Generation of (Trimethylsiloxy)(phenylethynyl)ketene and (Trimethylsiloxy)cyanoketene and Their Reactions with Some Alkynes

Daniel J. Pollart and Harold W. Moore*

Department of Chemistry, University of California, Irvine, California 92717

Received March 16, 1989

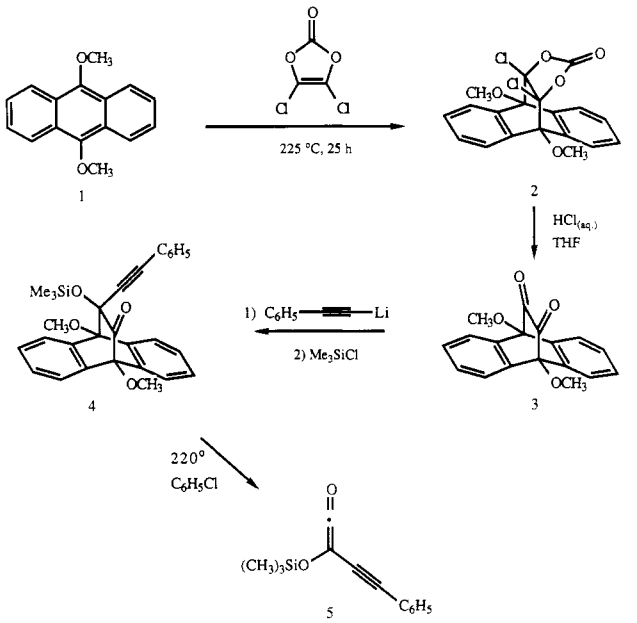
9,10-Dihydro-9,10-dimethoxy-9,10-ethanoanthracene-11,12-dione (**3**) is shown to be a valuable precursor to the (trialkylsiloxy)ketenes **5** and **21**. Conversion of the dione to 9,10-dihydro-9,10-dimethoxy-11-oxo-12-(phenylethynyl)-12-(trimethylsiloxy)-9,10-ethanoanthracene (**4**) and thermolysis at 220 °C resulted in a retro-Diels–Alder fragmentation, giving 9,10-dimethoxyanthracene and the ketene **5**. (Trimethylsiloxy)cyanoketene (**21**) was generated in an analogous manner from 12-cyano-9,10-dimethoxy-11-oxo-12-(trimethylsiloxy)-9,10-ethanoanthracene (**19**). Reactions of these ketenes with alkynes are reported.

Reported here is the generation of the ketenes (trimethylsiloxy)(phenylethynyl)ketene (**5**) and (trimethylsiloxy)cyanoketene (**21**) using the retro-Diels–Alder fragmentations of appropriately substituted 9,10-ethanoanthracene derivatives.[1] These ketenes are members of rare classes. For example, only one previous example of a (trialkylsilyloxy)ketene has been reported, and the only examples of alkynylketenes to appear are alkynylcyanoketenes.[2,3] Both of the ketenes described here are of synthetic interest, but (trimethylsilyloxy)ketene **21** is of particular note since it is a potential ethenedione synthon and could thus be of potential use as a reagent for the synthesis of cyclic α-diketones.

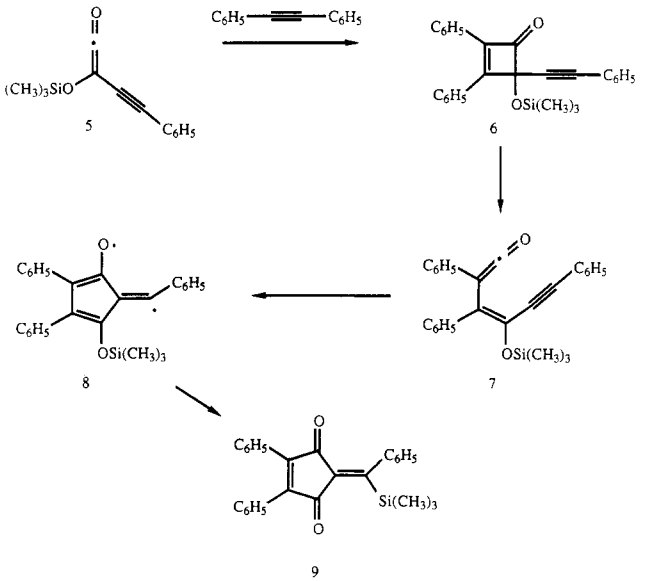
Several reports have appeared attesting to the efficacy of the retro-Diels–Alder reaction for the generation of olefins from ethanoanthracenes.[4,5] In this regard, a recent study described by Chung et al. observed acceleration of the rate of such fragmentations as a function of increased electron-donating ability of the substituents at the bridgehead positons.[4] With this in mind, dione **3** was prepared by the cycloaddition of 9,10-dimethoxyanthracene (**1**) to dichlorovinylenecarbonate (Scheme I).[6,7] Acidic hydrolysis of the resulting adduct **2** gave the desired dione **3** as a bright orange solid in 72% overall yield.

