induce rate enhancement by virtue of coordination to the phosphoryl oxygen atoms. However, β_{nuc} for the catalyzed processes (0.21 and 0.17, respectively) was found to be practically identical with that of the uncatalyzed reaction (0.18). It was therefore concluded that both reactions have essentially the same TS structure. Similarly, the work of Jorgensen and Buckner[31] showed that, for the reaction of chloride ion with methyl chloride, the TS structure remains essentially constant on going from the gas phase to aqueous medium. Thus, it is not surprising that in the present case variation in the intensity of solvent interactions with the transition state, e.g., by hydrogen bonding, while changing its energy does not affect its structure.

Finally, it should be pointed out that the magnitude of β_{nuc} cannot be used to deduce the degree of nucleophile–substrate bond formation at the transition state. This parameter can be obtained from the normalized β_{nuc} value, i.e., β_{nuc}/β_{eq}, where β_{eq} refers to the equilibrium for the formation of the tetrahedral intermediate. The latter, however, is not available for the present system.

Conclusions. Two goals were achieved in this study: (a) we have shown that, under certain conditions, the TS structure of the title reaction is insensitive to variation in the reaction medium, and (b) a novel strategy for the construction of Brønsted type plots was devised. The latter involves *variation of the pK_a of the nucleophile by changing the solvent composition rather than by variation of substituents.* This method is applicable in cases where no drastic and capricious changes of solvent properties occur. In water–DMSO mixtures, the range 40–90 mol % DMSO was found to comply with this requirement.

Using a statistical analysis it was shown that the unique β_{nuc} value obtained by the method proposed herein is by far more reliable than the individual values derived by the traditional method. The linearity obtained in this case, together with the nearly constant value of the normalized ρ values for substituent variation on the leaving group, indicates a nearly constant structure of the transition state. This conclusion derives strong support from the aforementioned studies by Jencks[30] and Jorgensen.[31]

The major advantage of this novel method for construction of Brønsted type plots is that it enables an extension of the pK_a range beyond the one set by the limited number of substituents and that within this range more data points can be obtained. These two features increase significantly the reliability of the derived β_{nuc} parameter, providing a more solid basis for mechanistic interpretation. We believe that this strategy is of general nature and can be applied to other systems as well.

(31) Jorgensen, W. L.; Buckner, J. K. *J. Phys. Chem.* **1986**, *90*, 4651.

Experimental Section

The aryl acetates in this study were prepared by literature procedures and their purity was checked by means of their physical constants and IR and ^1H NMR characteristics. The phenols were of the highest quality available and were generally recrystallized before use. Doubly glass-distilled water was boiled and cooled under nitrogen just before use. Dioxane was first refluxed and distilled from anhydrous stannous chloride and then from metallic sodium. Dimethyl sulfoxide was refluxed over calcium hydride, distilled, collecting the fraction of bp 64–66 °C (6–7 mmHg), and stored under nitrogen. All solutions were prepared and stored under nitrogen and transferred by means of syringes. DMSO–water solutions of various mol % DMSO compositions were prepared by weight. Only freshly prepared solutions were used in the kinetic studies.

The rates of relatively slow reactions ($T_{1/2} > 10$ s) were followed spectrophotometrically with a Beckman 25, Acta IV, or Perkin-Elmer 552 spectrophotometer equipped with thermostated cell holders. Generally, reactions were followed at a fixed wavelength (λ_{max} of ArO^-). Typically, reaction was initiated by adding 5 μL of a 0.02 M solution of the aryl acetate in dioxane by syringe to a 10-mm quartz cuvette containing the reaction mixture made up of DMSO–water, the phenol, and 0.5 equiv of aqueous NaOH or aqueous Me_4NOH for DMSO-rich media. Generally, the phenoxide concentration was varied over the range $(1-30) \times 10^{-3}$ M while the ester concentration was 2×10^{-5}–2×10^{-4} M, depending on λ_{max} and molar extinction values, with the nucleophile concentration at least 15 times that of the substrate. Usually, five values of $[ArO^-]$ were employed and replicate values of k_{obsd} were determined to obtain the second-order rate coefficients from linear k_{obsd} vs $[ArO^-]$ plots. For reactions with $T_{1/2} < 10$ s, a stopped-flow technique was used with a Can-Tech module, spectral traces being displayed on an oscilloscope and data stored on a transient recorder coupled to a computer to yield the pseudo-first-order rate constant k_{obsd}.

Acknowledgment. Financial support of this research by the Natural Sciences and Engineering Research Council of Canada and the award of an Ontario graduate scholarship (I.H.U.) are gratefully acknowledged.

Registry No. $4\text{-}ClC_6H_4^-$, 24573-38-4; $4\text{-}CNC_6H_4^-$, 14609-76-8; PhO^-, 3229-70-7; $4\text{-}CH_3C_6H_4O^-$, 22113-51-5; $CH_3C(O)OC_6H_4\text{-}4\text{-}NO_2$, 830-03-5; $CH_3C(O)OC_6H_4\text{-}3\text{-}NO_2$, 1523-06-4; $CH_3C(O)OC_6H_4\text{-}4\text{-}CHO$, 878-00-2; $CH_3C(O)OC_6H_4\text{-}3\text{-}CHO$, 34231-78-2; $CH_3C(O)OC_6H_4\text{-}4\text{-}COCH_3$, 13031-43-1.

Rearrangement of 4-Alkynylcyclobutenones. A New Synthesis of 1,4-Benzoquinones

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Contribution from the Department of Chemistry, University of California, Irvine, California 92717. *Received June 24, 1988*

Abstract: A new convergent synthesis of 1,4-benzoquinones from 4-alkynyl-4-alkoxy(or hydroxy or trimethylsilyloxy)cyclobutenones is described. The required cyclobutenones are prepared from squaric acid and converted to the quinones upon mild thermolysis. The reaction proceeds via electrocyclic ring opening of the required cyclobutenones to (2-alkynylethenyl)ketenes, which then ring close to unique diradical intermediates. These then give the quinone products. The scope and mechanism of this unusual rearrangement are discussed.

Reported here are details of a new reaction having significant utility for the synthesis of substituted 1,4-benzoquinones **6** and 2-alkylidene-1,3-cyclopentenediones **7** (Scheme I).[2,3] These products arise from 4-alkynylcyclobutenones **2** which are envisaged to undergo a remarkably selective electrocyclic ring opening upon mild thermolysis to generate (2-alkynylethenyl)ketenes **3**. These reactive ketenes then undergo ring closure to produce the unique diradicals (or zwitterions) **4** and **5**, which, in turn, proceed to

(1) This work was taken primarily from the Ph.D. Dissertation research of L.D.F.

(2) A preliminary account of this work has appeared. See: Karlsson, J. O.; Nguyen, N. V.; Foland, L. D.; Moore, H. W. *J. Am. Chem. Soc.* **1985**, *107*, 3392.

(3) For a review of related chemistry, see: Moore, H. W.; Decker, O. H. W. *Chem. Rev.* **1986**, *86*, 821.

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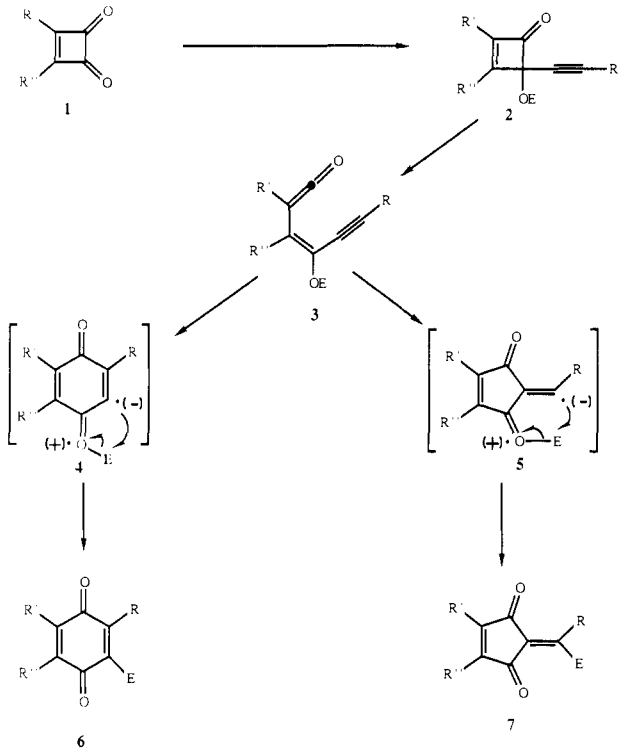
Scheme I

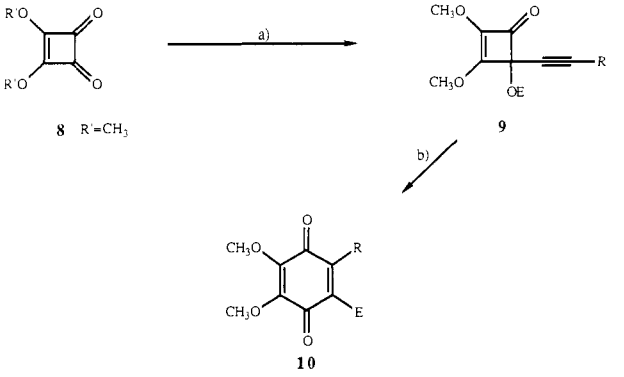


products **6** and **7** via an intramolecular transfer of the E substituent (proton, trimethysilyl, or allyl) from oxygen to carbon. The selectivity of this rearrangement to give either benzoquinones or cyclopentenediones is significantly influenced by the R substituent of the alkyne moiety in that radical-stabilizing groups tend to favor cyclopentenedione formation. The method is convergent, of particular use as a benzoquinone synthesis, and starts with cyclobutenediones **1**, a class of compounds which are easily prepared in a variety of substitution patterns from commercially avaiable squaric acid.[4-6]

Results and Discussion

1. Synthetic Scope. Specific examples illustrating the synthetic utility of this method as a route to benzoquinones are given in Schemes II and III. Those in Scheme II employ dimethyl squarate as a starting material, which is easily converted to the 4-alkynyl-2,3-dimethoxy-4-(trimethylsiloxy)(or hydroxy)cyclobutenones **9** in 50–90% yield upon treatment with the corresponding lithium acetylide (THF, −78 °C) followed by quenching of the reaction mixture with trimethylsilyl chloride or ammonium chloride, respectively.[6] The realized cyclobutenones were then thermolyzed (*p*-xylene, 138 °C) to give the 1,4-benzoquinones **10** as the only isolable products in the indicated purified yields. This is a useful reaction, having apparent generality for the synthesis of benzoquinones having a variety of substitution patterns. Particular note is made of the trimethylsilyl-substituted 1,4-benzoquinones since they constitute members of a rare class of compounds and warrant further study.[7] It is also noteworthy that the method is ideally suited for the synthesis of benzoquinones having those structural features deemed necessary for potential bioreductive alkylating agents, i.e., quinones such as **10c–i**, which

Scheme II

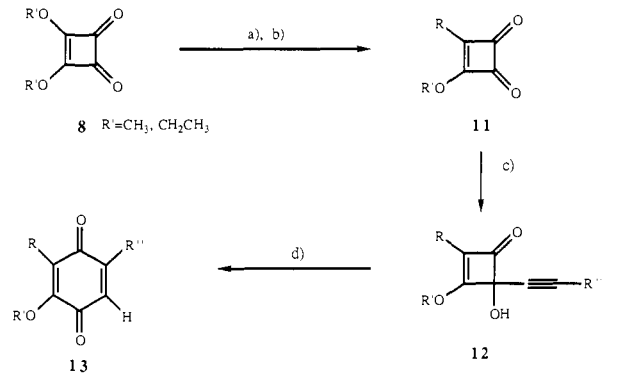


	R	E	% YIELD
a	-n-C_4H_9	- H	78
b	-n-C_4H_9	-$Si(CH_3)_3$	75
c	-CH_2OTMS	-H	36
d	-CH_2OTMS	-$Si(CH_3)_3$	80 (54)*
e	-CH_2OTHP	-H	47
f	-CH_2OTHP	-$Si(CH_3)_3$	41
g	- $CH(CH_3)OTMS$	- H	64
h	-CH(CH3)OTHP	-H	46*
i	-$CH(CH_3)OTHP$	-$Si(CH_3)_3$	36
j	-$Si(CH_3)_3$	-$Si(CH_3)_3$	55
k	-$CH_2CH_2CH{\equiv}CH$	- $Si(CH_3)_3$	42*
l	-$CH_2C_6H_5$	- H	71
m	-$CH_2C_6H_5$	-$Si(CH_3)_3$	74
n	-H	- H	48
o	-H	- $Si(CH_3)_3$	75

* Yield obtained from **8** in a "one Pot" sequence

a) Li$C{\equiv}$C-R, THF, -78° b) 138°, p-xylene

Scheme III



	R'	R	R''	%13
a	-CH_3	-C_6H_5	-n-C_4H_9	57
b	-CH_3	-$C{\equiv}C$-C_6H_5	-n-C_4H_9	57
c	-CH_2CH_3	-C_6H_5	-$CH_2C_6H_5$	46
d	-CH_2CH_3	-n-C_4H_9	-$CH_2C_6H_5$	47
e	-CH_2CH_3	-$C_{10}H_7$	-$CH_2C_6H_5$	65
f	-CH_3	-n-C_4H_9	-$CH_2C_6H_5$	84*
g	-CH_3	-$C{\equiv}CC_6H_5$	-$CH_2C_6H_5$	50*

* Yield obtained from **11** in a "one pot" sequence

a) LiR', THF, -78° b) TFAA, -78° c) Li$C{\equiv}$C-R'', THF, -78° d) 138°, p-xylene

are reasonable precursors to electrophilic quinone methides (alkylating agents) subsequent to an in vivo reduction.[8,9]

The examples shown in Scheme III illustrate another dimension of the synthetic scope of this method. Here, either dimethyl or diethyl squarate (**8**, R′ = CH_3 or CH_2CH_3) was converted to the respective cyclobutenediones **11a–g** in good yield upon treatment with the corresponding organolithium reagent at −78 °C in THF followed by trifluoroacetic anhydride and standard workup conditions.[4,5] These were then taken on to the alkynyl adducts **12a–g**,

(4) Reed, M.; Perri, S. T.; Pollart, D.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477.

(5) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482.

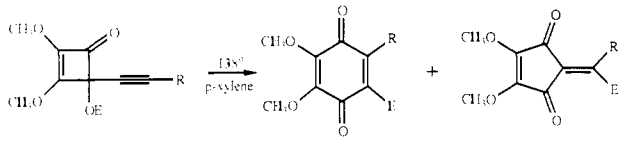
(6) Dimethyl squarate is readily available from the commercially available diethyl analogue upon refluxing in methanol. Caution should be used in handling diethyl squarate since we have found it to cause severe contact dermatitis.

(7) Hashimoto, T. *Yakugaku Azsshi* **1967**, *87*, 535. Vasikiskaya, N. S.; Gorbunova, L. V.; Mamysheva, O. N.; Bortnikov, G. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, 2755. Back, H.; Alt, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 944.

(8) Moore, H. W. *Science* **1977**, *197*, 527.

(9) Moore, H. W.; Czernick, R. *Med. Res. Rev.* **1981**, *1*, 249.

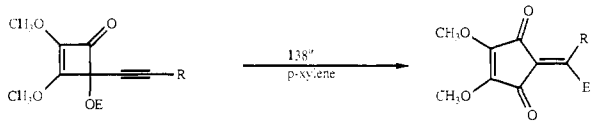
Scheme IV



14 15 16

	R	E	% 15	% 16
a	$-C_6H_5$	-H	21	46
b	$-C_6H_5$	-TMS	52	13
c	$-OC_2H_5$	-H	25	50
d	$-OC_2H_5$	-TMS	23	55
e	-TMS	-H	21	5

Scheme V



17 18

	R	E	% 18
a	$-CO_2C_2H_5$	-H	66
b	$-Cl_2C_2H_5$	-TMS	33
c	$-CH=CHOCH_3$	-H	49

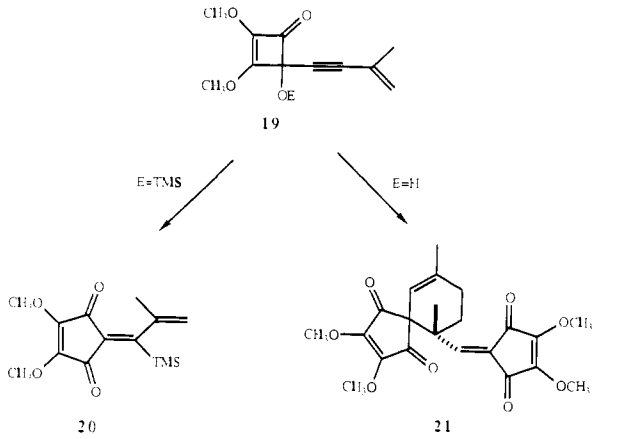
which readily rearranged to the quinones **13a–e** under the standard conditions (*p*-xylene, 138 °C). An important point with regard to this chemistry is that benzoquinones of structural type **13** can now be prepared *regiospecifically* since it was observed that **11** reacts selectively with organolithium reagents at the more reactive non-vinylogous ester carbonyl group. Thus, alkoxybenzoquinones having different alkyl groups disposed in a 2,6 relationship are now readily available. This method complements one previously reported for the synthesis of 2,5-dialkylated 1,4-benzoquinones.[10]

Although thermolyses of the cyclobutenones **9** and **12** were conveniently accomplished in refluxing *p*-xylene, it is noteworthy that the rearrangements of the **12** series could be accomplished at much lower temperatures. For example, it was observed that a diethyl ether solution of **12f** rearranged to **13f** at ambient temperature over a period of several hours while **9l** was unreactive under these conditions.

For all of the above examples the alkyne moiety is substituted with an alkyl group or a proton, and in these cases only the corresponding benzoquinones were detected as products of the thermolyses. Interestingly, when the substituent R of **14** (Scheme IV) is an alkoxy, phenyl, or trimethylsilyl group, a mixture of the benzoquinones **15a–e** and 2-alkylidene-1,3-cyclopentenediones **16a–e** resulted. Furthermore, the rearrangement can be driven completely to the cyclopentenediones **18a–c** when the cyclobutenones **17a–c** are employed (Scheme V). These results are best explained by the generalized mechanism represented in Scheme I, i.e., the intermediate **5** becomes favored over **4** when the substituent R becomes more and more capable of stabilizing an adjacent radical site. Apparently, the presumed aromatic stabilization associated with six-membered ring formation (**4**) is overcome by direct stabilization of one of the radical centers by the adjacent R substituent when five-membered ring formation (**5**) takes place.

