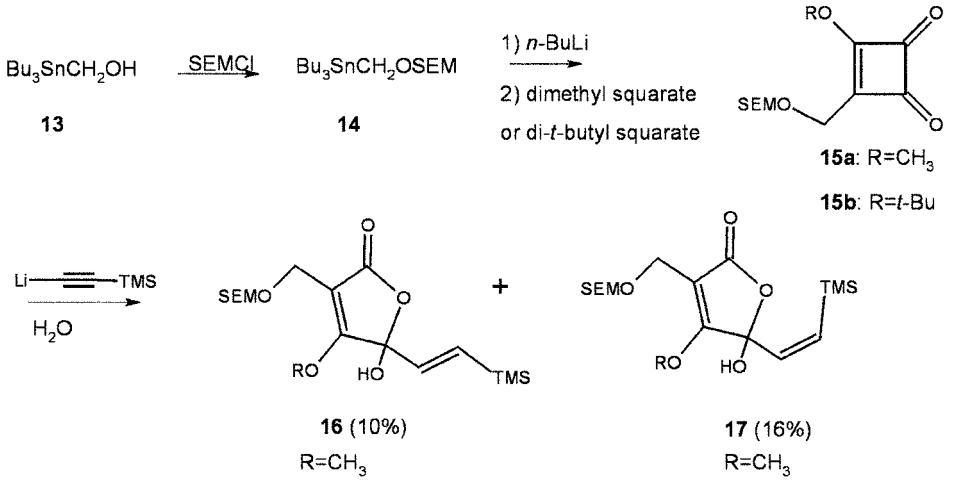


Scheme 1. Synthesis of quinones from alkenyl or aryl compounds with cyclobutenediones.



Scheme 2. Synthesis of quinones from alkynyl compounds with cyclobutenediones.

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 3. Unusual transformation from cyclobutenedione.

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 cyclobutediones react with lithium trimethylsilylacetylene, an unusual transformation can take place. We report an unusual transformation of cyclobutenediones into butenolides in this article.

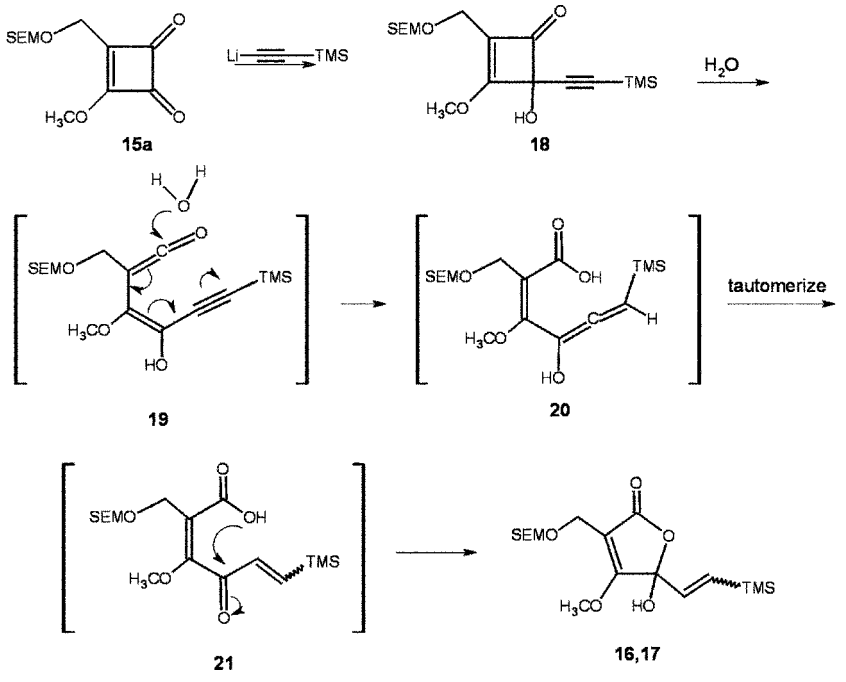
RESULTS AND DISCUSSION

An unexpected transformation took place when lithium trimethylsilylacetylene was treated with 3-methoxy-4-[(trimethylsilylethoxymethoxy)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]