The utility of **3** as a ketene precursor was demonstrated following its conversion to **4** upon sequential treatment with lithium phenylacetylide (THF, −78 °C) and trimethylsilyl chloride. Thermolysis of **4** in the presence of diphenylacetylene gave the known cyclopentenedione **9** in 70% isolated yield (Scheme II).[1] The formation of **9** was anticipated on the basis of previous studies, and its formation thus lends evidence for the generation of **5** from **4**. On the basis of work previously reported from this laboratory, a mechanism for the formation of **9** is outlined in Scheme I.[8-10] It is envisaged to involve the initial cycloaddition of the **5** to diphenylacetylene to give the cyclobutenone **6**. Under the thermal conditions of the reaction **6** is not stable but undergoes electrocyclic ring opening to the conjugated ketene **7**, which then ring closes to the diradical **8**. This then suffers an intramolecular

Scheme I



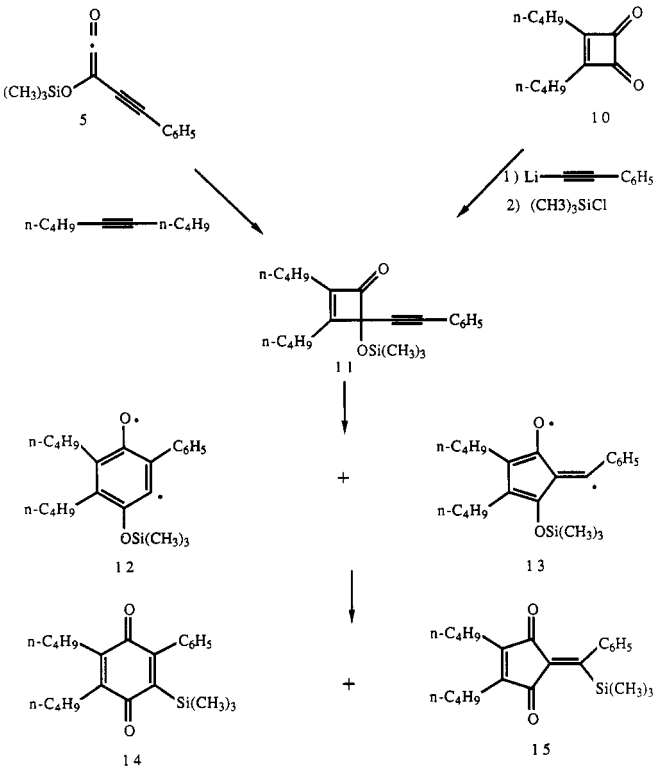
Scheme II



(1) The generation of **5** has previously been reported: Fernandez, M.; Pollart, D. J.; Moore, H. W. *Tetrahedron Lett.* **1988**, *29*, 2765.
(2) Wright, B. B. *J. Am. Chem. Soc.* **1988**, *110*, 4456.
(3) Moore, H. W.; Chow, K.; Nyueyn, N. V. *J. Org. Chem.* **1987**, *52*, 1315.
(4) Chung, Y.-S.; Duerr, B. F.; Nanjappan, P.; Czarnik, A. W. *J. Org. Chem.* **1988**, *53*, 1334, and references therein.
(5) Strating, J.; Zwanenburg, B.; Wagenaar, A.; Udding, A. C. *Tetrahedron Lett.* **1969**, 125. Hart, H.; Dean, D. L.; Buchanan, D. N. *J. Am. Chem. Soc.* **1973**, *95*, 6294, and references therein. Ripoll, J. L. *Tetrahedron* **1977**, *33*, 389.
(6) Meek, J. S.; Monroe, P. A.; Bouboulis, C. J. *J. Org. Chem.* **1963**, *28*, 2572.
(7) Scharf, H.-D.; Droste, W.; Liebig, R. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 215. Scharf, H.-D.; Pinske, W.; Feilen, M.-H.; Droste, W. *Chem. Ber.* **1972**, *105*, 554.
(8) Foland, L.; Karlsson, J. O.; Perri, S.; Patil, S.; Schwabe, R.; Xu, S.; Moore, H. W. *J. Am. Chem. Soc.*, in press, and references therein.