Although generation of the cyclopentenediones by the method given here is of interest, it is of more mechanistic value than of synthetic utility since a related and more general route to this class of compounds is now available upon treatment of 4-alkynylcyclobutenones with a catalytic amount of palladium trifluoroacetate.[11] In any regard, an interesting example of cyclopentenedione formation is represented in Scheme VI. Here, the cyclobutenones **19** were each thermolyzed at 138 °C in refluxing *p*-xylene. For the (trimethylsilyl)oxy derivative, rearrangement took place as expected to give the cyclopentenedione **20** (69% yield) along with a small amount of the corresponding benzoquinone (16% yield) (9:2). However, for the sterically less congested

Scheme VI



19 20 21

Table I. Experimental Data for the X-ray Diffraction Study

formula: $C_{12}H_{24}O_8$	monochromator: highly oriented graphite
fw: 416.0	data collected: $+h,+k,\pm l$
crystal system: monoclinic	scan type: coupled θ (crystal) – 2θ (counter)
space group: $P2_1/c$ (No. 14; C_{2h}^5)	scan width: symmetrical $[2\theta(K\alpha_1) - 1.2] \rightarrow [2\theta(K\alpha_2) + 1.2]$
a = 13.3028 (41) Å	scan speed: 4.0 deg min^{-1} (in 2θ)
b = 10.5491 (24) Å	$2\theta_{max}$: 55.0°
c = 14.5381 (40) Å	μ(Mo Kα) = 0.98 cm^{-1}
β = 94.501 (23)°	unique reflections: 4697
V = 2033.5 (9) Å^3	no. of variables: 367
Z = 4	R_F = 6.6%
D_{calcd} = 1.38 g/cm^3	R_{wF} = 6.4%
diffractometer: Nicolet P3	goodness of fit: 1.52
radiation: Mo Kα ($\bar{\lambda}$ = 0.710730 Å)	

Table II. Final Positional Parameters

atom	x	y	z
C(01)	0.5183 (1)	0.1876 (1)	0.1442 (1)
c(02)	0.4625 (1)	0.2556 (1)	0.2015 (1)
C(03)	0.5293 (1)	0.3129 (1)	0.2752 (1)
C(04)	0.6362 (1)	0.2569 (1)	0.2734 (1)
C(05)	0.6240 (1)	0.1794 (1)	0.1841 (1)
C(06)	0.7113 (1)	0.3632 (2)	0.2645 (1)
C(07)	0.7717 (1)	0.4078 (1)	0.3340 (1)
C(08)	0.7736 (1)	0.3526 (2)	0.4294 (1)
C(09)	0.6861 (1)	0.2641 (2)	0.4434 (1)
C(10)	0.6634 (1)	0.1737 (1)	0.3611 (1)
C(11)	0.7590 (1)	0.1001 (1)	0.3477 (1)
C(12)	0.8064 (1)	0.0125 (1)	0.4013 (1)
C(13)	0.7850 (1)	−0.0515 (2)	0.4884 (1)
C(14)	0.8630 (1)	−0.1506 (2)	0.5054 (1)
C(15)	0.9312 (1)	−0.1467 (2)	0.4406 (1)
C(16)	0.9020 (1)	−0.0446 (2)	0.3742 (1)
C(17)	0.3937 (1)	0.1236 (2)	0.0271 (1)
C(18)	0.3075 (1)	0.2881 (2)	0.2687 (1)
C(19)	0.8430 (2)	0.5155 (2)	0.3210 (2)
C(20)	0.5751 (1)	0.0855 (2)	0.3798 (1)
C(21)	0.9258 (3)	−0.3221 (4)	0.5994 (2)
C(22)	1.0686 (2)	−0.2327 (3)	0.3632 (2)
O(01)	0.4969 (1)	0.1313 (1)	0.0638 (1)
O(02)	0.3631 (1)	0.2804 (1)	0.1878 (1)
O(03)	0.5052 (1)	0.3961 (1)	0.3265 (1)
O(04)	0.6895 (1)	0.1202 (1)	0.1496 (1)
O(05)	0.7200 (1)	−0.0310 (1)	0.5406 (1)
O(06)	0.8540 (1)	−0.2236 (2)	0.5789 (1)
O(07)	1.0131 (1)	−0.2211 (2)	0.4407 (1)
O(08)	0.9477 (1)	−0.0128 (1)	0.3089 (1)

(10) Moore, H. W.; Sing, Y. L.; Sidhu, R. S. *J. Org. Chem.* **1980**, *45*, 4483.

(11) Liebeskind, L. S.; Mitchell, D.; Foster, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 7908.

Table III. Anisotropic Temperature Factors (×10e4)[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(01)	380 (7)	319 (7)	281 (7)	1 (6)	40 (6)	21 (6)
C(02)	340 (7)	339 (8)	349 (7)	41 (6)	35 (6)	10 (6)
C(03)	375 (8)	337 (8)	329 (7)	64 (6)	55 (6)	-3 (6)
C(04)	339 (7)	339 (7)	294 (7)	47 (6)	44 (6)	-5 (6)
C(05)	369 (7)	339 (8)	295 (7)	25 (6)	80 (6)	19 (6)
C(06)	382 (8)	373 (8)	388 (8)	36 (6)	67 (6)	34 (7)
C(07)	345 (8)	362 (8)	502 (9)	47 (6)	52 (7)	-34 (7)
C(08)	400 (9)	455 (9)	444 (9)	36 (7)	-29 (7)	-71 (8)
C(09)	401 (8)	446 (9)	307 (7)	86 (7)	32 (6)	-39 (7)
C(10)	336 (7)	362 (8)	300 (7)	49 (6)	55 (6)	14 (6)
C(11)	358 (7)	378 (8)	313 (7)	36 (6)	52 (6)	-9 (6)
C(12)	359 (7)	396 (8)	326 (7)	55 (6)	55 (6)	-10 (6)
C(13)	412 (9)	536 (10)	373 (8)	113 (8)	71 (7)	66 (7)
C(14)	474 (9)	621 (11)	408 (9)	143 (8)	82 (7)	158 (8)
C(15)	389 (8)	589 (11)	423 (9)	164 (8)	59 (7)	87 (8)
C(16)	374 (8)	507 (9)	370 (8)	80 (7)	66 (7)	41 (7)
C(17)	426 (9)	651 (13)	442 (10)	-10 (9)	-21 (8)	-138 (9)
C(18)	376 (10)	683 (13)	545 (11)	3 (9)	119 (8)	-69 (11)
C(19)	451 (10)	454 (11)	767 (15)	-60 (8)	48 (10)	-14 (10)
C(20)	384 (8)	428 (9)	457 (9)	3 (7)	70 (7)	55 (8)
C(21)	1090 (24)	1285 (27)	869 (20)	757 (22)	431 (19)	688 (21)
C(22)	652 (14)	1007 (21)	653 (15)	461 (15)	235 (12)	183 (14)
O(01)	402 (6)	477 (6)	310 (5)	-15 (5)	41 (4)	-63 (5)
O(02)	344 (6)	582 (7)	417 (6)	73 (5)	31 (5)	-56 (5)
O(03)	458 (7)	487 (7)	492 (7)	127 (5)	-5 (5)	-173 (6)
O(04)	418 (6)	558 (7)	377 (6)	97 (5)	87 (5)	-58 (5)
O(05)	616 (8)	880 (10)	486 (7)	324 (8)	249 (6)	196 (7)
O(06)	717 (9)	1016 (12)	676 (9)	448 (9)	293 (8)	497 (9)
O(07)	648 (9)	1140 (13)	665 (9)	557 (9)	270 (7)	364 (9)
O(08)	576 (8)	846 (10)	640 (9)	265 (7)	309 (7)	293 (8)

[a] The anisotropic displacement exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*bU_{12})$.

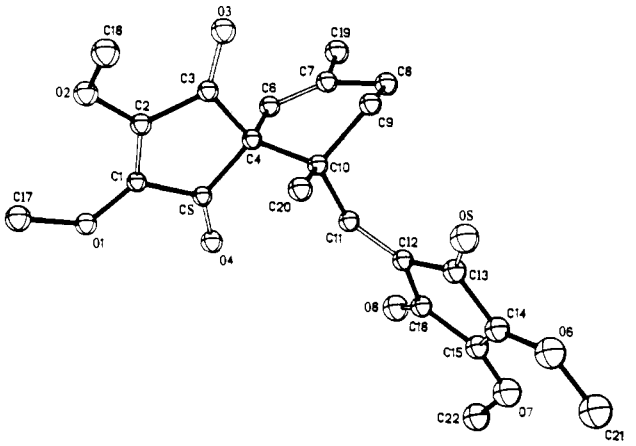


Figure 1. ORTEP plot of dimer **21**.

hydroxy derivative (E = H), the Diels–Alder dimer **21** was realized as the main product. The structure of **20** is based upon its characteristic spectral data, which are listed in the Experimental Section. The structure of **21** was not amenable to simple spectral analysis and thus a complete X-ray crystal structure determination was necessary (see Figure 1 and Tables I–VI).

In conclusion, the 4-alkynylcyclobutenone rearrangement described here provides an especially useful route to substituted benzoquinones; 2-alkyl-5,6-dialkoxy- and 2,6-dialkyl-5-alkoxy-1,4-benzoquinones are conveniently prepared by this regiospecific method. The reaction should gain even further attention since alkoxy groups on quinone nuclei are also easily replaced by a variety of nucleophiles (addition–elimination). Thus, a general route to highly substituted benzoquinones is now available. Additional specific applications of this rearrangement to targets in the natural products arena are presented in the following paper.

Attention is now turned to mechanistic consideration of this unusual rearrangement.

2. Mechanism A number of questions can be formulated from the mechanistic paradigm outlined in Scheme I. For example, it predicts an intramolecular migration of the E substituent in the

Table IV. Interatomic Distances (Å) with Esd's

C(01)–O(01)	1.322 (2)	C(01)–C(02)	1.363 (2)
C(01)–C(05)	1.481 (2)	C(02)–O(02)	1.347 (2)
C(02)–C(03)	1.468 (2)	C(03)–O(03)	1.211 (2)
C(03)–C(04)	1.542 (2)	C(04)–C(06)	1.514 (2)
C(04)–C(05)	1.532 (2)	C(04)–C(10)	1.567 (2)
C(05)–O(04)	1.212 (2)	C(06)–C(07)	1.327 (2)
C(07)–C(19)	1.501 (2)	C(07)–C(08)	1.503 (2)
C(08)–C(09)	1.518 (2)	C(09)–C(10)	1.541 (2)
C(10)–C(11)	1.516 (2)	C(10)–C(20)	1.539 (2)
C(11)–C(12)	1.335 (2)	C(12)–C(13)	1.482 (2)
C(12)–C(16)	1.488 (2)	C(13)–O(05)	1.214 (2)
C(13)–C(14)	1.480 (2)	C(14)–O(06)	1.330 (2)
C(14)–C(15)	1.359 (2)	C(15)–O(07)	1.343 (2)
C(15)–C(16)	1.478 (2)	C(16)–O(08)	1.214 (2)
C(17)–O(01)	1.436 (2)	C(18)–O(02)	1.440 (2)
C(21)–O(06)	1.427 (3)	C(22)–O(07)	1.400 (3)

Table V. Interatomic Angles (Deg) with Esd's

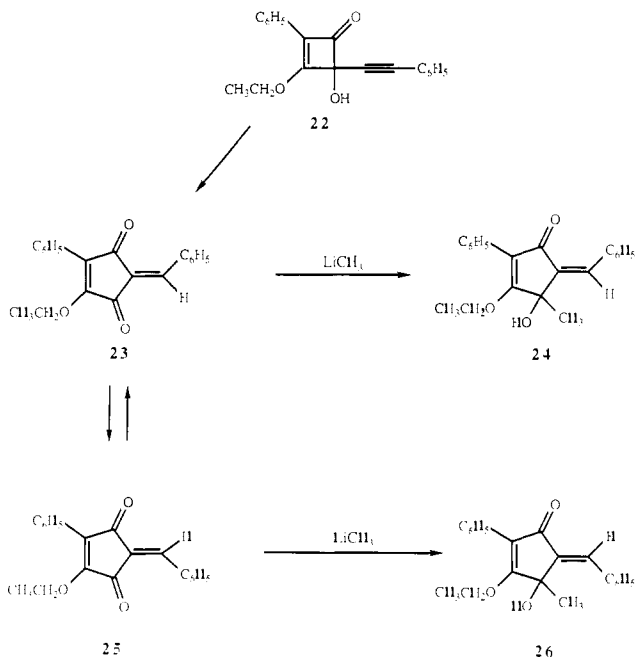
O(01)–C(01)–C(02)	133.41 (14)	O(01)–C(01)–C(05)	116.87 (13)
C(02)–C(01)–C(05)	109.72 (13)	O(02)–C(02)–C(01)	125.96 (14)
O(02)–C(02)–C(03)	123.99 (13)	C(01)–C(02)–C(03)	109.60 (13)
O(03)–C(03)–C(02)	125.01 (14)	O(03)–C(03)–C(04)	125.25 (14)
C(02)–C(03)–C(04)	109.65 (12)	C(06)–C(04)–C(05)	110.46 (12)
C(06)–C(04)–C(03)	109.47 (12)	C(06)–C(04)–C(10)	111.88 (12)
C(05)–C(04)–C(03)	100.50 (11)	C(05)–C(04)–C(10)	113.14 (12)
C(03)–C(04)–C(10)	110.81 (11)	O(04)–C(05)–C(01)	124.00 (14)
C(04)–C(05)–C(04)	126.43 (14)	C(01)–C(05)–C(04)	109.57 (12)
C(07)–C(06)–C(04)	124.18 (15)	C(06)–C(07)–C(19)	121.55 (17)
C(06)–C(07)–C(08)	122.06 (15)	C(19)–C(07)–C(08)	116.39 (16)
C(07)–C(08)–C(09)	113.86 (14)	C(08)–C(09)–C(10)	112.46 (13)
C(11)–C(10)–C(20)	111.88 (13)	C(11)–C(10)–C(09)	107.55 (12)
C(11)–C(10)–C(04)	108.96 (11)	C(20)–C(10)–C(09)	110.04 (13)
C(20)–C(10)–C(04)	110.59 (13)	C(09)–C(10)–C(04)	107.69 (12)
C(12)–C(11)–C(10)	129.97 (14)	C(11)–C(12)–C(13)	134.47 (14)
C(11)–C(12)–C(16)	120.01 (14)	C(13)–C(12)–C(16)	105.50 (13)
O(05)–C(13)–C(14)	123.09 (15)	O(05)–C(13)–C(12)	130.31 (15)
C(14)–C(13)–C(12)	106.58 (13)	O(06)–C(14)–C(15)	132.97 (16)
O(06)–C(14)–C(13)	115.91 (15)	C(15)–C(14)–C(13)	111.12 (15)
O(07)–C(15)–C(14)	124.57 (16)	O(07)–C(15)–C(16)	126.76 (15)
C(14)–C(15)–C(16)	108.62 (14)	O(08)–C(16)–C(15)	126.16 (15)
O(08)–C(16)–C(12)	125.88 (15)	C(15)–C(16)–C(12)	107.96 (13)
C(01)–O(01)–C(17)	119.16 (13)	C(02)–C(02)–C(18)	116.83 (14)
C(14)–O(06)–C(21)	119.24 (17)	C(15)–O(07)–C(22)	121.96 (16)

Table VI. Hydrogen Atom Coordinates and $U(iso) \times 10e^{3}$[a]

atom	x	y	z	U(iso)
H(06)	0.7116 (14)	0.4071 (17)	0.2010 (12)	18 (5)
H(08A)	0.8390 (15)	0.3053 (19)	0.4421 (13)	27 (5)
H(08B)	0.7746 (14)	0.4213 (20)	0.4771 (13)	24 (5)
H(09A)	0.6257 (13)	0.3133 (17)	0.4481 (11)	14 (4)
H(09B)	0.7014 (13)	0.2106 (17)	0.5000 (12)	14 (4)
H(11)	0.7946 (13)	0.1226 (17)	0.2922 (12)	15 (4)
H(17A)	0.3946 (15)	0.0644 (20)	-0.0268 (14)	27 (5)
H(17B)	0.3677 (17)	0.2058 (25)	0.0135 (15)	42 (6)
H(17C)	0.3529 (19)	0.0929 (24)	0.0744 (16)	47 (7)
H(18A)	0.3233 (19)	0.3669 (27)	0.2999 (18)	53 (7)
H(18B)	0.3243 (20)	0.2235 (27)	0.3094 (19)	55 (8)
H(18C)	0.2390 (19)	0.2866 (22)	0.2514 (15)	40 (6)
H(19A)	0.8255 (17)	0.5864 (23)	0.3614 (15)	37 (6)
H(19B)	0.8425 (17)	0.5416 (22)	0.2581 (17)	36 (6)
H(19C)	0.9147 (21)	0.4916 (25)	0.3400 (17)	58 (8)
H(20A)	0.5938 (15)	0.0300 (19)	0.4318 (14)	28 (5)
H(20B)	0.5550 (14)	0.0349 (18)	0.3267 (14)	20 (5)
H(20C)	0.5167 (16)	0.1339 (19)	0.3946 (13)	25 (5)
H(21C)	0.9028 (22)	-0.3667 (31)	0.6469 (13)	76 (9)
H(21A)	0.9933 (53)	-0.2590 (62)	0.6220 (43)	215 (27)
H(21B)	0.9413 (23)	-0.3666 (30)	0.5426 (22)	75 (10)
H(22A)	1.0928 (24)	-0.1533 (37)	0.3395 (24)	88 (11)
H(22B)	1.1165 (20)	-0.2851 (26)	0.3769 (17)	50 (7)
H(22C)	1.0267 (22)	-0.2496 (28)	0.3105 (20)	68 (10)

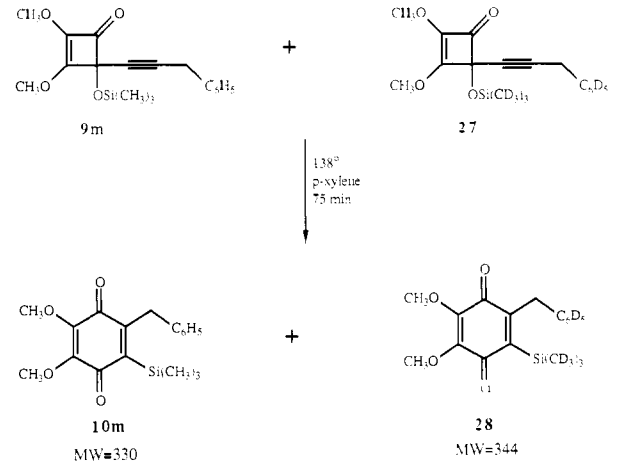
[a] The complete temperature factor is exp $[-U^{*}8\pi^{2*} \sin(\theta^2)/(\lambda^2)]$.

Scheme VII



product-forming step, leading to both **6** and **7**. This translates to the expectation that one stereoisomer of the 4-alkylidene-1,3-cyclopentenediones should be formed as the kinetic product when suitably substituted 4-alkynylcyclobutenediones are thermolyzed. This was, in fact, established for the rearrangement of **22** in that only **23** (46%, Scheme VII) was observed (^{1}H NMR) in the crude reaction mixture immediately following thermolysis. The stereochemistry of **23** was determined as follows. Treatment of **23** with silica gel resulted in its facile equilibration with **25**. These two isomers were then treated with methyllithium to give **24** and **26**, respectively. The regioselectivity of addition is controlled by the difference in reactivity of the two carbonyl groups, one being a vinylogous ester and the other being a more reactive enone. The *Z* configuration of **24** and the *E* configuration of **26** were then established from their respective ^{1}H NMR spectrum. The vinyl proton of the former absorbed at 6.96 ppm and the latter showed an analogous absorption further downfield at 7.51 ppm. This difference is expected due to the deshielding anisotropy effect of the proximal carbonyl group of the *E* isomer.[11] These assignments

Scheme VIII



No crossover products were detected at m/e 335 and/or 339.

were confirmed by NOE studies on **24**; preiiradiation of the vinylic proton absorption at 6.96 ppm resulted in the net enhancement of the hydroxy proton absorption at 2.25 ppm (5%) and the methyl absorption at 1.73 ppm (2.5%). The *Z* stereochemistry of **24** translates to the indicated *E* stereochemistry of **23** and thus allows the conclusion that **23** is formed stereospecifically, a result most likely involving an intramolecular migration of the hydrogen atom in the diradical or zwitterionic intermediate.

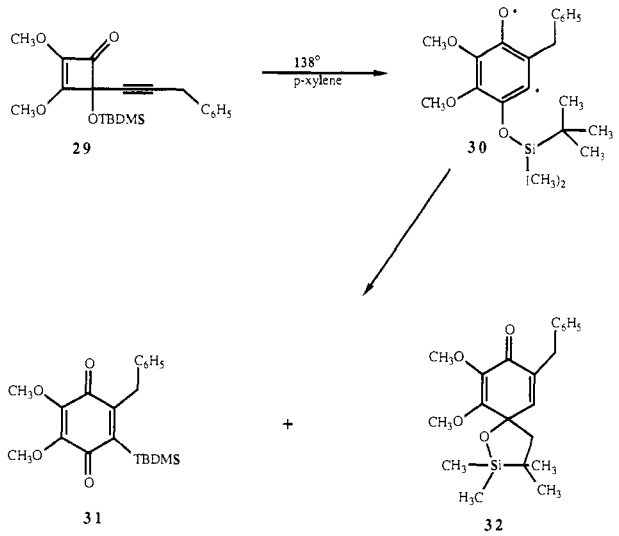
Evidence was also obtained which establishes an analogous intramolecular migration in the quinone-forming rearrangement. As mentioned above, and as shown in Schemes II and IV, the formation of trimethylsilyl-substituted 1,4-benzoquinones may be accomplished from the thermolysis of 4-alkynyl-4-[(trimethylsilyl)oxy]cyclobutenones. As a prototype for all of the benzoquinone syntheses outlined here, it was of interest to probe mechanistic details of this transformation, specifically with regard to the trimethylsilyl transfer step. The intramolecular nature of this transfer was established by subjecting a mixture containing equimolar amounts of **9m** and its deuteriated analogue **27** to thermolysis at 138 °C in refluxing *p*-xylene and by analyzing the crude reaction mixture for the presence of crossover products by mass spectroscopy (Scheme VIII). None were observed—a result *required* for an intramolecular transfer of the trimethylsilyl group. Also, since the rates of formation of **10m** and **28** were observed to be nearly equivalent (^{1}H NMR), the interpretation is not complicated by the presence of an isotope effect in the rearrangement. From these results it is reasoned that the diradical or zwitterionic intermediate analogous to **4** (Scheme I) suffers front-side intramolecular displacement of the trimethylsilyl group to give the corresponding quinones **10m** and **28**.[12,13] It is further assumed that analogous intermolecular migrations also take place in the other rearrangements leading to 1,4-benzoquinones as well as to 2-alkylidene-1,3-cyclopentenediones.