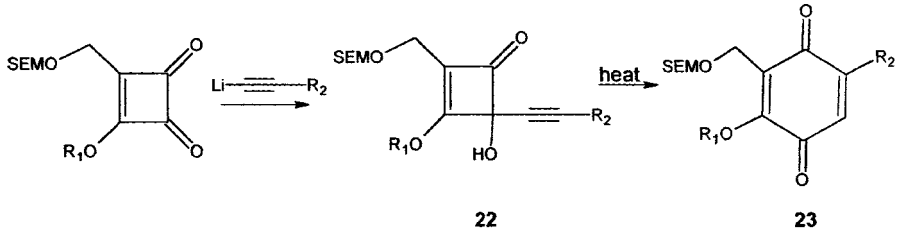
TLC analysis of the reaction revealed some interesting change. The single spot which formed upon addition of lithium trimethylsilylacetylene to **15** splits into two new spots upon quenching the reaction with water. It thus appears that a water molecule plays an important role in the above transformation. 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 trimethylsilylacetyl 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



Scheme 4. Proposed mechanism for the unexpected transformation.



Entry	R_1	R_2	Yields(%)23*
a	CH_3	n-C_4H_9	40
b	CH_3	n-C_3H_7	16
c	t-Bu	n-C_4H_9	38
d	t-Bu	n-C_3H_7	18
e	t-Bu	$CH_2Si(CH_3)_3$	15

* yields from cyclobutenediones

Scheme 5. Products from various alkynyl derivatives.

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

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 Ω 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.

[(Trimethylsilylethoxymethoxy)methyl]tributylstannane (14). The solution of **13** (0.57 g, 2.0 mmol) in 10 mL of dry CH_2Cl_2 were added *i*-Pr_2NEt (2.74 mL, 10 mmol) and SEMCl (0.38 mL, 2.4 mmol) and warmed up to 40 °C. The reaction mixture was stirred for 3 hrs (color of the reaction solution changed from colorless to orange) at 40 °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}; ^1H NMR ($CDCl_3$, 500 MHz) δ 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 ($CDCl_3$) δ 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.

3-Methoxy-4-[(trimethylsilylethoxymethoxy)-methyl]-3-cyclobutene-1,2-dione (15a). To a solution of Bu_3SnCH_2OSEM (3.25 g, 7.2 mmol) in dry THF (30 mL) in 50 mL round bottom flask was added *n*-BuLi (1.6 M in hexanes, 4.0 mL, 7.2 mmol) slowly for 20 min at −78 °C. The reaction mixture was stirred for 30 min at −78 °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 °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 °C and stirred for 30 min and quenched with 5% NH_4Cl 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}; ^1H NMR ($CDCl_3$, 500 MHz) δ 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 ($CDCl_3$) δ 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), 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-trimethylsilylvinyl-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 °C *via* syringe. After stirring for 20 min at −78 °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 °C *via* cannula. Immediately after the completion of transfer, the reaction mixture was quenched with 5% NH_4Cl 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), 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 ($CHCl_3$) 3600, 3019, 2400, 1761, 1734, 1670, 1521, 1422, 1210, 1046 cm^{-1} on the mixture of *cis* and *trans*; ^1H NMR ($CDCl_3$, 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), 4.22 (s, 3H), 3.62 (t, *J*=8.3 Hz, 2H), 0.95 (t, *J*=8.3 Hz, 2H), 0.18 (s, 9H), 0.02 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 174.5, 171.2, 139.1, 138.4, 100.5, 98.8, 94.5, 65.6, 59.5, 57.5, 18.0, 0.6, -1.5 for *cis* isomer **17**. ^1H NMR ($CDCl_3$, 500 MHz) δ 6.42 (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); ^{13}C NMR ($CDCl_3$) 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 $C_{17}H_{32}Si_2O_6$, 388.1737; found, 388.1745.