(9) Karlsson, J. O.; Nguyen, N. V.; Foland, L. D.; Moore, H. W. *J. Am. Chem. Soc.* **1985**, *107*, 3392.
(10) Nguyen, N. V.; Chow, K.; Karlsson, J. O.; Doedens, R.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 419.

0022-3263/89/1954-5444$01.50/0

Scheme III



trimethylsilyl transfer to give the observed product **9**.

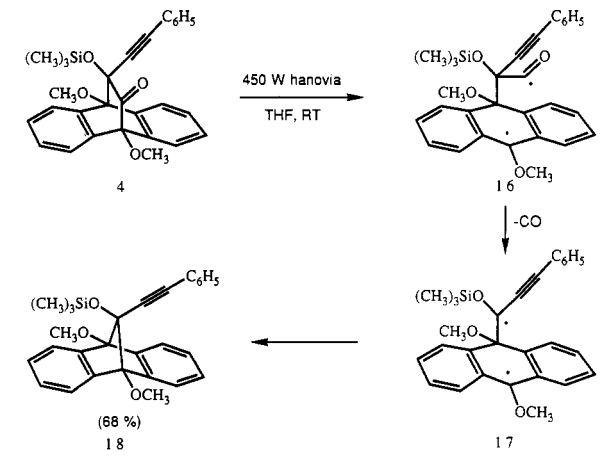
In a related experiment **5** was reacted in the presence of 5-decyne (Scheme III). In this case, the quinone **14** as well as the cyclopentenedione **15** were realized as products in a respective ratio of 1:7. This transformation is again viewed as involving the cyclobutenone **11**, which leads to the diradicals **12** and **13** after electrocyclic ring opening and subsequent ring closure of the resulting conjugated ketene. These respective diradicals then proceed to **14** and **15** upon intramolecular trimethylsilyl transfer.

The mechanism proposed above is supported by the results obtained from a study of the thermolysis of the proposed cyclobutenone intermediate **11**, which was independently prepared from di-*n*-butylcyclobutenedione **10**.[11] Specifically, mild thermolysis of **11** in refluxing ether for 1 h gave the di-*n*-butylcyclopentenedione **15** and quinone **14** in a respective ratio of 3:1 (NMR analysis), a result in approximate agreement with the 7:1 ratio of these products when generated from the cycloaddition of **5** to 5-decyne.

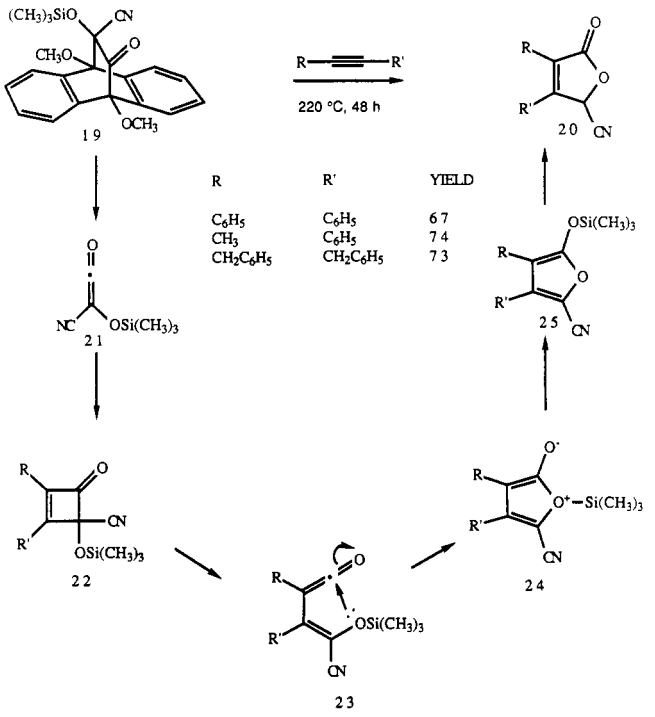
It was hoped that the cycloreversion of **4** to the ketene **5** could also be accomplished under photolytic conditions since this would allow the ketene cycloadditions to be accomplished at ambient temperature or below. However, the most efficient photoprocess observed was the extrusion of carbon monoxide from **4** to give **18** (Scheme IV). This transformation is thought to involve an initial homolytic carbon–carbon bond cleavage to give the acyl radical **16**, which then undergoes loss of carbon monoxide and ring closure to the final product.[12]