An important mechanistic point concerns the electronic nature of the unique intermediate **4** (and **5**); is it a diradical, a zwitterion, or a strained allene? The results presented here do not allow an unambiguous resolution. However, the data most reasonably suggest that the intermediate is a diradical or at least a species having appreciable radical character. In this regard, some crucial information was inadvertently obtained from investigations designed to further probe the scope of the trialkylsilyl quinone synthesis. For example, when the cyclobutenone **29** was thermolyzed in an attempt to prepare the bulky trialkylsilyl quinone **31**, the expected product was indeed realized in 49% yield, but

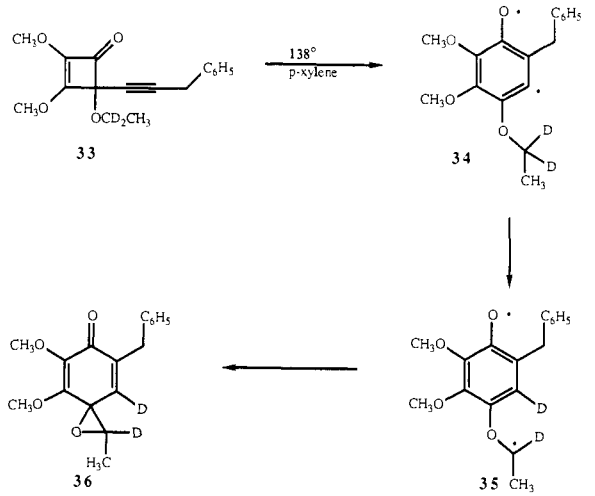
(12) For other examples of the migration of a trimethylsilyl group from oxygen to carbon, see: Shih, C.; Swenton, J. S. *J. Org. Chem.* **1982**, *47*, 2668. Anderson, G.; Cameron, D. W.; Feutrill, G. I.; Read, R. W. *Tetrahedron Lett.* **1981**, 4347.

(13) Sommer, L. H. *Stereochemistry, Mechanism and Silicon*; McGraw-Hill: New York, 1965.

Scheme IX



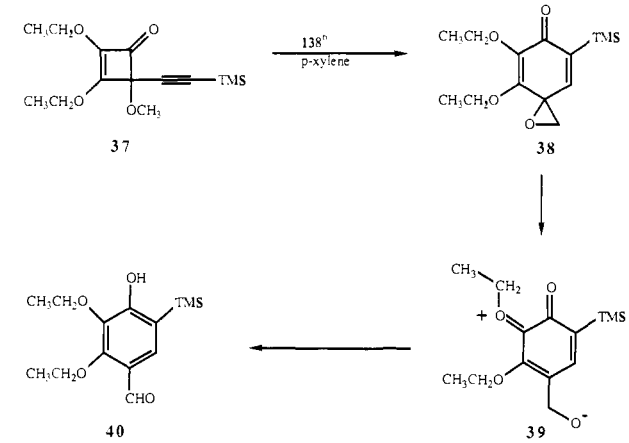
Scheme X



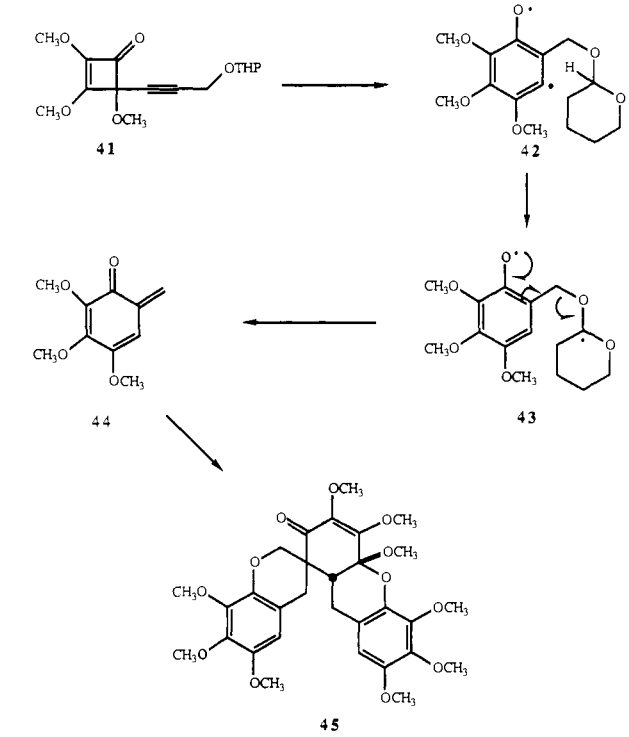
significantly, the unexpected spiro compound **32** was also isolated in 7% yield (Scheme IX). Formation of the quinone could conceivably take place from a diracial, a zwitterionic intermediate (Scheme I), or a strained allene. In contrast, **32** most reasonably would arise from an intermediate having significant diradical character. On the basis of these data, as well as those given below, it is assumed that the rearrangements all involve the diradical forms of the intermediates **4** or **5**.

Additional evidence for the intermediacy of a diradical, as well as the discovery of an interesting new variant of the cyclobutenone/benzoquinone rearrangement, comes from a study of the thermal chemistry of 4-alkynyl-4-alkoxycyclobutenones. For example, when 4-(3-phenylpropynyl)-4-ethoxy-2,3-dimethoxycyclobutenone was thermolyzed, it gave a spiroepoxide. This study was continued with the deuteriated analogue **33** in order to probe the specific site of hydrogen or deuterium atom abstraction (Scheme X). For example, the ring-based radical center in **34** could abstract a hydrogen atom from the methyl group or a deuterium atom from the methylene group of the ethoxy substituent. The former process would give a new intermediate having a primary radical center. Conceivably, its stabilization could be achieved by deuterium atom migration and subsequent ring closure to give the spiro compound. The result of such a process would be a product having the two deuterium atoms equally distributed between the epoxide ring and the methyl group. On the other hand, the latter process would lead to the specific mechanism outlined in Scheme X, and this was, in fact, shown to be the case on the basis of the labeling study. Specifically, the product arising from **33** was shown by ^{1}H NMR analysis to be **36**. Thus the

Scheme XI



Scheme XII

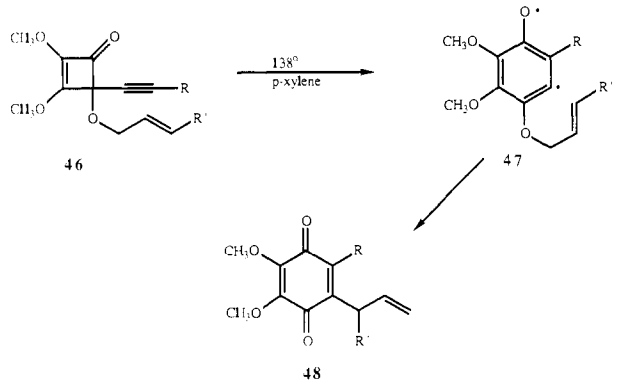


ring-based radical center abstracts a deuterium atom directly from the methylene position to give **35**, and this proceeds directly to product upon ring closure.

An interesting twist to this unusual spiroepoxide-forming reaction is outlined in Scheme XI. Here, the cyclobutenone **37** was thermolyzed under conditions analogous to those used for **33** except the reaction time was extended to 2 h rather than 30 min. ^{1}H NMR and TLC analyses of the reaction solution during the course of the reaction showed the presence of the spiroepoxide **38**, but this slowly disappeared, and the ultimate product was established to be the highly functionalized aromatic aldehyde **40**. This is rationalized as arising via the zwitterionic intermediate **39**, which gives the observed product after proton loss and tautomerism.

Still another variation on the above theme is outlined in Scheme XII. Here, the cyclobutenone **41** was subjected to thermolysis. On the basis of the above results, spiroexpodie formation is deemed possible, but it is not necessarily anticipated since the alkynyl substituent (tetrahydropyranyl, THP) is also favorably disposed to interact with the ring-based radical center in **42**. This, in fact, was established since the product was the trimer **45** and this is viewed as arising from the diradical **42**, followed by a favorable 1,6-hydrogen abstraction from the THP group to give **43**. This

Scheme XIII



	R	R'	% 48
a	-H	-H	60
b	$-CH_2C_6H_5$	-H	76
c	$-CH_2C_6H_5$	$-CH_3$	54

intermediate then undergoes the indicated loss of the δ-lactone with concomitant formation of the reactive quinone methide **44**, which gives the product **45** in 49% yield upon trimerization.[14]

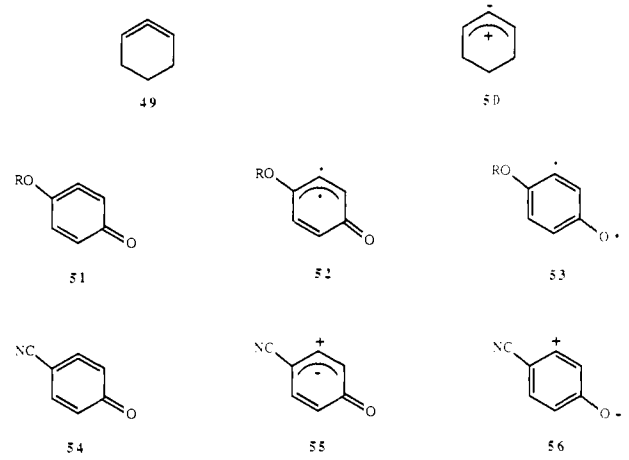
The structure of **45** is tentatively assigned on the basis of its ^1H and ^{13}C NMR spectral data as well as analogous results reported for the trimerization of quinone methides. The diagnostic peaks in the ^1H NMR spectrum are the nine methoxy singlets appearaing between 4.05 and 3.60 ppm, along with the two aromatic proton absorptions at 6.36 and 6.34 ppm. The ^{13}C NMR spectrum shows nine methyl carbons, three methylene carbons, three methine carbons, and one carbonyl carbon, all of which are consistent with the proposed structure. Also, the EI and CI mass spectra show a peak whose molecular weight corresponds to the molecular weight of the trimer as a parent ion as well as fragments that correspond to the dimer and monomer units.

The connectivity of the trimer is based on reports for the trimerization of quinone methides. For example, oxidation of 4-methoxy-2,6-dimethylphenol gives a quinone methide which also trimerizes to a product having a reported structure analogous to that proposed for **45**.[15]

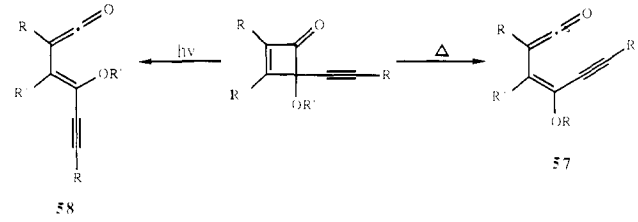
The last variation of the benzoquinone synthesis having both synthetic and mechanistic significance was discovered when 4-alkynyl-4-allyloxycyclobutenones were studied (Scheme XIII).[16] For example, thermolysis of **46a–c** gave the quinones **48a–c** in 54–60% purified yields. from a synthetic perspective this reaction is noteworthy since it allows the construction of alkoxybenzoquinones having a 2,3-dialkylated pattern. The transformation is also of mechanistic importance and is envisaged to proceed via the diradical intermediate **47**. Unlike th above thermolyses of 4-alkoxycyclobutenones, hydrogen abstraction is now less favorable than intramolecular radical addition to the alkene bond, thus initiating allyl group migration to give the allyl-substituted quinones **48a–c**. Special note is made of the conversion of **46c** to **48c** since this example shows the allyl group to invert during the rearrangement, a result consistent with the above suggested mechanism.

The data presented above all point to the diradicals **4** and **5** as being pivotal intermediates in the rearrangements presented in this work. These are unique species and of interest from a mechanistic point of view. This is especially true of **4** since its structure relates to a growing interest in the bonding and reactivity of strained cyclic allenes. For example, cyclic allenes in rings of

Chart I



Scheme XIV



less than nine members cannot attain their normally preferred linear geometry. As an illustration, the highly strained 1,2-cyclohexadiene (**49**) could conceivable find relief by reorganizing to the zwitterionic form **50** (Chart I). This is an intriguing possibility, but until now no experimental evidence has been reported to establish the presence of this species, and calculations suggest it to be unfavorable until the ring size has been reduced to five members.[17,18] However, the results presented here can be interpreted as providing evidence for the "charge separated" form of a highly strained allene. That is, ring closure of the conjugated ketene could result in the allene generally represented as **51** or in the diradical **52**. Formation of the diradical, i.e., "charge separated form", would be expected to be favored over the "allene form" on the basis of a lower strain energy as well as a gain in aromatic-resonance energy, as depicted by structure **53**. As outlined above, the diradical form is consistent with the observed results. It is of further interest to note that the electronic character of these intermediates appears to be significantly influenced by the substituents on the ring. For example, replacement of the alkoxide in **51** with a nitrile gives **54**, and this species has previously been shown to exhibit characteristics of a zwitterion rather than that of a diradical. Furthermore, rather than having vinyl anionic/allyl cationic properties, as represented generally by **49** and **50**, it is surprisingly best represented as a vinyl cationic/allyl anionic species as represented by **55** and **56**.[19]

A final point of mechanistic concern focuses attention on the electrocyclic ring opening of the 4-alkynyl-4-alkoxycyclobutenones **2** to the corresponding (2-alkynylethenyl)ketenes **3**. The marvelous selectivity of this ring opening is of key importance since it dictates the course of the reactions encountered in this study. Under the thermal conditions described, such ring opening takes place to give products which appear to arise from only the ketene **57** having *Z* stereochemistry, i.e., those having a configuration such that the electrophilic carbonyl group can directly interact with the proximal alkyne moiety to proceed to the diradical intermediate described above (Scheme XIV). This mode of ring opening is reasonable

(14) Westra, J. G.; Huysmans, W. G. B.; Mijis, W. J.; Gaur, H. A.; Vriend, J.; Smidt, J. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 1121.

(15) For other examples of the dimer- and trimerizations of *o*-quinone methides, see: Chauthan, M. S.; Dean, F. M.; McDonald, S.; Robinson, M. S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 359. Dean, F. M.; Matkin, D. A.; Osrabi, M. O. A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1437. Cavitt, S. B.; Sarrafizadeh, H.; Gardner, P. D. *J. Org. Chem.* **1962**, *27*, 1211.

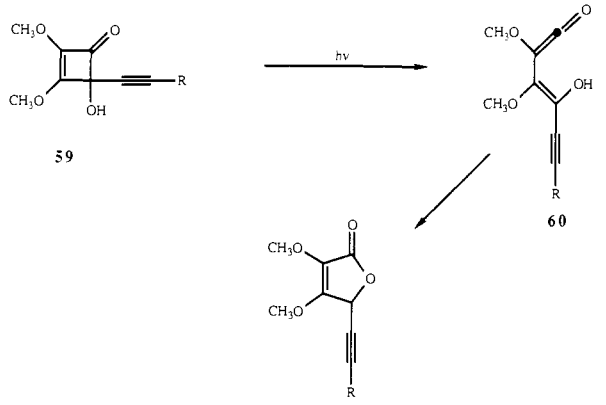
(16) A preliminary account of this work has appeared. See: Perri, S. T.; Foland, L. D.; Decker, O. H. W. *J. Org. Chem.* **1986**, *51*, 3067.

(17) Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 7607.

(18) Johnson, R. P. In *Molecular Structures and Energetics*; Vol. 3, Liebman, J. F., Greenberg, A., Eds.; Verlag Chemie: Deerfield Beach, FL, 1985.

(19) Moore, H. W.; Chow, K.; Nguyen, N. V. *J. Org. Chem.* **1987**, *52*, 3491.

Scheme XV



	R	% 61
a	$-CH_2C_6H_5$	52
b	$-C_6H_5$	28
c	$-n-C_4H_9$	50

on the basis of analogies to the extensively studied electrocyclic ring opening of cyclobutenes.[20-24] That is, the related, but less studied, ring opening of cyclobutenones would be expected to take place by the specific contrarotatory mode in which the electron-donating substituent at position 4 rotates outward, thus giving **57**. It was of concern, however, that such selectivity may not be operative during the ring opening and that, rather, an equilibrating mixture of the (*Z*)- and (*E*)-(2-alkynylethenyl)ketenes are formed under the thermal reaction conditions employed. In such a case the selectively could then be envisaged to arise from the possibility that only the *Z* isomer finds a productive pathway to products. This possibility does, however, seem unlikely, particularly for the transformations associated with 4-alkynyl-4-hydroxycyclobutenones, since the *E* isomer **58** (R′ = H, Scheme XIV) would be expected to rapidly ring close to the corresponding butenolides. In fact, exactly that was substantiated by data obtained from a study of the photolysis of selected examples of this series (Scheme XV). Specifically, the cyclobutenones **59a–c** were subjected to photolysis through quartz (450-W Hanovia lamp) in anhydrous THF at 0 °C. Selective ring opening to **60a–c** is proposed since the only isolable products were the butenolides **61a–c**, and no quinones could be detected in the crude reaction mixture. Thus, electrocyclic ring opening of the cyclobutenones can be controlled to proceed by either an inward (photolysis) or outward (thermolysis) rotation of the 4-alkoxy group to give, respectively, the ketene stereoisomeric intermediates **58** and **57**.

Conclusions

The thermal ring expansion of 4-alkynyl-4-hydroxy(or trialkylsilyloxy or allyloxy)cyclobutenones to 1,4-benzoquinones is a transformation of synthetic importance. It is notably useful for the regiospecific construction of highly substituted benzoquinones and starts from readily available materials. This rearrangement is complimentary to the ring expansion of 4-aryl-4-hydroxycyclobutenones to annelated hydroquinones.[25] Indeed, together, these two methods rank among the most versatile and useful known routes to benzoquinones and annelated derivatives.

One final point of caution is noted. On two occasions contact dermatitis was encountered when working with diethyl squarate (2,3-diethoxycyclobutenedione). As a result, dimethoxy-, diethoxy-, diisopropoxy-, dihydroxy-, and 3-methoxy-4-phenylcyclobutenedione were tested for skin irritancy with 4–6-month-old male Hartly strain guinea pigs.[26] The compounds were all found to be very active and to compare favorably with pentadecylcatechol, the active ingredient of poison ivy. Further studies are under way to investigate these and related compounds for allerginicity using the Freund's Complete Adjuvant Test as described by Klecak.[27]

Experimental Section

Melting points were determined on a Thomas-Hoover or a Büchi 510 capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 sodium chloride spectrophotometer using chloroform solution cells as a KBr pellet or as a neat thin film. In describing some of the infrared spectra the following abbreviations were used: s, strong; m, medium; and w, weak absorptions. Infrared absorptions are reported in cm^{-1} with polystyrene as the external standard (1601.8 cm^{-1}). Proton and carbon NMR spectra were obtained on Varian FT-80, Bruker WM-250, and GE 300-MHz and 500-MHz spectrometers. the multilicity of the carbon NMR spectra were obtained by using the DEPT 45, 90, and 135 pulse sequences on the GE 500-MHz spectrometer. All NMR spectra were recorded for $CDCl_3$ or C_6D_6 solutions and are reported relative to the internal standard tetramethylsilane for the proton spectra and as the center peak in the deuteriochloroform signal in the carbon spectra. All values are reported in parts per million. In describing the NMR data the following abbreviations were used: s, singlet; d, doubet; t, triplet; q, quartet; m, multiplet; and br, broad. Mass spectra were determined with a medium-resolution Finnigan 4000 GC/MS quadrupole spectrometer interfaced to a Nova 312 data system. High-resolution mass spectra were obtained from a 7070 VG Analytical Organic Mass Spectrometer interfaced to a VG Analytical LTD 11/250 data system.