3-*t*-Butoxy-4-[(trimethylsilylethoxymethoxy)-methyl]-3-cyclobutene-1,2-dione (15b). To the solution of Bu_3SnCH_2OSEM (5.40 g, 12 mmol) in dry THF (50 mL) was added *n*-BuLi (2.5 M in hexanes, 5.0 mL, 13 mmol) slowly *via* syringe at −78 °C. After stirring for 20 min at that temperature, the reaction mixture was transferred to the solution of di-*t*-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% NH_4Cl solution (5 mL) and 100 mL of diethyl ether was added. 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 (3/1 hexanes/ethyl acetate) and gave 1.12 g (36%) of the desired cyclobutenedione **15b** as a pale yellow liquid: IR (neat) 2953, 2894, 1798, 1756, 1586, 1400, 1375, 1337, 1249, 1153, 1109, 1061 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 4.77 (s, 2H), 4.60 (s, 2H), 3.67 (t, *J*=8.5 Hz, 2H), 1.62 (s, 9H), 0.97 (t, *J*=8.5 Hz, 2H), 0.02 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 198.8, 193.3, 192.8, 180.6, 95.1, 88.8, 65.9, 59.0, 28.9, 18.3, -1.2; MS (CI), m/z 257 (MH^+-*t*-Bu); MS (EI), m/z (rel. intensity) 200(4), 185(4), 171(2), 147(2), 141(2), 129(5), 103(7), 101(7), 75(54), 73(100), 57(64), 56(21); HRMS, m/z calculated for $C_{15}H_{26}SiO_5$, 314.1549; found, 314.1381.

6-*n*-Butyl-3-methoxy-2-(trimethylsilylethoxy-methoxy)methyl]benzoquinone (23a). 1) With 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 **15a** (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% NH_4Cl 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 ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$) 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 benzoquinone compound **23a** as a pale yellow liquid. **2) Without purification of the hydroxycyc-lobutenone.** To a solution of 1-hexyne (0.07 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 °C *via* syringe. After stirring for 20 min, the

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% NH_4Cl 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 ($CHCl_3$) 2955, 2874, 1654, 1608, 1460, 1323, 1249, 1059 cm^{-1}; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$) 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(4), 208(16), 207(16), 165(14), 137(50), 101(6), 73(100), 58(6); HRMS, m/z calculated for $C_{18}H_{30}SiO_5$, 354.1862; found, 354.1837.

3-Methoxy-6-*n*-propyl-2-[(trimethylsilylethoxy-methoxy)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 ($CHCl_3$) 2952, 2893, 1740, 1657, 1612, 1596, 1461, 1331, 1267, 1248, 1103, 1038, 860, 836 cm^{-1}; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$) 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 (CI), m/z 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 $C_{17}H_{28}SiO_5$, 340.1706; found, 340.1888.

3-*t*-Butoxy-6-*n*-butyl-2-[(trimethylsilylethoxy-methoxy)methyl]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 ($CHCl_3$) 2930, 2875, 1670, 1656, 1605, 1465, 1394, 1366, 1248, 1139, 1104, 1059, 1028 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.45 (s, 1H), 4.73 (s, 2H), 4.42 (s, 2H), 3.65 (t, *J*=7.1 Hz, 2H), 2.41 (m, 2H), 1.5 (m, 4H), 1.4 (s, 9H), 0.96 (m, 5H), 0.01 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 187.4, 185.7, 156.0, 150.0, 132.4, 131, 95.2, 85.2, 65.2, 58.7, 29.8, 29.2, 28.6, 22.4, 18.0, 13.7, -1.5; MS (CI), m/z 342 (MH^+-*t*-Bu); 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 $C_{21}H_{36}SiO_5$, 396.2332; found, 396.2305.

3-*t*-Butoxy-6-*n*-propyl-2-[(trimethylsilylethoxy-methoxy)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 ($CHCl_3$) 2959, 2933, 2877, 1669, 1655, 1605, 1459, 1395, 1370, 1319, 1250, 1137, 1058, 1021, 862, 838 cm^{-1}; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$) 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 (CI), m/z 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 $C_{20}H_{34}SiO_5$, 384.2332; found, 384.2315.

3-*t*-Butoxy-6-*n*-trimethylsilylmethyl-2-[(trime-thylsilylethoxymethoxy)methyl]benzoquinone (23e). Compound **23e** was prepared (32 mg, 50%) from 3-trimethylsilylpropyne (0.06 mL, 0.6 mmol) by the similar process for the synthesis of **23c** as a yellow oil: IR ($CHCl_3$) 2956, 2898, 1655, 1597, 1464, 1370, 1251, 1135, 1059 cm^{-1}; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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(20), 103(3), 101(2), 75(35), 73(100), 57(30); HRMS, m/z calculated for $C_{21}H_{38}Si_2O_5$, 426.2258; found, 426.2286.

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