Dione **3** was also employed as the starting point for the generation of (trimethylsiloxy)cyanoketene (**21**), a potential

Scheme IV



Scheme V



R	R'	YIELD
C_6H_5	C_6H_5	67
CH_3	C_6H_5	74
$CH_2C_6H_5$	$CH_2C_6H_5$	73

ethenedione synthon. To this end, the dione **3** was converted to **19** in excellent yield upon treatment with trimethylsilyl cyanide (Scheme V).[13]

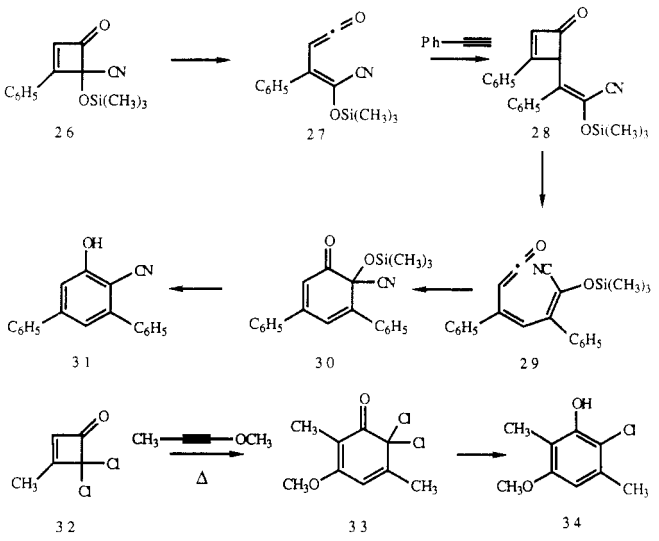
Surprisingly, thermolysis of **19** in the presence of excess diphenylacetylene did not give the expected cyclobutenone, but rather the 5-oxo-2-furancarbonitrile **20a** was realized in 67% isolated yield. The mechanism of this transformation is suggested to involve an initial cycloaddition of the ketene to the alkyne to give **22**, which undergoes subsequent electrocylic ring opening under the reaction conditions to the vinylketene **23**. Ring closure involving intramolecular attack of the electrophilic ketene moiety on the oxygen of the trimethylsiloxy group gives the zwitterion **24**. Silyl migration then results in the siloxycyanofuran **25**. Examination of the crude product (R = R = C_6H_5) by ^1H NMR spectroscopy showed the presence of an electron-deficient trimethylsilyl group (singlet at 0.327 ppm) and the absence of the furanone ring proton. Evidently hydrolysis to the furan **25** to the butenolides **20** occurs during purification (silica gel chromatography).

(11) For synthetic methods for the conversion of squaric acid to substituted cyclobutendiones see: (a) Reed, M. W.; Pollart, D. P.; Perri, S. T.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477. (b) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shaw, T. T. *J. Org. Chem.* **1988**, *53*, 2482.

(12) Precedence for homolytic cleavage of similar ethanoanthracenes can be found in the work of: Hart, H.; Dean, D. L.; Buchanan, D. N. *J. Am. Chem. Soc.* **1973**, *95*, 6294.

(13) Evans, D. A.; Hoffman, J. M.; Truesdale, L. K. *J. Am. Chem. Soc.* **1973**, *95*, 5822.