Representative Procedure for the Synthesis of Cyclobutenones 9. 2,3-Dimethoxy-4-(1-hexynyl)-4-hydroxy-2-cyclobuten-1-one, 9a. A solution of 0.32 g (3.87 mmol) of freshly distilled 1-hexyne and 50 mL of freshly distilled THF in a dry 100-mL round-bottom flask was stirred under an atmosphere of nitrogen in a dry ice–acetone bath. A 1.6-mL portion of 2.29 M *n*-BuLi (3.70 mmol) solution was introduced dropwise via a syringe. The resulting light yellow solution was stirred for 30 min. This solution was then transferred under a positive pressure of nitrogen, via a cannula, to a solution of 0.50 g (3.52 mmol) of dimethyl squarate in 50 mL of freshly distilled THF also under an atmosphere of nitrogen in a dry ice–acetone bath. The resulting yellow solution was stirred for 45 min and then quenched with 30 mL of 5% NH_4Cl and 50 mL of diethyl ether. The aqueous layer was separated and extracted with 2 × 15 mL portions of ethyl ether, and the combined organic layers were washed with 2 × 25 mL portions of brine and then dried over $MgSO_4$. Removal of the solvent in vacuo yielded a light yellow oil. Column chromatography of this oil (3:1 hexanes/ethyl acetate) yielded a clear oil that was triturated with ether/hexanes to give 0.70 g (3.12 mmol) (89% yield) of **9a** as white prisms: mp 53–54 °C; IR ($CHCl_3$) 3500, 2980, 2830, 2255, 1795, 1656, 1483, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.20 (s, 3 H), 3.97 (s, 3 H), 3.06 (br s, 1 H) 2.26 (t, 2 H, J = 7.02 Hz), 1.43 (m, **4** H), 0.91 (t, 3 H, J = 7.13 Hz); MS, *m/e* (relative intensity) EI 224 (11), 207 (9), 195 (49), 149 (49), 139 (86), 109 (37), 91 (43), 79 (100), 67 (97); exact mass calcd for $C_{12}H_{16}O_4$ (M^+) 224.1048, found 224.1040.

2,3-Dimethoxy-4-[(trimethylsilyl)oxy]-4-(1-hexynyl)-2-cyclobuten-1-one, 9b. Compound **9b**: oil; 79% yield; IR ($CHCl_3$) 2960, 2220, 1780, 1640, 1465, 1350, 1250, 1155, 1050, 840 cm^{-1}; ^1H MNR ($CDCl_3$) δ 4.15 (s, 3 H), 3.94 (s, 3 H), 2.25 (br t, J = 7 Hz, 2 H), 1.6–1.1 (m, 4 H), 0.90 (br t, J = 7 Hz, 3 H), 0.22 (s, 9 H); MS, *m/e* (relative intensity) EI 296 (6), CI 297 (13).

2,3-Dimethoxy-4-hydroxy-4-[3-((trimethylsilyl)oxy)prop-1-ynyl]-2-cyclobuten-1-one, 9c. Compound **9c**: This compound was very unstable upon attempted purification by chromatography. Therefore it was used directly without purification. See this section for the synthesis of **10c**.

2,3-Dimethoxy-4-[(trimethylsilyl)oxy]-4-[3-((trimethylsilyl)oxy)prop-1-ynyl]-2-cyclobuten-1-one, 9d. Compound **9d**: oil; 85% yield; IR ($CHCl_3$) 2950, 2200, 1780, 1640, 1340, 1250, 1150, 1050, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.30 (s, 2 H), 4.10 (s, 3 H), 3.89 (s, 3 H), 0.22 (s, 9

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H), 0.16 (s, 9 H); MS, *m/e* (relative intensity) EI 342 (1), CI 343 (11); exact mass calcd for $C_{15}H_{26}O_5Si_2$ 342.1319, found 342.1324.

2,3-Dimethoxy-4-hydroxy-4-[((tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-ynyl]-2-cyclobuten-1-one, 9e. Compound **9e**: oil; 0.88 g (3.19 mmol); 84% yield; IR ($CHCl_3$) 3580, 3500–3200, 3030, 2950, 1785, 1640, 1355, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.83 (m, 1 H), 4.35 (d, J = 2 Hz, 2 H), 4.20 (s, 3 H), 3.98 (s, 3 H), 3.82 (m, 1 H), 3.52 (m, 1 H), 1.65 (m, 6 H); MS, *m/e* (relative intensity) EI 166 (35), 138 (44), 123 (100), CI 167 (100), 121 (20); exact mass calcd for $C_{14}H_{18}O_6$ (M^+) 282.1103, found 282.1080.

2,3-Dimethoxy-4-[((tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-ynyl]-4-[(trimethylsilyl)oxy]-2-cyclobuten-1-one, 9f. Compound **9f**: oil; 1.64 g (4.63 mmol); 66% yield; IR ($CHCl_3$) 2970 (s), 2880 (m), 1794 (s), 1653 (s), 1450 (s), 1135 (s), 850 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.77 (t, 1 H, J = 3.08 Hz), 4.30 (s, 2 H), 4.13 (s, 3 H), 3.93 (s, 3 H), 3.80 (m, 1 H), 3.45 (m, 1 H), 1.9–1.4 (m, 6 H), 0.21 (s, 9 H); MS, *m/e* (relative intensity) EI 354 (0.04), 311 (10), 255 (41), 239 (54), 211 (25), 89 (38), 85 (100), CI 355 (0.15), 354 (0.5), 266 (15), 265 (100), 181 (15), 85 (10); exact mass calcd for $C_{17}H_{26}O_6Si$ (M^+) 354.1498, found 354.1507.

2,3-Dimethoxy-4-hydroxy-4-[3-((trimethylsilyl)oxy)-2-methyl-1-propynyl]-2-cyclobuten-1-one, 9g. Compound **9g**: oil; 0.85 g (2.90 mmol); 1:1 mixture of diastereomers (82% yield); IR ($CHCl_3$) 3700–3100 (m), 2965 (m), 2870 (m), 1785 (s), 1650 (s), 1474 (s), 1350 (s), 849 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.57 (q, J = 6.55 Hz, 1 H), 4.18 (s, 3 H), 3.96 (s, 3 H), 3.46 (s, 1 H), 1.43 (d, J = 6.55 Hz, 3 H), 0.16 (s, 9 H); MS, *m/e* (relative intensity) EI 241 (0.20), 194 (70), 179 (67)8 151 (66), 95 (19), 73 (100), CI 285 (7), 267 (9), 195 (100); exact mass calcd for $C_{13}H_{20}O_5Si$ (M^+) 284.1080, found 284.1079.

2,3-Dimethoxy-4-hydroxy-4-[3-((tetrahydro-2*H*-pyran-2-yl)oxy)-2-methyl-1-propynyl]-2-cyclobuten-1-one, 9h. Compound **9h**: oil; 0.72 g (2.40 mmol); 69% yield; IR (neat) 3360 (br s), 1785 (s), 1473 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 4.91 (br t, 1 H), 4.62 (q, J = 6.8 Hz, 1 H), 4.18 (s, 3 H), 3.97 (s, 3 H), 3.80 (m, 1 H), 3.50 (m, 1 H), 1.90–1.50 (m, 6 H), 1.47 (d, J = 6.8 Hz, 3 H); MS, *m/e* (relative intensity) EI 194 (28), 151 (39), 85 (100), 67 (31), 57 (39), CI 297 (0.35), 213 (80), 195 (36), 85 (100); exact mass calcd for $C_{15}H_{20}O_6$ (M^+) 296.1260, found 293.1263.

2,3-Dimethoxy-4-[(trimethylsilyl)oxy]-4-[3-((tetrahydro-2*H*-pyran-2-yl)oxy)-2-methyl-1-propynyl]-2-cyclobuten-1-one, 9i. Compound **9i**: clear oil; 1.02 g (2.78 mmol); 72% yield; IR ($CHCl_3$) 2962 (s), 1793 (s), 1655 (s), 1257 (s); ^1H NMR ($CDCl_3$) major diastereomer reported, δ 4.89 (br t, 1 H), 4.62 (q, J = 6.5 Hz, 1 H), 4.17 (s, 3 H), 3.97 (s, 3 H), 3.82 (m, 1 H), 3.51 (m, 1 H), 1.9–1.4 (m, 6 H), 1.49 (d, J = 6.5 Hz, 3 H), 0.25 (s, 9 H); MS, *m/e* (relative intensity) EI 368 (0.51), 269 (20), 225 (23), 85 (32), 83 (100), CI 368 (0.11), 279 (100), 195 (19), 185 (20).

2,3-Dimethoxy-4-[(trimethylsilyl)oxy]-4-[2-(trimethylsilyl)-1-ethynyl]-2-cyclobuten-1-one, 9j. Compound **9j**: oil; 1.75 g (5.60 mmol); 72% yield; IR ($CHCl_3$) 2961 (m), 2157 (w), 1784 (m), 1650 (s), 1352 (s), 1050 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.17 (s, 3 H), 3.96 (s, 3 H), 0.24 (s, 9 H), 0.19 (s, 9 H); ms, *m/e* (relative intensity) EI 312 (1), 297 (19), 89 (26), 73 (100), CI 313 (22), 223 (100); exact mass calcd for $C_{14}H_{24}O_4Si_2$ 312.1213, found 312.1218.

2,3-Dimethoxy-4-hydroxy-4-(3-phenyl-1-propynyl)-2-cyclobuten-1-one, 9l. Compound **9l**: mp 86–87 °C; 0.74 g (2.87 mmol); 82% yield; UV (CH_3OH) 253 nm, ϵ = 10 500; IR ($CHCl_3$) 3575, 3439, 2997, 2950, 2230, 1780, 1640, 1420, 1035, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 5 H), 4.15 (s, 3 H), 3.95 (s, 3 H), 3.63 (s, 2 H), 3.07 (br s, 1 H); MS, *m/e* (relative intensity) EI 258 (0.1), 198 (2), 127 (22), 77 (7), CI 259 (10), 243 (10), 228 (15), 227 (100); exact mass calcd for $C_{15}H_{14}O_4$ (M^+) 258.0892, found 258.0876.

2,3-Dimethoxy-4-(3-phenyl-1-propynyl)-4-[(trimethylsilyl)oxy]-2-cyclobuten-1-one, 9m. Compound **9m**: oil; 1.69 g (5.11 mmol); 72% yield; IR ($CHCl_3$) 2950, 2223, 1792, 1467, 1251, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29 (m, 5 H), 4.15 (s, 3 H), 3.95 (s, 3 H), 3.52 (s, 2 H), 0.20 (s, 9 H); MS, *m/e* (relative intensity) EI 226 (38), 198 (33), 183 (78), 155 (59), 127 (100), 77 (33), CI 227 (100).

2,3-Dimethoxy-4-ethynyl-4-hydroxy-2-cyclobuten-1-one, 9n. Compound **9n**: mp 75.5–77 °C; 0.51 g (3.02 mmol); 86% yield; IR (neat) 3600–3200 (br s), 2960 (m), 1790 (s), 1630 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.22 (s, 3 H), 4.04 (s, 1 H), 3.97 (s, 3 H), 2.83 (s, 1 H); MS, *m/e* (relative intensity) EI 169 (1.4) 153 (31), 139 (31), 125 (77), 97 (100), 82 (89), 53 (83), CI 169 (100), 151 (19); exact mass calcd for $C_8H_8O_4$ (M^+) 168.0422, found 168.0399.

2,3-Dimethoxy-4-ethynyl-4-[(trimethylsilyl)oxy]-2-cyclobuten-1-one, 9o. Compound **9o**: oil; 0.75 g (3.11 mmol); 88% yield; IR (neat) 3290 (m), 2960 (m), 2120 (w), 1795 (s), 1645 (s), 1346 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.18 (s, 3 H), 3.97 (s, 3 H), 2.79 (s, 1 H), 0.25 (s, 9 H); MS, *m/e* (relative intensity) EI 240 (1), 197 (35), 154 (25), 126 (27), 89 (56), 73 (100), CI 241 (36), 151 (100); exact mass calcd for $C_{11}H_{16}O_4Si$ 240.0818, found 240.0828.

Representative Procedure for the Synthesis of Quinones 10. 2,3-Dimethoxy-5-butyl-2,5-cyclohexadiene-1,4-dione, 10a. A solution of 0.22 g (0.98 mmol) of **9a** and 10 mL of freshly distilled *p*-xylene was refluxed for 15 min. During this time the initially colorless solution became deep red. The solvent was removed in vacuo (70 °C). The resulting red oil was purified by column chromatography (5:1 hexanes/ethyl acetate) to yield 0.17 g (0.76 mmol) of **10a** as a red oil: 78% yield; IR (neat) 2980, 2890, 1673, 1612, 1463, 1145, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.38 (t, J = 1.50 Hz, 1 H), 4.02 (s, 3 H), 4.00 (s, 3 H), 2.41 (dt, J = 1.37 Hz, J_t = 7.46 Hz, 2 H), 1.44 (m, 4 H), 0.93 (t, J = 6.85 Hz, 3 H); MS, *m/e* (relative intensity) EI 224 (100), 153 (58), 139 (60), 137 (99), 123 (50), 81 (90), 79 (49); exact mass calcd for $C_{12}H_{16}O_4$ (M^+) 224.1048, found 224.1038.

4-Butyl-2,3-dimethoxy-5-[((trimethylsilyl)oxy)methyl]-2,5-cyclohexadiene-1,4-dione, 10b. Compound **10b**: yellow oil; 75% yield; IR ($CHCl_3$) 2940, 1630, 1525, 1445, 1245, 1185, 1115, 1080, 840 cm^{-1}; ^1H NMR ($CDCl_3$) 4.47 (s, 2 H), 3.98 (s, 3 H), 2.97 (s, 3 H), 0.32 (s, 9 H), 0.14 (s, 9 H); MS, *m/e* (relative intensity) 342 (14); CI 343 (54).

Anal. Calcd for $C_{15}H_{24}O_4Si$: C, 60.77; H, 8.16. Found: C, 61.09; H, 8.40.

2,3-Dimethoxy-5-[((trimethylsilyl)oxy)methyl]-2,5-cyclohexadiene-1,4-dione, 10c, and 2,3-Dimethoxy-5-(hydroxymethyl)-2,5-cyclohexadiene-1,4-dione. A solution of 0.95 g (7.39 mmol) of freshly distilled, trimethylsilyl-protected propargyl alcohol and 50 mL of freshly distilled THF in a dry 100-mL round-bottom flask was stirred under an atmosphere of nitrogen in a dry ice–acetone bath. A 3.7-mL portion of a 2.0 M *n*-BuLi (7.39 mmol) solution was introduced dropwise via a syringe. The resulting light yellow solution was stirred for 60 min. This solution was then transferred under a positive pressure of nitrogen, via a cannular, to a solution of 1.00 g (7.04 mmol) of dimethyl squarate in 100 mL of freshly distilled THF (N_2) in a dry ice–acetone bath. The resulting yellow solution was stirred for 60 min in the cold bath and then was quenched with 40 mL of 5% NH_4Cl and 30 mL of diethyl ether. The aqueous layer was extracted with 3 × 20 mL portions of ethyl ether, and the combined organic layers were washed with 30 mL of brine and then dried over $MgSO_4$. Removal of the solvent in vacuo yielded a light yellow oil. This oil was diluted with 50 mL of freshly distilled *p*-xylene. The light yellow solution then refluxed for 60 min. The *p*-xylene was removed in vacuo (70 °C). The resulting red oil was purified by column chromatography (5:1 hexanes/ethyl acetate) and yielded two products. Compound **10c**: red oil; R_f = 0.68; 0.68 g (2.53 mmol); 36% yield; IR (neat) 3010, 2970, 1668, 1610, 1455, 1270, 1055, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.59 (t, 1 H, J = 2.66 Hz), 4.45 (d, 2 H, J = 2.66 Hz), 4.05 (s, 3 H), 3.95 (s, 3 H), 0.18 (ns, 9 H); MS, *m/e* (relative intensity) EI 270 (34), 255 (100), 182 (64), 169 (34), 113 (22), 89 (33), CI 271 (100), 199 (30), 183 (100); exact mass calcd for $C_{12}H_{18}O_5Si$ (M^+) 270.0923, found 270.09254. 2,3-Dimethoxy-5-(hydroxymethyl)-2,5-cyclohexadiene-1,4-dione: red-orange needles, mp 69–70 °C (ethyl ether); R_f = 0.07; 0.26 g (1.31 mmol); 19% yield; IR ($CHCl_3$) 3460, 3045, 2960, 1665, 1610, 1370, 1245, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.63 (t, J = 1.89 Hz, 1 H), 4.54 (br d, J = 1.93 Hz, 2 H), 4.04 (s, 3 H), 4.00 (s, 3 H), 2.23 (br, 1 H); MS, *m/e* (relative intensity) EI 198 (65), 180 (51), 150 (65), 125 (39), 84 (100), Cl 199 (100), 183 (26).

Anal. Calcd for $C_9H_{10}O_5$: C, 54.56; H, 5.09. Found: C, 54.46; H, 5.20.

2,3-Dimethoxy-5-(trimethylsilyl)-6-[((trimethylsilyl)oxy)methyl]-2,5-cyclohexadiene-1,4-dione, 10d. A solution of 0.99 g (7.74 mmol) of freshly distilled trimethylsilyl propargyl ether and 35 mL of freshly distilled THF was delivered to a dry 100-mL round-bottom flask and was stirred under an atmosphere of nitrogen in a dry ice–acetone bath. A 4.8-mL portion of a 1.55 M *n*-BuLi (7.39 mmol) solution was introduced dropwise via a syringe. The resulting light yellow solution was stirred for 20 min. This solution was then transferred under a positive pressure of nitrogen, via a cannula, to a solution of 1.00 g (7.04 mmol) of dimethyl squarate in 70 mL of freshly distilled THF also under an atmosphere of nitrogen in a dry ice–acetone bath. The resulting yellow solution was stirred for 30 min in the cold bath and then was quenched with 1.35 mL (1.14 g, 10.6 mmol) of trimethylsilyl chloride at −78 °C. The colorless solution was allowed to warm to room temperature and the solvent was removed in vacuo. The resulting light yellow oil was diluted with 100 mL of ether and then passed through a plug of Florisil (30 g, 100–200 mesh). The filtrate was concentrated and then diluted with 50 mL of freshly distilled *p*-xylene. The light yellow xylene solution was refluxed for 40 min. The initially light yellow solution became deep red during the thermolysis. The reaction mixture was cooled to room temperature and the solvent was removed in vacuo at 70 °C. The resulting red oil was purified by column chromatography (10:1 hexanes/ethyl acetate) to yield 1.30 g (3.80 mmol) of **10d** as a red oil. This represents a 54% yield from dimethyl squarate: IR (neat) 2940 (s), 1630 (s), 1580 (m), 1450 (m), 1310 (m), 1250 (s), 1190 (m), 1120 (s), 1080 (s), 840 (s) cm^{-1}; ^1H

NMR ($CDCl_3$) δ 4.47 (s, 2 H), 3.99 (s, 3 H), 3.98 (s, 3 H), 0.33 (s, 9 H), 0.15 (s, 9 H); MS, *m/e* (relative intensity) EI 342 (14), CI 343 (54); exact mass calcd for $C_{12}H_{18}O_5Si$ (fragment) 270.0923, found 270.09254.

Anal. Calcd for $C_{15}H_{26}O_5Si_2$: C, 52.59; H, 7.65. Found: C, 52.95; H, 7.83.

The quinones were also prepared in 80% yield upon thermolysis of **9d**.

2,3-Dimethoxy-5-[((tetrahydro-2*H*-pyran-2-yl)oxy)methyl]-2,5-cyclohexadiene-1,4-dione, 10e. Compound **10e**: red oil; 0.40 g (1.42 mmol); 47% yield; IR (neat), 2965, 2870, 1640, 1608, 1445, 1140 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.90 (t, J = 1.80 Hz, 1 H), 4.72 (br t, 1 H), 4.63 (dd, 1-4 J = 1.80 Hz, 1-2 J_d = 17.86 Hz, 1 H), 4.36 (dd, 1-4 J_d = 1.80 Hz, 1-2 J_d = 17.86 Hz, 1 H), 4.05 (s, 3 H), 4.00 (s, 3 H), 3.83 (m, 1 H), 3.55 (m, 1 H), 1.65 (m, 6 H); MS, *m/e* (relative intensity) EI 282 (5), 198 (13), 182 (60), 167 (16), 154 (34), 85 (100), CI 283 (15), 200 (10), 199 (49), 183 (61), 85 (100); exact mass calcd for $C_{14}H_{18}O_6$ (M^+) 282.1103, found 282.1102.

2,3-Dimethoxy-5-[((tetrahydro-2*H*-pyran-2-yl)oxy)methyl]-6-[(trimethylsilyl)oxy]-2,5-cyclohexadiene-1,4-dione, 10f. Compound **10f**: red oil; 81.0 mg (0.23 mmol); 41% yield; IR (neat) 2975 (s), 1675 (s), 1655 (s), 1645 (s), 1600 (m), 1265 (s), 1036 (s), 860 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.74 (br t, 1 H), 4.64 (d, 1 H, J = 10.9 Hz), 4.26 (d, 1 H, J = 10.9 Hz), 3.99 (s, 3 H), 3.98 (s, 3 H), 3.89 (m, 1 H), 3.53 (m, 1 H), 1.90-1.40 (m, 6 H), 0.33 (m, 9 H); MS, *m/e* (relative intensity) EI 354 (0.83), 255 (15), 254 (11), 226 (14), 85 (100), 75 (20), 73 (47).

Anal. Calcd for $C_{17}H_{26}O_6Si$: C, 57.61; H, 7.39. Found: C, 57.81; H, 7.50.

2,3-Dimethoxy-5-[1-((trimethylsilyl)oxy)ethyl]-2,5-cyclohexadiene-1,4-dione, 10g. Compound **10g**: red oil; 0.30 g (1.06 mmol); 64% yield; IR (neat) 2965 (m), 1664 (s), 1607 (s), 1260 (s), 1062 (s), 852 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 6.61 (d, J = 1.39 Hz, 1 H), 4.77 (dq, J_d = 1.38 Hz, J_q = 6.38 Hz, 1 H), 3.96 (s, 3 H), 3.93 (s, 3 H), 1.25 (d, J = 6.26 Hz, 3 H), 0.05 (s, 9 H); MS, *m/e* (relative intensity) EI 284 (26), 269 (91), 251 (22), 211 (23), 182 (25), 75 (30), 73 (100), 53 (21), CI 285 (100), 197 (98), 91 (34).

Anal. Calcd for $C_{13}H_{20}O_5Si$: C, 54.91; H, 7.09. Found: C, 55.00; H, 7.04.

2,3-Dimethoxy-5-[1-((tetrahydro-2*H*-pyran-2-yl)oxy)ethyl]-2,5-cyclohexadiene-1,4-dione, 10h. Compound **10h**: red oil; 85 mg (0.29 mmol); 42% yield; IR ($CHCl_3$) 2955 (s), 1665 (s), 1609 (s), 1310 (s), 899 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.57 (d, J = 1.4 Hz, 1 H), 4.93 (dq, J_d = 1.4 Hz, J_q = 6.6 Hz, 1 H), 4.52 (br t, 1 H), 4.03 (t, 3 H), 4.00 (t, 3 H), 3.90 (m, 1 H), 3.52 (m, 1 H), 1.90-1.50 (m, 6 H), 1.3. (d, 3 H, J = 6.6 Hz); MS, *m/e* (relative intensity) EI 296 (0.7), 212 (11), 196 (38), 85 (100), CI 297 (16), 213 (61), 197 (47), 103 (16), 85 (100); exact mass calcd for $C_{15}H_{20}O_6$ (M^+) 296.1260, found 296.1256.

2,3-Dimethoxy-5-(trimethylsilyl)-6-[1-((tetrahydro-2*H*-pyran-2-yl)-oxy)ethyl]-2,5-cyclohexadiene-1,4-dione, 10i. Compound **10i**: red oil; 90 mg (0.24 mmol); 36% yield; IR (neat) 2950 (s), 1650 s), 1255 (s), 845 (s) cm^{-1}; ^1H NMR ($CDCl_3$) major diastereomer, δ 5.04 (q, J = 7.1 Hz, 1 H), 4.43 (br t, 1 H), 4.01 (s, 3 H), 3.98 (s, 3 H), 3.90 (m, 1 H), 3.48 (m, 1 H), 1.9-1.4 (m, 6 H), 1.57 (d, 3 H, J = 7.1 Hz), 0.35 (m, 9 H); MS, *m/e* (relative intensity) EI 368 (0.01), 269 (14), 85 (100), 73 (31), CI 369 (0.05)8 285 (38), 269 (65), 103 (18), 85 (100).

2,3-Dimethoxy-5,6-bis(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione, 10j. Compound **10j**: mp, 49-50 °C; 65.4 mg (0.209 mmol); 55% yield; IR (Nujol mull) 2989, 1649, 1607, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.99 (s, 6 H) 0.33 (s, 18 H); MS, *m/e* (relative intensity) EI 312 (8), 297 (50), 163 (17), 89 (33), 73 (100), CI 313 (100), 297 (23); exact mass calcd for $C_{14}H_{24}O_4Si_2$ 312.1213, found 312.1188.

2-(3-Butynyl)-5,6-dimethoxy-3-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione, 10k. The same procedure as employed for the synthesis of **10d** was used. Compound **10k**: orange oil; 290 mg; 46% yield; IR ($CHCl_3$) 3320, 2960, 2245, 1735, 1665, 1650, 1590, 1470, 1440, 1255, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.02 (s, 3 H), 3.97 (s, 3 H), 2.81 (t, J = 7.3 Hz, 2 H), 2.38 (dt, J = 7.3, 2.7 Hz, 1 H), 2.00 (t, J = 2.7 Hz, 1 H), 0.34 (s, 9 H); MS, *m/e* (relative intensity) EI 294 (42), 293 (14), 292 (12), 279 (19), 278 (17), 277 (81), 264 (32), 263 (20), 262 (24), 249 (33), 247 (23), 233 (20), 219 (22), 73 (100), CI 295 (40), 294 (33), 293 (100), 279 (36), 255 (73), 203 (35), 183 (21); exact mass calcd for $C_{15}H_{20}O_4Si$ 292.1131, found 292.1167.

2,3-Dimethoxy-5-(phenylmethyl)-2,5-cyclohexadiene-1,4-dione, 10l. Compound **10l**: red oil; 71 mg (0.276 mmol); 71% yield; IR ($CHCl_3$) 2980, 2930, 1695, 1595, 1445, 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2 (m, 5 H), 6.12 (t, J = 1.6 Hz, 1 H), 4.01 (s, 6 H), 3.72 (d, J = 1.6 Hz, 2 H); MS, *m/e* (relative intensity) EI 258 (70), 243 (74), 228 (26), 144 (28), 115 (100), CI 259 (100), 183 (29); exact mass calcd for $C_{15}H_{14}O_4$ (M^+) 258.0892, found 258.0883.

2,3-Dimethoxy-5-(phenylmethyl)-6-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione, 10m. Compound **10m**: yellow crystals, 74% yield; mp 59.5-60 °C; IR ($CHCl_3$) 2920, 1630, 1525, 1445, 1245, 1185, 1115, 1089, 840 cm^{-1}; ^1H NMR ($CDCl_3$) 7.5-6.9 (m, 5 H), 3.95 (s, 3 H), 3.90 (s, 2 H), 3.82 (s, 3 H), 0.32 (s, 9 H); MS, *m/e* (relative intensity) EI 330 (7), CI 331 (100).

2,3-Dimethoxy-2,5-cyclohexadiene-1,4-dione, 10n. Compound **10n**: orange needles; 200 mg (1.19 mmol); 66% yield; IR (Nujol) 1650 (s), 1592 (s), 1305 (s), 846 (m), 837 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.62 (s, 2 H), 4.03 (s, 6 H); MS, *m/e* (relative intensity) EI 170 (33), 168 (65), 153 (24), 123 (100), 82 (36), 69 (55), CI 169 (100).

Anal. Calcd for $C_8H_8O_4$: C, 57.16; H, 4.80; found: C, 57.25; H, 4.63.

2,3-Dimethoxy-5-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione, 10o. A solution of 180 mg (0.749 mmol) of **9o** and 5 mL of freshly distilled *p*-xylene was refluxed for 20 min under an atmosphere of nitrogen. During this time the initialy colorless solution became red. The product was concentrated to yield a red oil. ^1H NMR analysis of the crude reaction mixture showed only a single isomer. The red oil was purified by flash column chromatography (8:1 hexanes/ethyl acetate) and gave 135 mg (0.562 mmol) (75% yield) of **10o**: yellow oil; IR (CCl_4) 2940, 1660, 1640, 1620, 1580, 1255, 1110, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.85 (s, 1 H), 3.98 (s, 3 H), 3.95 (s, 3 H), 0.24 (s, 9 H); MS, *m/e* (relative intensity) EI 240 (53), CI 241 (100); exact mass calcd for $C_{11}H_{16}O_4Si$ 240.0818, found 240.0826.

The product has physical (TLC) and spectral properties identical with those of an authentic sample prepared from the thermolysis of 2,3-dimethoxy-4-hydroxy-4-[(trimethylsilyl)ethynyl]-2-cycloubuten-1-one.

4-(1-Hexynyl)-4-hydroxy-3-methoxy-2-phenyl-2-cyclobuten-1-one, 12a. Compound **12a**: pale yellow powder; 82% yield; mp 114-116 °C; IR (KBr) 3590, 2975, 2945, 2240, 1795, 1765, 1640, 1600, 1505, 1455, 1370, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25-7.45 (m, 5 H), 4.41 (s, 3 H), 2.28 (t, 2 H), 1.45 (m, 4 H), 0.88 (t, 3 H); MS, *m/e* (relative intensity) EI 270 (80), 241 (85), 227 (25), 2132 (23), 185 (46), 161 (24), 157 (21), 145 (39), 141 (29), 139 (30), 129 (76), 128 (47), 118 (53), 105 (58), 89 (100), CI 271 (100). Exact mass calcd for $C_{17}H_{18}O_3$ 270.1256, found 270.1251.

4-(1-Hexynyl)-4-hydroxy-3-methoxy-2-(phenylethynyl)-2-cyclobuten-1-one, 12b. Compound **12b**: orange oil; 90% yield; IR ($CHCl_3$) 3590, 2980, 2950, 2880, 2230, 2210, 1775, 1630, 1600, 1500, 1460, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29-7.48 (m, 5 H), 4.44 (s, 3 H), 2.28 (t, 2 H), 1.45 (m, 4 H), 0.91 (t, 3 H); MS, *m/e* (relative intensity) EI 296 (58), 294 (100), 281 (27), 253 (70), 251 (71), 239 (27), 238 (39), 225 (21), 224 (37), 223 (52), 207 (30), 195 (22), 181 (19), 165 (39), 152 (30), 141 (24); CI 295 (100). Exact mass calcd for $C_{19}H_{18}O_3$ 294.1256, found 294.1244.

3-Ethoxy-4-hydroxy-2-phenyl-4-(3-phenyl-1-propynyl)-2-cyclobuten-1-one, 12c. Compound **12c**: yellow solid; mp 80-81 °C dec (pentane); 310 mg; 65% yield; IR ($CHCl_3$) 3320, 3020, 2240, 1757, 1638, 1605, 1500, 1459, 1419, 1390, 1356, 1340, 1320, 1230, 1155, 1018, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.73 (m, 2 H), 7.15-7.39 (m, 8 H), 4.77 (q, J = 7.1 Hz, 2 H), 4.68 (s, 1 H), 3.66 (s, 2 H), 1.52 (t, 3 H, J = 7.1 Hz); MS, *m/e* (relative intensity) EI 320 (35), 318 (M^+, 64), 303 (27), 289 (29), 273 (32), 261 (11), 215 (32), 202 (21), 189 (9), 172 (14), 145 (39), 144 (19), 129 (24), 117 (26), 115 (100), 91 (93), 90 (24), 89 (88), 77 (33)8 CI 320 (16), 319 (100), 301 (11), 203 (8); exact mass calcd for $C_{21}H_{18}O_3$ (M^+) 318.1256, found 318.1261.

2-Ethoxy-4-hydroxy-2-(1-naphthyl)-4-(3-phenyl-1-propynyl)-2-cyclobuten-1-one, 12d. Compound **12d**: semisolid; 0.153 g; 72% yield; IR ($CHCl_3$) 3310, 3020, 3035, 2244, 1761, 1620, 1578, 1514, 1500, 1468, 1458, 1423, 1387, 1340, 1135, 1033, 1021, 1005, 915, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.25 (dd, J = 7.7, 1.4 Hz, 1 H), 7.80-7.87 (m, 2 H), 7.74 (dd, J = 7.2, 1.2 Hz, 1 H), 7.42-7.57 (m, 3 H), 7.18-7.37 (m, 5 H), 4.74 (dq, J = 7.2, 1.0 Hz, 2 H), 4.21 (s, 1 H), 3.72 (s, 2 H), 1.48 (t, J = 7.1 Hz, 3 H); MS, *m/e* (relative intensity) EI 370 (75), 368 (M^+, 81), 353 (19), 342 (25), 340 (14), 339 (29), 265 (20), 263 (24), 252 (14), 239 (11), 195 (14), 167 (16), 140 (17), 139 (64), 128 (14), 127 (15), 115 (46), 91 (100), 65 (11), CI 371 (19), 370 (32), 369 (88), 294 (19), 293 (100). Exact masss calcd for $C_{25}H_{20}O_3$ (M^+) 368.1412, found 368.1393.

2-*n*-Butyl-3-ethoxy-4-hydroxy-4-(3-phenyl-1-propynyl)-2-cyclobuten-1-one, 12e. Compound **12e**: yellow oil; 0.188 g; 64% yield; IR ($CHCl_3$) 3330, 2975, 2945, 2880, 2245, 1775, 1625, 1500, 1460, 1420, 1392, 1351, 1330, 1145, 1027, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2-7.35 (m, 5 H), 4.58 (q, 2 H, J = 7.0 Hz), 4.3 (s, 1 H), 3.67 (s, 2 H), 2.06 (t, 2 H, J = 7.3 Hz), 1.5 (m, 2 H), 1.44 (t, 3 H, J = 7.1 Hz), 1.31 (m, 2 H), 0.88 (t, 3 H, J = 7.3 Hz); MS, *m/e* (relative intensity) EI 298 (M^+, 52), 268 (34), 255 (18), 241 (12), 227 (53), 211 (18), 209 (23), 181 (15), 155 (20), 153 (17), 141 (15), 128 (19), 115 (77), 91 (100), 77 (17), 69 (17), 65 (20), 57 (41), 55 (65); exact mass calcd for $C_{19}H_{22}O_3$ (M^+) 298.1568, found 298.1558.

3-Butyl-2-methoxy-5-phenyl-2,5-cyclohexadiene-1,4-dione, 13a. Compound **13a**: orange oil; 53 mg; 57% yield; IR ($CHCl_3$) 2970, 2940, 1685, 1675, 1600, 1500, 1455, 1360, 1335 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25-7.45 (m, 5 H), 6.55 (t, J = 1.3 Hz, 1 H), 3.77 (s, 3 H), 2.47 (dt, J = 1.3 Hz,

2 H), 1.45 (m, 4 H), 0.93 (t, 3 H), MS, *m/e* (relative intensity) CI 273 (88), 271 (100); exact mass calcd for $C_{17}H_{18}O_3$ 270.1256, found 270.1247.

3-Butyl-2-methoxy-5-(phenylethynyl)-2,5-cyclohexadiene-1,4-dione, 13b. Compound **13b**: red oil; 49 mg; 57% yield; IR ($CHCl_3$) 2975, 2950, 2210, 1675, 1665, 1595, 1335, 1215 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.56 (m, 5 H), 6.52 (t, J = 1.5 Hz, 1 H), 4.43 (s, 3 H), 2.47 (dt, J = 7.2, 1.5 Hz, 2 H), 1.45 (m, 4 H), 0.94 (t, J = 7.2 Hz, 3 H); MS, *m/e* (relative intensity) EI 294 (100), 253 (32), 251 (88), 224 48), 223 (53), 206 (20), 195 (25), 165 (46), 153 (25), 152 (33), CI 297 (100, corresponding to hydroquinone), 296 (29), 295 (62), 293 (13); exact mass calcd for $C_{19}H_{18}O_3$ 294.1256, found 294.1252.

2-Ethoxy-3-phenyl-5-(phenylmethyl)-2,5-cyclohexadiene-1,4-dione, 13c. Compound **13c**: red oil; 58 mg; 46% yield; IR ($CHCl_3$) 3030, 1675, 1655, 1600, 1571, 1500, 1458, 1385, 1323, 1285, 1217, 1166, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2–7.45 (m, 10 H), 6.32 (t, J = 1.7 Hz, 1 H), 4.01 (q, J = 7.0 Hz, 2 H), 3.78 (d, J = 1.5 Hz, 2 H), 1.15 (t, J = 7.0 Hz, 3 H); MS, *m/e* (relative intensity) EI 320 (53), 318 (M^+, 100), 303 (61), 301 (31), 290 (30), 289 (54), 273 (62), 115 (48), 91 (78); exact mass calcd for $C_{21}H_{18}O_3$ (M^+) 318.1256, found 318.1269.

3-Butyl-2-ethoxy-5-(phenylmethyl)-2,5-cyclohexadiene-1,4-dione, 13d. Compound **13d**: orange oil; 55 mg; 47% yield; IR ($CHCl_3$) 2943, 2975, 1659, 1610, 1500, 1475, 1430, 1388, 1327, 1193, 1143, 1108, 1026, 945 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13–7.39 (m, 5 H), 6.13 (t, J = 1.6 Hz, 1 H), 4.26 (q, J = 7.1 Hz, 2 H), 3.72 (d, J = 1.2 Hz, 2 H), 2.45 (t, J = 7.3 Hz, 2 H), 1.28–1.46 (m, 4 H), 1.33 (t, J = 7.1 Hz, 3 H), 0.91 (t, J = 7.1 Hz, 3 H); MS, *m/e* (relative intensity) EI 298 (M^+, 100), 296 (9), 269 (52), 255 (39), 227 (30), 211 (23), 151 (42), 113 (17), 91 (35), 70 (10), 57 (12); exact mass calcd for $C_{19}H_{22}O_3$ (M^+) 298.1568, found 298.1541.

2-Ethoxy-3-(1-naphthyl)-5-(phenylmethyl)-2,5-cyclohexadiene-1,4-dione, 13e. Compound **13e**: orange oil; 92 mg; 65% yield; IR ($CHCl_3$) 3070, 3040, 3015, 3000, 2925, 1674, 1657, 1607, 1593, 1580, 1500, 1396, 1318, 1250, 1194, 1170, 1160, 1010, 955, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87–7.92 (m, 2 H), 7.4–7.58 (m, 4 H), 7.2–7.39 (m, 6 H), 6.39 (t, J = 1.6 Hz, 1 H), 3.79 (d, J = 1.3 Hz, 2 H), 3.67–3.88 (m, 2 H), 0.96 (t, J = 7.0 Hz, 3 H) MS, *m/e* (relative intensity) EI 370 (15), 368 (M^+, 86), 353 (24), 339 (34), 165 (9), 152 (12), 140 (18), 139 (82), 132 (10), 128 (18), 127 (18), 116 (13), 115 (75), 105 (15), 91 (100), 89 (19), 77 (18), 69 (10), 65 (27), 63 (15), 57 (14), 55 (12), 51 (12), CI 371 (13), 370 (35), 369 (100), 294 (14), 293 (94), 91 (15); exact mass calcd for $C_{25}H_{20}O_3$ (M^+) 368.1412, found 368.1402.

3-Butyl-2-methoxy-5-(phenylmethyl)-2,5-cyclohexadiene-1,4-dione, 13f. This compound was prepared from the cyclobutenedione **11g** in the "one pot" sequence of rections analogous to that used for the synthesis of **10d**. Compound **13f**: gold oil; 284 mg (1.00 mmol); 84% yield; IR ($CHCl_3$) 3030, 2922, 1642, 1597, 1136 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29 (m, 5 H), 6.14 (t, J = 1.6 Hz, 1 H), 3.98 (s, 3 H), 3.73 (d, J = 1.6 Hz, 2 H), 2.42 (t, J = 7 Hz, 2 H), 1.36 (m, 4 H), 0.91 (t, J = 7 Hz, 3 H); MS, *m/e* (relative intensity) EI 284 (100), 241 (97), 227 (39), 115 (69), 91 (98), CI 285 (100), 209 (6).

Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.04; H, 7.09. Found C, 76.09; H, 7.24.

2-Methoxy-3-(phenylethynyl)-5-(phenylmethyl)-2,5-cyclohexadiene-1,4-dione, 13g. This compound was prepared by the "one pot" procedure described above. Compound **13g**: maroon threads; mp 123–124.5 °C (ether); 0.32 g (0.96 mmol); 50% yield; IR ($CHCl_3$) 1665 (s), 1595 (m), 1333 (s), 975 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.55 (m, 2 H), 7.27 (m, 8 H), 6.31 (t, 1 H, J = 1.56 Hz), 4.41 (s, 3 H), 3.78 (d, J = 1.48 Hz, 2 H); MS, *m/e* (relative intensity) EI 328 (100), 268 (32), 228 (50), 115 (48).

Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.48; H, 4.91. Found: C, 80.46; H, 5.20.

2,3-Dimethoxy-4-hydroxy-4-(phenylethynyl)-2-cyclobuten-1-one, 14a. The cyclobutenones **14** were prepared in the same manner as was used for the synthesis of the cyclobutenones 9. Compound **14a**: gold oil; 1.36 g (5.57 mmol); 79%; IR ($CHCl_3$) 3580, 3380, 3030, 2960, 2238, 1785, 1635, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33 (m, 5 H), 4.20 (s, 3 H), 3.95 (s, 3 H), 3.38 (s, 1 H); MS, *m/e* (relative intensity) EI 244 (3), 243 (5), 229 (21), 158 (13), 145 (27), 129 (100), CI 245 (100), 227 (45), 143 (14); exact mass calcd for $C_{14}H_{12}O_4$ (M^+) 244.07354, found 244.07356.

2,3-Dimethoxy-4-[(trimethylsilyl)oxy]-4-(phenylethynyl)-2-cyclobuten-1-one, 14b. Compound **14b**: oil; 85% yield; IR (CCl_4) 2950, 2210, 1780, 1630, 1460, 1330, 1250, 1095, 1035, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–7.3 (m, 5 H), 4.20 (s, 3 H), 3.98 (s, 3 H), 0.28 (s, 9 H); MS, *m/e* (relative intensity) EI 316 (8), CI 317 (20); exact mass calcd for $C_{17}H_{20}O_4Si$ 316.1131, found 316.1125.

2,3-Dimethoxy-4-(2-ethoxy-1-ethynyl)-4-hydroxy-2-cyclobuten-1-one, 14c. Compound **14c**: yellow oil; 0.73 g (3.44 mmol); 49% yield; IR ($CHCl_3$) 3400 (br), 2990 (m), 2270 (s), 1770 (s), 1665–1615 (s, multiplet), 1475 (s), 860 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.19 (s, 3 H), 4.17 (q, J = 7.09 Hz, 2 H), 3.96 (s, 3 H), 3.06 (s, 1 H), 1.39 (t, J = 7.12 Hz, 3 H); MS, *m/e* (relative intensity) EI 212 (0.09), 183 (100), 140 (11), 127 (19), 99 (14), 85 (10), 84 (13), 69 (62), 53 (10), CI 213 (100), 183 (14), 167 (10), 71 (12); exact mass calcd for $C_{10}H_{12}O_5$ (M^+) 212.0685, found 212.0680.

2,3-Dimethoxy-4-(2-ethoxy-1-ethynyl)-4-[(trimethylsilyl)oxy]-2-cyclobuten-1-one, 14d. Compound **14d**: clear oil; 1.00 g (3.53 mmol); 50% yield; IR ($CHCl_3$) 2960 (s), 2265 (s), 1785 (s), 1645 (s), 1253 (s), 900 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.16 (s, 3 H), 4.15 (q, J = 7.09 Hz, 2 H), 3.94 (s, 3 H), 1.39 (t, J = 7.10 Hz, 3 H), 0.23 (s, 9 H); MS, *m/e* (relative intensity) EI 284 (0.46), 255 (37), 73 (100), CI 285 (30), 255 (13), 195 (94), 167 (100), 73 (11); exact mass calcd for $C_{13}H_{20}O_5Si$ (M^+) 284.1080, found 284.1088.

2,3-Dimethoxy-4-hydroxy-4-[(trimethylsilyl)ethynyl]-2-cyclobuten-1-one, 14e. Compound **14e**: clear oil; 1.44 g (5.98 mmol); 85% yield; IR (neat) 3400 (m, br), 2965 (s), 2161 (w), 1780 (s), 1650 (s), 1350 (s), 1070 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.19 (s, 3 H), 3.97 (s, 3 H), 3.09 (s, 1 H), 0.18 (s, 9 H); MS, *m/e* (relative intensity) EI 240 (1), 225 (91), 197 (34), 111 (49), 75 (100), CI 241 (100), 225 (12), 223 (22); exact mass calcd for $C_{11}H_{16}O_4Si$ (M^+) 240.0818, found 240.0820.

Representative Procedure for the Synthesis of Quinones 15 and Cyclopentenediones 16. 2,3-Dimethoxy-5-phenyl-2,5-cyclohexadiene-1,4-dione, 15a, and 4,5-Dimethoxy-2-(phenylmethylene)-4-cyclopentene-1,3-dione, 16a. A solution of 160 mg (0.665 mmol) of **14a** and 10 mL of freshly distilled *p*-xylene was heated and then refluxed for 30 min, during which time the solution became reddish-brown. The solvent was removed in vacuo at 70 °C. The resulting red oil was diluted with 25 mL of ethyl ether and extracted with a solution of 0.57 g (3.28 mmol) of sodium dithionite in 15 mL of water. The aqueous layer was extracted with 3 × 10 mL of ether, and the combined organic layers were washed with 3 × 15 mL of brine and then dried over $MgSO_4$. Removal of the solvent and column chromatography of the yellow oil (4:1 hexanes/ethyl acetate) yielded two products. 2,3-Dimethoxy-5-phenyl-1,4-benzenediol: yellow powder; R_f = 0.45; mp 104–105 °C; 73.0 mg (0.299 mmol); 46% yield; IR ($CHCl_3$) 2963, 1677, 1650, 1473, 1342, 1144, 1118, 1101, 1074, 1054 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.19 (m, 2 H), 7.45 (m, 3 H), 7.41 (s, 1 H), 4.67 (s, 6 H); MS, *m/e* (relative intensity) EI 244(100), 229(25), 215(46), 145(24), 131(25), 102(29). Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95; found: C, 68.65; H, 5.10. Compound **16a**: white needles (hexane/chloroform); R_f = 0.20; mp 148–149 °C; 34.4 mg (0.140 mmol); 46% yield; IR ($CHCl_3$) 3560, 3030, 2940, 1612, 1497, 1300, 1093, 962 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57 (m, 2 H), 7.42 (m, 2 H), 7.35 (m, 1 H), 6.72 (s, 1 H), 5.48 (s, 1 H), 5.27 (s, 1 H), 3.97 (s, 3 H), 3.96 (s, 3 H); MS, *m/e* (relative intensity) EI 246 (96), 199 (100), 171 (34), 131 (26), 115 (35), 102 (39) 77 (30); exact mass calcd for $C_{14}H_{14}O_4$ (M^+) 246.0892, found 246.0892.

The quinone **15a** was generated from the above described benzenediol as outlined here. A solution of 47.5 mg (1.93 mmol) of the benzenediol and 20 mL of freshly distilled benzene was stirred under an atmosphere of nitrogen at room temperature. To this colorless solution was added 89 mg (3.86 mmol) of Ag_2O and 53 mg (3.86 mmol) of potassium carbonate, and the suspension was stirrred at room temperature under an atmosphere of nitrogen for 45 min. The resulting orange solution was diluted with 30 mL of ether and filtered through a short pad of Celite. The filtrate was washed with 2 × 15 mL portions of brine and the was dried with $MgSO_4$. The solvent was removed on a rotavap to give a solid that was recrystallized from hexanes to yield 31.4 mg (1.29 mmol) of **15a** as orange threads: mp 90–91 °C; 67% yield; IR ($CHCl_3$) 2960, 1668, 1605, 1275, 1108 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45 (m, 5 H), 6.70 (s, 1 H), 4.09 (s, 3 H), 4.04 (s, 3 H); MS, *m/e* (relative intensity) EI 244 (38), 201 (21), 199 (46), 145 (53), 115 (24), 102 (100).

Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.71; H, 5.04.

2,3-Dimethoxy-5-phenyl-6-[(trimethylsilyl)oxy]-2,5-cyclohexadiene-1,4-dione, 15b, and 4,5-Dimethoxy-2-[(trimethylsilyl)phenylmethylene]-4-cyclopentene-1,3-dione, 16b. Compound **15b**: mp, 89.5–90.5 °C; IR (CCl_4) 2950, 1655, 1645, 1630, 1570, 1450, 1265, 1245, 1100, 840 cm^{-1}; ^1H NMR δ 7.5–6.9 (m, 5 H), 4.06 (s, 3 H), 3.98 (s, 3 H), −0.08 (s, 9 H); MS, *m/e* (relative intensity) EI 316 (43), CI 317 (60).

Anal. Calcd for $C_{17}H_{20}O_4Si$: C, 64.53; H, 6.37. Found: C, 64.57; H, 6.67.

Compound **16b**: mp, 95–95.5 °C; IR (CCl_4) 2940, 1675, 1620, 1460, 1330, 1070, 835 cm^{-1}; ^1H NMR δ ($CDCl_3$) 7.4–7.2 (m, 3 H), 6.9–6.7 (m, 2 H), 4.25 (s, 3 H), 4.14 (s, 3 H), 0.11 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 186.3, 184.2, 163.5, 151.7, 151.6, 142.1, 134.2, 127.7, 126.2, 124.6, 59.9, 59.8, −0.4; MS, *m/e* (relative intensity) EI 316 (11), CI 317 (100).

Anal. Calcd for $C_{17}H_{20}O_4Si$: C, 64.53; H, 6.37. Found: C, 64.45; H, 6.61.

2,3-Dimethoxy-5-ethoxy-2,5-cyclohexadiene-1,4-dione, 15c, and 4,5-Dimethoxy-2-(ethoxymethylene)-4-cyclopentene-1,3-dione, 16c. ^1H NMR analysis of the crude reaction mixture showed a 4:3 ratio of five- to six-membered ring products. Column chromatography of the orange oil (1.5:1 hexanes/ethyl acetate) yielded two products. Compound **15c**: mp 79–80.5 °C (ethyl ether); R_f = 0.24; 25 mg (0.12 mmol); 25% yield; IR (KBr), 3000 (m), 1660 (s), 1595 (s), 1218 (s), 1078 (s), 850 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.72 (s, 1 H), 4.09 (s, 3 H), 3.98 (q, 2 H, J = 7.03 Hz), 3.94 (s, 3 H), 1.48 (t, 3 H, J = 7.06 Hz); MS, m/e (relative intensity) EI 212 (42), 183 (21), 169 (28), 141 (31), 139 (35), 113 (49), 85 (32), 69 (100), 53 (29), CI 213 (100).

Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.61; H, 5.70. Found: C, 56.33; H, 5.61.

Compound **16c**: mp 59–9 °C (ethyl ether); R_f = 0.20; 51 mg (0.24 mmol); 50% yield; IR (KBr) 2958 (m), 1732 (s), 1665 (s), 1610 (s), 1450 (s), 1204 (s), 1055 (s), 885 (s), 800 (m), 760 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.17 (s, 1 H), 4.28 (q, J = 7.12 Hz, 2 H), 4.19 (s, 3 H), 4.18 (s, 3 H), 1.43 (t, J = 7.13 Hz, 3 H); MS, m/e (relative intensity) EI 212 (76), 183 (26), 169 (100), 155 (48), 141 (23), 85 (42), 71 (26), 70 (19), 69 (52), 53 (51), CI 213 (100), 199 (3), 70 (6).

Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.61; H, 5.70. Found: C, 56.71; H, 5.78.

2,3-Dimethoxy-5-ethoxy-6-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione, 15d, and 4,5-Dimethoxy-2-[ethoxy(trimethylsilyl)methylene]-4-cyclopentene-1,3-dione, 16d. 2,3-Dimethoxy-5-ethoxy-6-(trimethylsilyl)-1,4-benzenediol: white flakes: R_f = 0.33; mp 134–135 °C (hexanes); 0.15 g (0.52 mmol); 23% yield; IR (KBr) 3480 (s), 3390 (s), 2980 (m), 2942 (m), 2890 (m), 1607 (m), 1430 (s), 1245 (s), 1035 (s), 844 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.56 (s, 1 H), 5.13 (s, 1 H), 3.95 (q, J = 7.05 Hz, 2 H), 3.94 (s, 3 H), 3.93 (s, 3 H), 1.38 (t, J = 7.09 Hz, 3 H), 0.34 (s, 9 H); MS, m/e (relative intensity) EI 286 (56), 270 (100), 255 (18), 241 (74), 227 (74), 75 (52), CI 287 (7), 286 (9), 271 (100).

Anal. Calcd for $C_{13}H_{22}O_4Si$: C, 54.52; H, 7.74. Found: C, 54.48; H, 8.04.

Compound **16d**: light yellow oil; R_f = 0.40; 0.36 mg (1.27 mmol); 55% yield; IR (neat) 3380 (w), 2960 (m), 1680 (s), 1672 (s), 1646 (s), 1544 (s), 1465 (s), 1327 (s), 1040 (s), 846 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.46 (q, 2 H, J = 7.00 Hz), 4.14 (s, 3 H), 4.12 (s, 3 H), 1.32 (t, 3 H, J = 7.00 Hz), 0.24 (s, 9 H); MS, m/e (relative intensity) EI 284 (8), 269 (64), 255 (29), 241 (17), 73 (100), CI 285 (100), 85 (29), 83 (17), 81 (27), 71 (33), 70 (21).

Anal. Calcd for $C_{13}H_{20}O_4Si$: C, 54.91; H, 7.09. Found: C, 54.97; H, 7.25.

Compound **15d**: red oil; 54 mg (0.19 mmol); 94% yield from the benzenediol; IR (neat) 2957 (s), 2906 (s), 2849 (m), 1650 (s), 1580 (s), 1045 (s), 692 (m), 627 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.31 (q, J = 7.06 Hz, 2 H), 4.04 (s, 3 H), 3.93 (s, 3 H), 1.36 (t, J = 7.01 Hz, 3 H), 0.26 (s, 9 H); MS, m/e (relative intensity) EI 284 (40), 269 (100), 241 (66), 213 (28), 197 (29), 98 (34), 75 (42), 73 (84), CI 285 (100), 271 (26).

Anal. Calcd for $C_{13}H_{20}O_4Si$: C, 54.91; H, 7.09 Found: C, 54.60; H, 7.07.

2,3-Dimethoxy-5-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione, 15e, and 4,5-Dimethoxy-2-[(trimethylsilyl)methylene]-4-cyclopentene-1,3-dione, 16e. Compound **16e**: orange oil; 37 mg (0.15 mmol); 5% yield; IR (neat) 2960 (s), 1690 (s), 1600 (s), 1250 (m), 1085 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.97 (s, 1 H), 4.30 (s, 3 H), 4.28, (s, 3 H), 0.24 (s, 9 H); MS, m/e (relative intensity) EI 240 (6), 225 (100), 182 (12), 152 (16), 89 (15), 83 (22), CI 241 (100), 225 (16); exact mass calcd for $C_{11}H_{16}O_4Si$ 240.0818, found 240.0807.

2,3-Dimethoxy-5-(trimethylsilyl)-1,4-benzenediol: white flakes; mp 73–74 °C (chloroform); 310 mg (1.28 mmol); 41% yield; IR (neat) 3490 (s), 3400 (s), 2960 (m), 1430 (s), 1037 (s), 940 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.68 (s, 1 H), 5.49 (s, 1 H), 5.23 (s, 1 H), 3.92 (s, 3 H), 3.91 (s, 3 H), 0.27 (s, 9 H); MS, m/e (relative intensity) EI 242 (44), 226 (100), 211 (65), 77 (24), 75 (85), CI 244 (2), 243 (22), 227 (100); exact mass calcd for $C_{11}H_{18}O_4Si$ 242.0974, found 242.0961.

Compound **15e**: red oil; 97 mg (0.40 mmol); 98% yield from the benzenediol; IR (neat) 2960 (m), 1670 (s), 1590 (s), 1370 (s), 1123 (s), 848 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.72 (s, 1 H), 4.03 (s, 3 H), 4.00 (s, 3 H), 0.24 (s, 9 H); MS, m/e (relative intensity) EI 240 (56), 225 (100), 182 (56), 83 (96), 73 (65), CI 241 (100), 227 (13); exact mass calcd for $C_{11}H_{16}O_4Si$ 240.0818, found 240.0804.

3-(2,3-Dimethoxy-1-hydroxy-4-oxo-2-cyclobuten-1-yl)-2-propynoic Acid Ethyl Ester, 17a. Compound **17a**: yellow oil; 0.23 g (0.96 mmol); 27% yield; IR ($CHCl_3$) 3490, 3020, 2995, 2245, 1790, 1710, 1640, 1473, 1350, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.73 (br s, 1 H), 4.22 (q, J = 7.15 Hz, 2 H), 4.18 (s, 3 H), 3.94 (s, 3 H), 1.28 (t, J = 7.15 Hz, 3 H); MS, m/e (relative intensity) EI 240 (35), 194 (100), 167 (40), 153 (38), 139 (34), 123 (36), 81 (33); exact mass calcd for $C_{11}H_{12}O_6$ (M^+) 240.0634, found 240.0637.

3-[2,3-Dimethoxy-4-[(trimethylsilyl)oxy]-4-oxo-2-cyclobuten-2-yl]-2-propynoic Acid Ethyl Ester, 17b. Compound **17a**: oil; IR (CCl_4) 2950, 2220, 1780, 1710, 1640, 1465, 1360, 1235, 1045, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.20 (q, J = 7 Hz, 2 H), 4.13 (s, 3 H), 3.92 (s, 3 H), 1.30 t, J = 7 Hz, 3 H), 0.26 (s, 9 H); exact mass calcd for $C_{14}H_{20}O_6Si$ 312.1029, found 312.1027.

2,3-Dimethoxy-4-hydroxy-4-(4-methoxybut-3(Z)-en-1-ynyl)-2-cyclobuten-1-one, 17c. Compound **17c**: yellow solid; mp 88–89.5 °C; 86% yield; IR ($CHCl_3$) 3400, 2940, 2200, 1780, 1640, 1465, 1340, 1102, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.28 (s, 1 H), 3.76 (s, 3 H), 3.95 (s, 3 H), 4.19 (s, 3 H), 4.55 (d, J = 6.5 Hz, 1 H), 6.31 (d, J = 6.5 Hz, 1 H); MS, m/e (relative intensity) EI 224 (100), 209 (48), 195 (94), 181 (47), 153 (29), 125 (74), 110 (62), 93 (42); exact mass calcd for $C_{11}H_{12}O_5$ 224.0685, found 224.0680.

(3,4-Dimethoxy-2,5-dioxo-3-cyclopenten-1-ylene)acetic Acid Ethyl Ester, 18a. A solution of 89.3 mg (0.372 mmol) of **17a** and 4 mL of freshly distilled *p*-xylene was heated and then refluxed for 30 min, during which time the solution became orange. The solvent was removed in vacuo at 70 °C. The resulting orange oil was purified by column chromatography (2.5:1 hexanes/ethyl acetate) to yield 58.6 mg (0.244 mmol) of **18a** as a pale yellow oil (66% yield): IR (neat) 3020, 2960, 1740, 1670, 1605, 1465, 1433, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.64 (s, 1 H), 4.35 (q, J = 7.19 Hz, 2 H), 4.33 (s, 3 H), 4.32 (s, 3 H), 1.36 (t, J = 7.14 Hz, 3 H); MS, m/e (relative intensity) EI 240 (45), 194 (100), 167 (33), 149 (26), 123 (21) 83 (20).

Anal. Calcd for $C_{11}H_{12}O_4$: C, 55.01; H, 5.04. Found: C, 54.78; H, 5.06.

(3,4-Dimethoxy-2,5-dioxo-3-cyclopenten-1-ylene)(trimethylsilyl)acetic Acid Ethyl Ester, 18b. Compound **18b**: mp 68.5–69.5 °C; IR (CCl_4) 2940, 1720–1675, 1630–1590, 1430, 1325 1215, 1150, 1090, 1020, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.36 (q, J = 7 Hz, 2 H), 4.27 (s, 6 H), 1.35 (t, J = 7 Hz, 3 H), 0.28 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 184.9, 182.8, 170.6, 153.2, 151.8, 135.4, 61.1, 60.1, 60.0, 14.2, −1.3; MS, m/e (relative intensity) EI 312 (7), CI 313 (16).

Anal. Calcd for $C_{14}H_{20}O_6Si$: C, 53.82; H, 6.45. Found: C, 53.57; H, 6.65.

4,5-Dimethoxy-2-[(2-methoxy-(Z)-ethenyl)methylene]-4-cyclopentene-1,2-dione, 18c. Compound **18c**: yellow needles (ether); mp 106–108 °C; 49% yield; IR ($CHCl_3$) 2950, 1665, 1610, 1452, 1330, 1232, 1035, 635 cm^{-1}; ^1H NMR ($CDCl_3$) 3.81 (s, 3 H), 4.21 (s, 3 H), 4.22 (s, 3 H), 6.88 (dd, J = 12.0, 12.0 Hz, 1 H), 6.97 (d, J = 12.0 Hz, 1 H), 7.17 (d, J = 12.0 Hz, 1 H); ES, m/e (relative intensity) EI 224 (100), 209 (18), 193 (40), 181 (18), 163 (12), 153 (13), 125 (61), 110 (19), 95 (31); exact mass calcd for $C_{11}H_{12}O_5$ 224.0685, found 224.0675.

Anal. Calcd for $C_{11}H_{12}O_5$: C, 58.91; H, 5.41. Found: C, 58.74; H, 5.33.

2,3-Dimethoxy-4-hydroxy-4-(3-methyl-3-buten-1-ynyl)-2-cyclobuten-1-one, 19 (E = H). Compound **19** (E = H): white crystals; mp 71–72 °C (ether/hexane); 2.10 g; 76% yield; IR ($CHCl_3$) 3400, 2960, 2220, 1783, 1660, 1650, 1630, 1470, 1440, 1350, 1045, 980, 885, 783 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.89 (s, 3 H), 2.94 (s, 1 H), 3.98 (s, 3 H), 4.20 (s, 3 H), 5.31 (t, J = 1.7 Hz, 1 H), 5.38 (t, J = 1.4 Hz, 1 H); MS, m/e (relative intensity) CI 209 (MH^+), EI 208 (1), 207 (1)8 193 (18), 165 (22), 137 (9), 122 (25), 109 (20), 94 (100), 77 (51), 65 (47), 51 (57); exact mass calcd for $C_{11}H_{12}O_4$ (M^+) 208.0735, found 208.0738.

2,3-Dimethoxy-4-[(trimethylsilyl)oxy]-4-[3-methyl-3-buten-1-ynyl]-2-cyclobuten-1-one, 19 (E = TMS). Compound **19** (E = TMS): pale yellow oil; 0.77 g; 51% yield; IR (film) 2980, 2210, 1790, 1660, 1650, 1470, 1350, 1255, 1130, 1050, 910, 850, 770, 760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.25 (s, 9 H), 1.89 (s, 3 H), 3.96 (s, 3 H), 4.17 (s, 3 H), 5.28 (t, J = 1.7 Hz, 1 H), 5.34 (t, J = 0.8 Hz, 1 H); MS, m/e (relative intensity) CI 281 (MH^+), EI 280 (8), 265 (10), 239 (75), 221 (5), 207 (5), 194 (9), 178 (5), 166 (14), 123 (15), 105 (12), 73 (100); exact mass calcd for $C_{14}H_{20}SiO_4$ 280.1131, found 280.1113.

4,5-Dimethoxy-2-[(1-methylethenyl)(trimethylsilyl)methylene]-4-cyclopentene-1,3-dione, 20, and 2,3-Dimethoxy-5-(1-methylethenyl)-6-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione. A solution of 239 mg of **19** (E = TMS) (0.853 mmol) and 60 mL of freshly distilled *p*-xylene was refluxed for 40 min. During this time, the initially colorless solution turned orange. The reaction mixture was allowed to cool to room temperature and the solvent was removed in vacuo. ^1H NMR analysis of the crude mixture revealed a 9:2 ratio of the five- to six-membered ring products. The orange oil was diluted with 20 mL ether and was washed with 20 mL of saturated sodium dithionite solution. The bilayer was shaken until no leucomethylene blue active spot was observed on the TLC plate (ca. 10 min). The aqueous layer was extracted with ether (2 × 20 mL), and the combined organic layers were washed with brine (2 × 10 mL) and dried ($MgSO_4$). Removal of the solvent and column chroma-

tography yielded two products. Compound **20**: yellow powder; mp 70–71 °C; 166 mg; 69% yield; IR (CCl_4) 2960, 1685, 1630, 1470, 1435, 1330, 1250, 1100, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.23 (s, 9 H), 1.87 (s, 3 H), 4.23 (s, 3 H), 4.24 (s, 3 H), 4.36 (s, 1 H), 4.86 (t, J = 1.4 Hz, 1 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ −0.75, 23.2, 59.8, 59.9, 107.0, 132.6, 146.4, 151.07, 151.14, 166.1, 184.6, 186.3; MS, m/e (relative intensity) CI 281, EI 280 (63), 265 (100), 207 (31), 194 (11), 179 (10), 166 (15), 151 (6), 123 (30), 111 (13), 89 (44), 73 (97); exact mass calcd for $C_{14}H_{20}O_4Si$ 280.1131, found 280.1130.

Anal. Calcd for $C_{14}H_{20}O_4Si$: C, 59.98; H, 7.20. Found: C, 59.90; H, 7.07.

2,3-Dimethoxy-5-(1-methylethenyl)-6-(trimethylsilyl)-1,4-benzenediol: white flakes; mp 95–97 °C; 38.9 mg; 16% yield; IR (CCl_4) 3550, 3080, 2950, 2900, 2850, 1695, 1610, 1470, 1450, 1410, 1380, 1315, 1270, 1250, 1100, 1075, 960, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.31 (s, 9 H), 2.05 (s, 3 H), 3.92 (s, 3 H), 3.94 (s, 3 H), 4.91 (s, 1 H), 5.26 (s, 1 H), 5.29 (s, 1 H), 5.64 (s, 1 H); MS, m/e (relative intensity) CI 283 (MH^+), EI 282 (53), 266 (100), 252 (17), 236 (42), 223 (17), 205 (6), 191 (6), 177 (3), 163 (3), 149 (3), 113 (7), 89 (10), 75 (29); exact mass calcd for $C_{14}H_{22}SiO_4$ 282.1281, found 282.1284.

2,3-Dimethoxy-5-(1-methylethenyl)-6-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione: To a colorless solution of 53.6 mg (0.190 mmol) of the above benzenediol in 10 mL of benzene were added 88.1 mg (0.380 mmol) of Ag_2O and 52.5 mg (0.380 mmol) of K_2CO_3. The mixture was stirred at room temperature for 2 h, and the resulting orange solution was filtered through a bed of Celite, rinsed with ether, and concentrated to afford a red oil. The red oil was purified by column chromatography (10:1 hexanes/ethyl acetate) to yield 49.6 mg (93%) of the quinone as a red oil: IR (film) 2960, 1650, 1570, 1450, 1320, 1280, 1250, 1220, 1120, 1070, 870, 850, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 9 H), 1.97 (s, 3 H), 3.97 (s, 3 H), 4.01 (s, 3 H), 4.87 (s, 1 H), 5.19 (d, J = 3.0 Hz, 1 H); MS, m/e (relative intensity) CI 281 (MH^+), EI 280 (58), 264 (89), 250 (89), 235 (69), 207 (54), 194 (14), 181 (20), 123 (40), 89 (47), 73 (100); exact mass calcd for $C_{14}H_{20}O_4Si$ 280.1131, found 280.1117.

Anal. Calcd for $C_{14}H_{20}O_4Si$: C, 59.98; H, 7.20. Found: C, 60.12; H, 7.14

Dimer, 21. A solution of 104 mg of **19** (E = H) (0.250 mmol) and 60 mL of freshly distilled *p*-xylene was heated and then refluxed for 35 min under an atmosphere of Ar. During this time, the initially colorless solution turned orange. The reaction mixture was allowed to cool to ambient temperature and the solvent was removed in vacuo. The reddish-orange oil was taken by 5 mL of CH_2Cl_2 to which was added 1 g of silica gel. The mixture was stirred for 2 h. Filtration followed by removal of the solvent gave a reddish-orange residue. To the residue was added 2 mL of ether, and crystals of **21** were collected after 30 min. slightly yellow prisms; mp 140–143 °C; 51.1 mg; IR (KBr) 3000, 2950, 2920, 2840, 1680, 1635, 1470, 1430, 1330, 1220, 1210, 1100, 960, 785 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (s, 3 H), 1.70 (s, 3 H), 1.80–1.92 (m, 1 H), 1.98–2.10 (m, 1 H), 2.21–2.30 (m, 1 H), 2.35–2.45 (m, 1 H), 4.18 (s, 3 H), 4.20 (s, 3 H), 4.22 (s, 3 H), 4.26 (s, 3 H), 5.06 (s, 1 H), 7.55 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 197.16, 195.49, 185.50, 184.27, 153.12, 151.66, 151.19, 148.98, 148.34, 142.17, 127.20, 116.67, 59.92, 59.88, 59.85, 59.78, 58.58, 41.88, 30.40, 28.01, 23.56, 21.82; MS, m/e (relative intensity) CI 417 (MH^+), EI 416 (23), 401 (5), 383 (3), 369 (2), 355 (3), 339 (3), 322 (10), 309 (2), 295 (3), 261 (12), 248 (57), 233 (27), 221 (22), 208 (100), 193 (40), 165 (32), 115 (23), 91 (29), 77 (29), 65 (23), 53 (30); exact mass calcd for $C_{22}H_{24}O_8$ 416.1471, found 416.1462.

Anal. Calcd for $C_{22}H_{24}O_8$: C, 63.45; H, 5.81. Found: C, 63.21; H, 5.89.

3-Ethoxy-4-hydroxy-2-phenyl-4-(phenylethynyl)-2-cyclobuten-1-one, 22. Compound **22**: yellow oil; 0.512 g; 85% yield; IR ($CHCl_3$) 3350, 3010, 2238, 1770, 1642, 1610, 1502, 1453, 1419, 1395, 1362, 1346, 1327, 1098, 1018, 873, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.76 (m, 2 H), 7.2–7.42 (m, 8 H), 5.3 (s, 1 H), 4.84 (q, J = 7.1 Hz, 2 H), 1.57 (t, J = 7.1 Hz, 3 H); MS, m/e (relative intensity) EI 304 (M^+, 100), 276 (32), 275 (23), 247 (10), 231 (9), 202 (9), 192 (12), 191 (21), 172 (34), 131 (16), 105 (8), 89 (12), CI 306 (21), 305 (100); exact mass calcd for $C_{20}H_{16}O_3$ (M^+) 104.1099, found 304.1085.

4-Ethoxy-5-phenyl-2-(phenylmethylene)-4-cyclopentene-1,3-dione, 23. A solution of 0.556 g (1.83 mol) of alcohol **22** and 125 mL of freshly distilled benzene was heated and then refluxed for 4 h under argon. During this time the initially yellow colored solution became orange-yellow. The solution was allowed to cool to room temperature and the solvent was removed in vacuo at 50 °C. The resulting orange-yellow oil was purified by recrystallization (methanol) to yield 0.256 g (46% yield) of the E isomer only, as yellow crystals: mp 223.5–225 °C; IR ($CHCl_3$) 3020, 1678, 1632, 1600, 1500, 1459, 1450, 1400, 1383, 1350, 1339, 1270, 1208, 1138, 1048 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.31 (m, 2 H), 7.94 (m, 2 H), 7.52 (s, 1 H), 7.38–7.5 (m, 6 H), 4.88 (q, J = 7.1 Hz, 2 H), 1.46 (t, J = 7.1 Hz, 3 H); MS, m/e (relative intensity) EI 304 (M^+, 100), 276 (27), 275 (41), 247 (15), 219 (13), 202 (14), 192 (16), 191 (51), 189 (19), 172 (54), 145 (20), 131 (16), 129 (17), 117 (18), 102 (24), 89 (71), 77 (16), 63 (16); exact mass calcd for $C_{20}H_{16}O_3$ (M^+): 304.1099, found: 304.1109.

(*Z*)-4-Ethoxy-3-hydroxy-3-methyl-5-phenyl-2-(phenylmethylene)-4-cyclopenten-1-one, 24. To a solution of 50 mg (0.17 mmol) of **23** in 50 mL of dry THF at −78 °C under argon was added 0.13 mL (0.18 mmol) of 1.40 M CH_3Li via a syringe over a period of 1 min. After 10 min the solution was diluted with 40 mL of ether and quenched with 40 mL of 10% NH_4Cl. The aqueous layer was separated and extracted with 2 × 25 mL of ether, and the combined organic layers were washed with 2 × 40 mL of brine and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, resulting in a light yellow oil which was purified by column chromatography (5:1 hexanes/ethyl acetate) to yield 33 mg (66% yield) of the alcohol (only the E isomer) as a light yellow oil: IR ($CHCl_3$) 3430, 2998, 1684, 1649, 1627, 1600, 1497, 1450, 1380, 1327, 1130, 1014, 910, 840, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.09 (m, 2 H), 7.3–7.42 (m, 8 H), 6.96 (s, 1 H), 3.99–4.15 (m, 2 H), 2.25 (s, 1 H), 1.73 (s, 3 H), 1.26 (t, J = 7.0 Hz, 3 H); MS, m/e (relative intensity) EI 320 (M^+, 31), 305 (15), 277 (26), 274 (32), 273 (21), 231 (20), 218 (41), 203 (20), 202 (18), 191 (11), 157 (13), 145 (34), 131 (71), 129 (42), 128 (26), 117 (20), 115 (35), 105 (100), 103 (40), 102 (15), 91 (28), 89 (53), 77 (67), 63 (14), 51 (16); exact mass calcd for $C_{21}H_{20}O_3$ (M^+) 320.1412, found 320.1398.

4-Ethoxy-3-hydroxy-3-methyl-5-phenyl-2-(phenylmethylene)-4-cyclopenten-1-one, 26. A solution of 50 mg (0.17 mmol) of a mixture of **23** and **25** (E/Z = 4/5) was treated with methyllithium as described for **24**. This resulted in a light yellow oil which was purified by column chromatography (5:1 hexanes/ethyl acetate) to yield 28 mg (56% yield) of the alcohol (E:Z = 1:2) as a light yellow oil. The following spectral data were obtained for this mixture: IR ($CHCl_3$) 3370, 3015, 2990, 2940, 1690, 1686, 1646, 1623, 1599, 1496, 1450, 1380, 1330, 1130, 1015, 690 cm^{-1}; ^1H NMR ($CDCl_3$) (the chemical shifts given are those obtained from the spectrum of the mixture of **24** and **26**. The NMR data for pure **24** are given above) δ 8.0 (m, 2 H), 7.51 (s, 1 H), 7.28–7.49 (m, 8 H), 4.0–4.2 (m, 2 H), 2.57 (s, 1 H), 1.70 (s, 3 H), 1.26 (t, J = 7.0 Hz, 3 H); MS, m/e (relative intensity) EI 320 (M^+, 51), 305 (32), 277 (44), 275 (25), 274 (45), 273 (30), 231 (23), 219 (18), 218 (57), 203 (26), 202 (26), 191 (16), 157 (17), 145 (46), 131 (100), 129 (60), 128 (37), 127 (18), 117 (28), 116 (16), 115 (49), 105 (44), 103 (55), 102 (22), 91 (40), 90 (20), 89 (71), 77 (60), 63 (19), 51 (19); exact mass calcd for $C_{21}H_{20}O_3$ (M^+) 320.1412, found 320.1410.

2,3-Dimethoxy-4-[3-(phenyl-d_5)-1-propynyl]-4-[(trimethylsilyl-d_9)-oxy]-2-cyclobuten-1-one, 27. This compound was prepared by the standard method except the appropriate deuteriated reagents were used. Compound **27**: 325 mg (0.943 mmol); 33% yield; IR ($CHCl_3$) 2970 (m), 2382 (m), 1795 (s), 1653 (s), 1350 (s), 810 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.16 (s, 3 H), 3.96 (s, 3 H), 3.39 (s, 2 H); MS, m/e (relative intensity) EI 344 (3), 248 (65), 82 (100), CI 345 (17), 246 (100), 82 (12); exact mass calcd for $C_{18}H_8D_{14}O_4Si$ 344.2166, found 344.2174.

2,3-Dimethoxy-5-[(phenyl-d_5)methyl]-6-(trimethylsilyl-d_9)-2,5-cyclohexadiene-1,4-dione, 28. Compound **28**: red crystals; mp 58–59 °C; 74.7 mg (0.217 mmol); 87% yield; IR ($CHCl_3$) 2975 (m), 1652 (s), 1588 (m), 1249 (s), 1002 (s), 696 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.02 (s, 3 H), 3.96 (s, 2 H), 3.90 (s, 3 H); MS, m/e (relative intensity) EI 344 (1), 329 (21), 95 (21), 82 (100), CI 345 (100), 328 (60), 265 (26); exact mass calcd for $C_{18}H_8D_{14}O_4Si$ 344.2166, found 344.2173.

2,3-Dimethoxy-4-(3-phenyl-1-propynyl)-4-[(*tert*-butyldimethylsilyl)-oxy]-2-cyclobuten-1-one, 29. Alkynylation of dimethyl squarate was accomplished in the normal manner using 0.58 g (4.99 mmol) of 3-phenylpropyne. To the reaction mixture was added, via a cannula under a positive pressure of nitrogen, a solution of 2.26 g (14.97 mmol) of *tert*-butyldimethylsilyl chloride in 30 mL of freshly distilled dry THF that had been precooled to −78 °C under an atmosphere of nitrogen. The reaction mixture was then slowly warmed to −20 °C by allowing the dry ice–acetone bath to warm. The dry ice bath was removed and replaced with an ice bath. The solution was then slowly warmed to room temperature and then was diluted with 50 mL of ether and 25 mL of a 50% solution of brine. The organic layer was dried with 25 mL of brine and with $MgSO_4$. The product was concentrated, and the resulting light yellow oil was purified by flash column chromatography (15:1 hexanes/ethyl acetate) to yield 0.30 g (3.11 mmol) of **29** as a colorless oil: 17% yield; IR (neat) 2960 (s), 2230 (w), 1786 (s), 1636 (s), 1335 (s), cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (m, 5 H), 4.16 (s, 3 H), 3.95 (s, 3 H), 3.68 (s, 2 H), 0.87 (s, 9 H), 0.20 (s, 3 H), 0.18 (s, 3 H); MS, m/e (relative intensity) EI 372 (7), 281 (50), 73 (100), CI 373 (42), 241 (100); exact mass calcd for $C_{21}H_{28}O_4Si$ 372.1757, found 372.1748.

2,3-Dimethoxy-5-(phenylmethyl)-6-(*tert*-butyldimethylsilyl)-2,5-cyclohexadiene-1,4-dione, 31, and 6,7-Dimethoxy-8-oxo-9-(phenylmethyl)-2,2,3,3-tetramethyl-1-oxa-2-silaspiro[4.5]-6,9-decadiene, 32. A

solution of 290 mg (0.779 mmol) of **29** and 20 mL of freshly distilled *p*-xylene was delivered to a dry 50-mL round-bottom flask. The solution was heated and then refluxed for 30 min under an atmosphere of nitrogen. During this time the initially light yellow solution turned orange-red. The solvent was removed in vacuo at 70 °C. ^{1}H NMR analysis of the crude reaction mixture showed a 2:1 ratio of **31** to **32**. Column chromatography of the orange oil (10:1 hexanes/ethyl acetate) yielded two products. Compound **31**: orange oil; 141 mg (0.379 mmol); 49% yield; IR (KBr) 2955 (m), 1650 (s), 1255 (s), 823 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.20 (m, 5 H), 4.03 (s, 3 H), 3.97 (s, 3 H), 3.86 (s, 2 H), 0.94 (s, 9 H), 0.26 (s, 6 H); MS, *m/e* (relative intensity) EI 315 (100), 285 (30), 75 (25), CI 411 (3), 373 (100), 359 (30); exact mass calcd for $C_{21}H_{28}O_4Si$ 372.1757, found 372.1725. Compound **32**: colorless oil; 21 mg (0.056 mmol); 7% yield; IR (KBr) 2960 (m), 1730 (s), 1638 (s), 786 (s) cm^{-1}; ^{1}H NMR $CDCl_3$) δ 7.25 (m, 2 H), 7.20 (m, 3 H), 6.21 (t, J = 1.4 Hz, 1 H), 4.01 (s, 3 H), 3.71 (s, 3 H), 3.64 (d, J = 15.9 Hz, 1 H), 3.53 (d, J = 16.0 Hz, 1 H), 2.26 (d, J = 13.9 Hz, 1 H), 1.54 (d, J = 13.9 Hz, 1 H), 1.11 (s, 3 H), 1.10 (s, 3 H), 0.23 (s, 3 H), 0.17 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 184.1 (s), 161.9 (s), 144.9 (d) 138.9 (s), 136.6 (s), 134.0 (s), 129.4 (d), 128.6 (d), 126.4 (d), 79.0 (s), 60.9 (q), 60.9 (q), 51.5 (t), 34.9 (t), 27.0 (q), 25.8 (q), 23.4 (s), −1.8 (q), −2.5 (q); MS, *m/e* (relative intensity) CI 373 (78), 317 (100), 299 (26); exact mass calcd for $C_{21}H_{28}O_4Si$ 372.1757, found 372.1756.

2,3-Dimethoxy-4-(ethoxy-*1,1-d*$_2$)-4-(3-phenyl-1-propynyl)-2-cyclobuten-1-one, 23. A solution of 200 mg (0.775 mmol) of **9m** and 6.5 mL of dioxane was delivered to a dry 25-mL round-bottom flask and stirred under an atmosphere of nitrogen at room temperature. To this solution was added 1.79 mg (7.75 mmol) of silver(I) oxide, 1.22 % (7.75 mmol) of iodoethane-*1,1-d*$_2$, and 1.07 g (7.75 mmol) of potassium carbonate, and the resulting black and white suspension was stirred for 36 h under an atmosphere of nitrogen. The black and white suspension was then filtered through a plug of Celite and then diluted with ether. The solvent was removed in vacuo, and after column chromatography (7:1 hexanes/ethyl acetate) 170 mg (0.590 mmol) of **33** was recovered as a clear oil. This represents a 76% yield from **9m**: IR ($CHCl_3$) 2980 (m), 2235 (w), 1783 (s), 1645 (s), 1419 (s), 1049 (s); ^{1}H NMR ($CDCl_3$) δ 7.40–7.20 (m, 5 H), 4.17 (s, 3 H), 3.97 (s, 3 H), 3.72 (s, 2 H), 1.22 (s, 3 H); MS, *m/e* (relative intensity) EI 288 (1.5), 272 (26), 257 (47), 197 (69), 172 (37), 115 (100).

2,8-Dideuterio-4,5-dimethoxy-2-methyl-6-oxo-7-(phenylmethyl)-1-oxaspiro[2.5]-4,7-octadiene, 36. A solution of 140.4 mg (0.487 mmol) of **33** and 10 mL of freshly distilled *p*-xylene was delivered to a dry 25-mL round-bottom flask. This solution was heated and then refluxed for 30 min. During this time the initially light yellow solution turned red-orange. The solvent was removed in vacuo at 70 °C. Column chromatography of the resulting red oil (6:1 hexanes/ethyl acetate) yielded 51.5 g (0.179 mmol) of **36** as a red oil. This represents a 37% yield from **33**: IR (neat) 2950 (m), 1650 (s), 1615 (s), 1209 (s); ^{1}H NMR ($CHCl_3$) major diastereomer reported, δ 7.38–7.14 (m, 5 H), 4.04 (s, 3 H), 3.77 (s, 3 H), 3.68 (s, 2 H), 1.35 (s, 3 H); ^{13}C NMR ($CDCl_3$) 183.4 (s), 156.0 (s), 143.4 (s), 138.4 (s), 135.4 (three-line multiplet of equal intensity), 129.6 (s), 129.4 (d), 128.7 (d), 126.6 (d), 61.1 (q), 61.0 (q), 57.3 (s), 35.6 (t), 14.1 (q); MS, *m/e* (relative intensity) EI 288 (100), 273 (9), 258 (10), 243 (8), 129 (7), 91 (9), 58 (33); exact mass calcd for $C_{17}H_{16}D_2O_4$ 288.1330, found 288.1326.

2,3-Diethoxy-4-methoxy-4-[(trimethylsilyl)ethynyl]-2-cyclobuten-1-one, 37. 2,3-Diethoxy-4-hydroxy-4-[(trimethylsilyl)ethynyl]-2-cyclobuten-1-one (prepared in a similar manner as **9** from diethyl squarate): white crystals (ether/hexanes); 93% yield; mp 90.5–91.5 °C; IR (KBr) 3400, 2975, 2160, 1780, 1625, 1385, 1340, 1035, 850 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 1.30 (t, J = 7.1 Hz, 3 H), 1.44 (t, J = 7.1 Hz, 3 H), 3.13 (s, 1 H), 4.30 (q, 7.1 Hz, 2 H), 4.52 (q, 7.1 Hz, 2 H); MS, *m/e* (relative intensity) EI 268 (6), 253 (19), 239 (16), 225 (39), 211 (100), 197 (49), 165 (35), 127 (34), 123 (26), 111 (46), 109 (32), 99 (90); exact mass calcd for $C_{13}H_{20}SiO_4$ (M^+) 268.1131, found 268.1121.

A solution of 0.30 g (1.12 mmol) of 2,3-diethoxy-4-hydroxy-4-[(trimethylsilyl)ethynyl]-2-cyclobuten-1-one in 18 mL of dioxane was placed under argon and treated with 1.54 g (11.1 mmol) of solid K_2CO_3, 2.60 g (11.2 mmol) of Ag_2O, and 0.70 mL (11.2 mmol) of CH_3I. The mixture was stirred for 33 h in the dark then filtered through Celite and rinsed with ether. The solution was concentrated under reduced pressure to afford a yellow oil. The oil was purified by column chromatography with 5/1 hexanes/ethyl acetate to obtain 0.23 g (72% yield) of **37** as a pale yellow oil: IR (neat) 2980, 1785, 1640, 1330, 1252, 1088, 1048, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9 H), 1.31 (t, J = 7.1 Hz, 3 H), 1.44 (t, J = 7.1 Hz, 3 H), 3.51 (s, 3 H), 4.32 (q, J = 7.1 Hz, 2 H), 4.46 (q, J = 7.1 Hz, 2 H); MS, *m/e* (relative intensity) EI 282 (1), 267 (9), 225 (19), 211 (19), 197 (18), 97 (21), 89 (28), 73 (100), CI 283 (100); exact mass calcd for $C_{14}H_{22}SiO_4$ (M^+) 282.1287, found 282.1286.

2,3-Diethoxy-4-hydroxy-5-(trimethylsilyl)benzaldehyde, 40. A solution of 165 mg (0.59 mmol) of **37** in 75 mL of dry *p*-xylene was heated at reflux for 2 h under argon. The solvent was removed under pressure (bath temperature 40 °C) to afford a yellow residue. Purification by column chromatography with 5/1 hexanes/ethyl acetate gave 124 mg (75% yield) of **40** as light yellow crystals: mp 92–93.5 °C; IR ($CHCl_3$) 3510, 2980, 1680, 1592, 1430, 1355, 1085, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (2 overlapping t, 6 H), 4.20 (2 overlapping q, **4** H), 6.56 (s, 1 H, exchangeable with D_2O), 0.30 (s, 9 H), 7.63 (s, 1 H), 10.21 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.7, 15.9, 69.5, 70.5, 121.4, 123.4, 130.4, 137.2, 155.9, 160.6, 189.2; MS, *m/e* (relative intensity) EI 282 (27), 267 (20), 253 (13), 211 (53), 195 (14), 181 (25), 151 (5), 99 (8), 85 (9), 75 (100); exact mass calcd for $C_{14}H_{22}SiO_4$ (M^+) 282.1287, found 282.1277.

Anal. Calcd for $C_{14}H_{22}O_4Si$: C, 59.55; H, 7.88. Found: C, 59.29; H, 7.60.

2,3,4-Trimethoxy-6-methylene-2,4-cyclohexadien-1-one and Its Trimerization Product, 45. A solution of 0.31 g (1.05 mmol) of **41** and 15 mL of freshly distilled *p*-xylene was heated and then refluxed for 30 min under an atmosphere of nitrogen. The initially colorless solution became light yellow. The solution was then cooled to room temperature and the solvent was removed in vacuo at 70 °C. The resulting light yellow oil was purified by flash column chromatography (1.5:1 hexanes:ethyl acetate) to yield 90 mg (0.15 mmol) of **45** as a white solid (mp 53–54 °C). This represents a 49% yield from **41**: IR ($CHCl_3$) 3000 (m), 2940 (m), 1730 (m), 1682 (m), 1613 (s), 1468 (s), 1130 (s); ^{1}H NMR ($CDCl_3$) δ 6.36 (s, 1 H), 6.34 (s, 1 H), 4.05 (s, 3 H), 3.98 (s, 3 H), 3.97 (s, 3 H), 3.90 (s, 3 H), 3.87 (s, 3 H), 3.79 (s, 3 H), 3.79 (s, 3 H), 3.69 (s, 3 H), 3.60 (s, 3 H), 3.12 (m, 1 H), 2.98–2.50 (m, 5 H), 2.28 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 193.2 (s), 157.9 (s), 148.2 (s), 147.0 (s), 142.5 (s), 142.3 (s), 141.8 (s), 141.8 (s), 141.5 (s), 139.7 (s), 137.3 (s), 117.6 (s), 116.3 (s), 107.0 (d), 106.1 (d), 99.5 (s), 80.7 (s), 61.7 (q), 6.16 (q), 61.5 (q), 61.4 (q), 61.0 (q), 60.8 (q), 56.5 (q) 56.5 (q), 51.4 (q) 44.4 (d), 29.8 (t), 26.4 (t), 22.0 (t); MS, *m/e* (relative intensity) EI 588 (1, trimer), 556 (13), 392 (35, dimer), 360 (71), 197 (99), 196 (39, monomer), 181 (86), 153 (100), 67 (59), CI 589 (65, trimer), 393 (0.07, dimer), 197 (100, monomer); exact mass calcd for $C_{30}H_{36}O_{12}$ 588.2206, found 588.2175.

2,3-Dimethoxy-4-ethynyl-4-(2-propenyloxy)-2-cyclobuten-1-one, 46a. A solution of 170 mg (0.61 mol) of **9n** and 10 mL of reagent-grade THF was treated with 0.61 mL (0.61 mmol) of a 1 M tetrabutylammonium fluoride solution at room temperature. Immediately after the addition the initially light gold solution became brown. The reaction mixture was stirred for 5 min and then was diluted with 25 mL of ether and 15 mL of a 10% ammonium chloride solution. The aqueous layer was separated and then extracted with 2 × 15 mL protions of ether, and the combined organic layer was dried with 2 × 10 mL of brine and $MgSO_4$. The product was concentrated to yield a brown oil that was purified by flash column chromatography (7:1 hexanes/ethyl acetate) to give 105 mg (0.506 mmol) of **46a** as a colorless oil. This represents a 83% yield from **9n**: IR (neat) 3000 (m), 2970 (m), 2118 (w), 1795 (s), 1650 (s), 1353 (s), 1046 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.94 (8-line multiplet, 1 H), 5.31 (d, 1 H, J = 17.7 Hz), 5.18 (d, 1 H, J = 10.2 Hz), 4.30 (m, 2 H), 4.18 (s, 3 H), 3.98 (s, 3 H), 2.84 (s, 1 H); MS, *m/e* (relative intensity) EI 208 (0.1), 167 (100), 151 (14), CI 209 (100), 151 (40); exact mass calcd for $C_{11}H_{12}O_4$ 208.0735, found 208.0721

2,3-Dimethoxy-4-(3-propynyl)-4-(2-propenyloxy)-2-cyclobuten-1-one, 46b. A solution of 0.40 g (1.55 mmol) of **9l** and 12 mL of dioxane was delivered to a dry 25-mL round-bottom flask and was stirred under nitrogen at room temperature. To this solution was added 1.42 mL (2.60 g, 15.5 mmol) of allyl iodide, 3.60 g (15.5 mmol) of silver oxide, and then 2.14 g (15.5 mmol) of potassium carbonate. The black and white suspension was stirred for 36 h at room temperature and then was filtered through Celite. Solvent removal in vacuo yielded a light yellow oil that was purified by column chromatography (8:1 heanes/ethyl acetate) to give 0.34 g (1.14 mmol) of **46b** as a light yellow oil. This represents a 74% yield from 9l: IR (neat) 3070 (w), 3035 (m), 2955 (m), 2865 (m), 2233 (w), 1785 (s), 1645 (s), 1350 (s), 840 (m), 733 (m), 695 (m); ^{1}H NMR ($CDCl_3$) δ 7.38–7.20 (m, 5 H), 6.95 (m, 1 H), 5.29 (m, 1 H), 5.18 (m, 1 H), 4.32 (m, 2 H), 4.16 (s, 3 H), 3.97 (s, 3 H), 3.73 (s, 2 H); MS, *m/e* (relative intensity) EI 258 (10), 257 (66), 207 (100), 171 (13), 155 (18), 115 (74), 91 (24), 77 (11), CI 299 (100), 241 (47); exact mass calcd for $C_{18}H_{18}O_4$ 298.1205, found 298.1199.

(*E*)-4-(Butenyloxy)-2,3-dimethoxy-4-(3-phenyl-1-propynyl)-2-cyclobuten-1-one, 46c. By the method described above the title compound was prepared in 72% yield: yellow oil; 87 mg (4.81 mmol); IR (neat) 3035 (m), 2954 (m) 2868 (m), 2222 (w), 1786 (s), 1646 (s), 1350 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 5 H), 5.8–5.5 (m, 2 H), 4.25 (m, 2 H), 4.15 (s, 3 H), 3.97 (s, 3 H), 3.72 (s, 3 H), 1.72 (d, 3 H); MS, *m/e* (relative intensity) EI 312 (0.54), 257 (35), 221 (24), 143 (45), 115 (100), 91 (27), 77 (16), CI 313 (100), 241 (86), 227 (23), 111 (20); exact

mass calcd for $C_{19}H_{20}O_4$ 312.1361, found 312.1364.

2,3-Dimethoxy-5-(2-propenyl)-2,5-cyclohexadiene-1,4-dione, 48a. A solution of 96.3 mg (0.463 mmol) of **46a** and 5 mL of freshly distilled *p*-xylene was heated and then refluxed for 17 min in a dry 25-mL pear-shaped flask under an atmosphere of nitrogen. The initially colorless solution became red during the thermolysis. The reaction mixture was allowed to cool to room temperature and the solvent was removed in vacuo at 65 °C. The product was purified by flash column chromatography (6:1 hexanes/ethyl acetate) to yield 58.0 mg (0.279 mmol) of **48a** as a red liquid. This represents a 60% yield from **46a**: IR (neat) 2950 (m), 1660 (s), 1605 (s), 1456 (m), 1390 (m), 1060 (m); ^{1}H NMR ($CDCl_3$) 6.40 (t, 1 H, J = 1.6 Hz), 5.78 (m, 1 H), 5.20 (m, 2 H), 4.03 (s, 3 H), 4.00 (s, 3 H), 3.18 (dd, 2 H, J = 1.4, 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 184.37, 184.01, 146.10, 145.19, 144.96, 132.80, 131.08, 119.28, 61.49, 61.40, 32.89; MS, *m/e* (relative intensity) EI 208 (100), 193 (47), 163 (35), 109 (35), 109 (32), 94 (28), CI 209 (100); exact mass calcd for $C_{11}H_{12}O_4$ 208.0735, found 208.0728.

2,3-Dimethoxy-5-(phenylmethyl)-6-(2-propenyl)-2,5-cyclohexadiene-1,4-dione, 48b. Compound **48b**: red oil; 0.13 g (0.44 mmol); 76% yield; IR (neat) 3300 (w), 3063 (m), 2951 (s), 2845 (m), 1663 (s), 1611 (s), 1496 (m), 1455 (s), 1270 (s), 1144 (s), 740 (s), 696 (s); ^{1}H NMR ($CDCl_3$) δ 7.15-7.35 (m, 5 H), 5.63-5.80 (m, 1 H), 5.06 (m, 1 H), 5.05-4.95 (m, 1 H), 4.00 (s, 3 H), 3.99 (s, 3 H), 3.87 (s, 2 H), 3.30 (dt, 2 H, J_t = 1.41 Hz, J_d = 4.90 Hz); MS, *m/e* (relative intensity) EI 298 (50), 283 (16), 207 (48), 165 (21), 128 (27), 115 (45), 91 (100), 65 (20), CI 299 (100); exact mass calcd for $C_{18}H_{18}O_4$ 298.1205, found 298.1200.

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.48; H, 6.08. Found: C, 72.24; H, 5.83.

2,3-Dimethoxy-5-(phenylmethyl)-6-(1-methyl-2-propenyl)-2,5-cyclohexadiene-1,4-dione, 48c. Compound **48c**: orange oil; 35 mg (0.11 mmol); 54% yield; IR (neat) 2950 (m), 1655 (s), 1607 (s), 1455 (s), 1265 (s); ^{1}H NMR ($CDCl_3$) δ 7.35-7.10 (m, 5 H), 6.08 (ddd, 1 H, J_{cis} = 10.18 Hz, J_{trans} = 17.19 Hz, J = 7.08 Hz), 4.95 (ddd, 1 H, $J_{gem} = J_{allylic}$ = 1.25 Hz, J_{cis} = 10.18 Hz), 4.85 (ddd, 1 H, $J_{gem} = J_{allylic}$ = 1.25 Hz, J_{trans} = 17.19 Hz), 4.00 (s, 3 H), 3.94 (s, 3 H), 3.72 (m, 1 H), 1.27 (d, 3 H, J = 7.06 Hz); MS, *m/e* (relative intensity) EI 312 (33), 265 (10), 207 (53), 189 (24), 165 (21), 115 (51), 91 (100), 77 (44), CI 313 (100), 237 (10); exact mass calcd for $C_{19}H_{20}O_4$ 312.1361, found 312.1338.

3,4-Dimethoxy-5-(3-phenyl-1-propynyl)-2(5*H*)-furanone, 61a. A solution of 0.25 g (0.97 mmol) of **9l** and 450 mL of freshly distilled THF was cooled to 0 °C in a photochemical reaction vessel under an atmosphere of nitrogen. The photochemical reaction vessel was fitted with a quartz immersion well and then the solution was photolyzed through the quartz immersion well with a 450-W, medium-pressure photochemical immersion lamp for 2 h at 0 °C. The initially colorless THF solution became light yellow during the photolysis. Solvent removal under reduced pressure yielded **61a** (0.13 g, 0.50 mmol) as a white solid (mp 73.5-74.0 °C) after flash column chromatography (5:1 hexanes/ethyl acetate) and recrystallization from ethyl ether. This represents a 52% yield from **9l**: IR (KBr) 2960, 2243, 1786, 1695, 1347, 1121, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 5 H), 5.30 (t, 1 H, J = 2.1 Hz), 4.16 (s, 3 H), 3.86 (s, 3 H), 3.68 (d, 2 H, J = 2.1 Hz); ^{13}C NMR ($CDCl_3$) δ 168.3, 156.4, 135.5, 128.8, 128.1, 127.1, 122.2, 87.4, 74.1, 65.4, 60.4, 59.8, 25.3; MS, *m/e* (relative intensity) EI 258 (50), 128 (53), 115 (100), 87 (38), CI 259 (100); exact mass calcd for $C_{15}H_{14}O_4$ 258.0892, found 258.0893.

3,4-Dimethoxy-4-(phenylethynyl)-2(5*H*)furanone, 61b. Compound **61b**: yellow oil; 62 mg, (0.25 mmol); 28% yield; IR (neat) 2963 (m), 2229 (m), 1780 (s), 1690 (s), 1344 (s); ^{1}H NMR ($CDCl_3$) δ 7.50-7.30 (m, 5 H), 5.47 (s, 1 H), 4.19 (s, 3 H), 3.88 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 168.2, 156.2, 132.1, 129.5, 128.5, 122.2, 121.3, 88.3, 80.4, 65.5, 60.4, 59.7; MS, *m/e* (relative intensity) EI 244 (6), 142 (52), 129 (62), 114 (100), 87 (42), CI 245 (100), 171 (2); exact mass calcd for $C_{14}H_{12}O_4$ 244.0735, found 244.0740.

3,4-Dimethoxy-4-(1-hexynyl)-2(5*H*)-furanone, 61c. Compound **61c**: yellow oil; 110 mg, (0.49 mmol); 50% yield; IR (neat) 2951 (s), 2240 (m), 1779 (s), 1690 (s), 1346 (s); ^{1}H NMR ($CDCl_3$) δ 5.23 (t, 1 H, J = 2.0 Hz), 4.15 (s, 3 H), 3.85 (s, 3 H), 2.24 (td, 2 H, J_t = 7.0 Hz, J_d = 2.0 Hz), 1.60-1.30 (m, 4 H), 0.91 (t, 3 H, J = 7.3 Hz); MS, *m/e* (relative intensity) EI 224 (15), 115 (100), 87 (89), CI 225 (100), 167 (2); exact mass calcd for $C_{12}H_{16}O_4$ 224.1048, found 224.1059.

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Synthesis of Isoarnebifuranone, Nanaomycin, and Deoxyfrenolicin. Structure Elucidation of Arnebifuranone

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Abstract: The synthesis of isoarnebifuranone is reported. This compound was established to have the *E* stereochemistry, which had previously been suggested for the natural product arnebifuranone. On the basis of a comparison of the spectral properties of the natural and synthetic products, arnebifuranone was shown to actually be the *Z* isomer. Also described is a new synthesis of naphthoquinones which involves the thermal rearrangement of alkynyl-substituted benzocyclobutenones. The reaction was employed as a key step in the synthesis of 2-(1-hydroxyethyl)- and 2-(1-hydroxybutyl)-8-methoxy-3-(2-propenyl)-1,4-naphthoquinones, which constitutes a formal synthesis of the natural isochroman-1,4-naphthoquinones nanaomycin and deoxyfrenolicin.

The rearrangement of 4-alkynylcyclobutenones to 1,4-benzoquinones described in the preceding paper has wide synthetic scope and can be utilized as a key step in the construction of quinones having a variety of substitution patterns.[1] Its utility is further illustrated here by specific syntheses related to selected targets in the natural products arena—arnebifuranone (**2**), nanaomycin D (**3**), and deoxyfrenolicin (**4**). Arnebifuranone is a natural benzoquinone reported to have *E* stereochemistry at the stereogenic alkene site.[2] However, this compound, **1**, *now referred to as isoarnebifuranone*, was prepared as outlined in Scheme III and

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