Scheme VI



Cycloaddition of (trimethylsiloxy)cyanoketene also proved amenable to other acetylenes. For example, thermolysis of **19** in the presence of dibenzylacetylene[14] provided the bis(phenylmethyl)furancarbonitrile **20c** in 73% yield, and in the presence of 1-phenylpropyne the furanone **20b** was isolated in 74% yield. Assignment of the regiochemistry of **20b** was based upon mechanistic consideration and the observed 1.8-Hz homoallylic coupling between the furanone ring proton and methyl protons.

Finally, thermolysis of **19** in the presence of excess phenylacetylene surprisingly did not give a furanone but rather the cyanophenol **31** was realized in 27% isolated yield (Scheme VI). The structure of **31** is based upon its characteristic IR, MS, and ^{1}H NMR data. Particularly important structural data are those obtained from a detailed NMR study. The ^{1}H NMR spectrum (500 MHz) of **31** shows a pair of doublets (1 H, J = 1.5 Hz) at 7.20 and 7.27 ppm due to the meta-disposed phenolic ring aromatic protons and multiplets at 7.40–7.51 (6 H) and 7.58–7.62 ppm (4 H). The four-proton multiplet was assigned to the ortho protons of the phenyl substituents on the basis of NOE studies. That is, presaturation of the phenolic ring proton doublet at 7.27 ppm caused a 16% NOE enhancement of the four-proton multiplet at 7.58–7.62 ppm. Analogously, presaturation of the upfield doublet at 7.20 ppm caused a 9% enhancement of this same four-proton multiplet, and presaturation of the multiplet caused a 7.5% and 19% enhancement of the upfield and downfield doublets, respectively. This suggests a structure in which the proton responsible for the upfield resonance (H_a) is adjacent to one of the phenyl groups, while the proton responsible for the downfield doublet (H_b) is adjacent to both. In addition, selective heteronuclear decoupling experiments provided the chemical shifts of the carbons bearing H_a (113.2 ppm), H_b (120.8 ppm), and the ortho protons (137.1 and 128.5 ppm). In conjunction with this information the calculated ^{13}C chemical shifts agree with those observed.[15] To confirm the structure, a series of long-range C–H correlation experiments were carried out with magnetization transfer optimized for a C–H coupling of 5 Hz. Soft pulse polarization at H_a caused the appearance of peaks at 97.4 (C_1), 113.2 (weak, due to the effect of a ^{13}C satellite of the C–H_b pair), 120.8, and 159.5 (C_2) ppm in the selective INEPT spectrum, while polarization at H_b caused the appearance of peaks at 97.4 and 113.3 ppm (intense). Significantly, these data show that the aromatic protons on the phenolic ring are thus not ortho to the nitrile group. Taken together, the above data allow an ambiguous assignment of the structure of **19**.

A possible mechanism for this reaction involves a Danheiser electrocyclic cascade,[16] i.e., regioselective cycloaddition of (trimethylsiloxy)cyanoketene to phenyl acetylene to give the cyclobutenone **26**, which undergoes ring opening to **27** and regioselective cycloaddition of a second equivalent of phenylacetylene. Ring opening of the resultant cyclobutenone **28** then gives the dienylketene **29**, which undergoes a six-electron electrocyclization to afford the cyclohexadienone **30**. The final step involves formal reduction and loss of silicon to give the cyanophenol, an unusual reaction that is currently under investigation. In similar experiments resorcinols have been reported to arise from the thermolysis of dichlorocyclobutenones in the presence of alkoxyacetylenes.[16] The mechanism reportedly involves ring opening of the cyclobutenone **32** and cycloaddition of the acetylene to ultimately provide the dichlorocyclohexadienone **33**, which was suggested to undergo a radical-mediated dechlorination to provide the final product **34**.

In summary, phenylethynyl(trimethylsiloxy)ketene (**5**) and (trimethylsiloxy)cyanoketene (**21**) have been generated from easily prepared precursors. In the presence of alkynes these ketenes undergo cycloaddition to give cyclobutenones which undergo subsequent unusual rearrangements under the reaction conditions.

Experimental Section

General Techniques. All air- or water-sensitive reactions were carried out in oven-dried (120 °C) glassware under a slight positive pressure of argon or in vacuo as indicated. Ethereal solvents were distilled from sodium (benzophenone indicator). Chlorobenzene and *p*-xylene were distilled from calcium hydride. All other solvents were of unpurified reagent grade. Removal of the solvents under vacuum was accomplished at either 15–30 Torr (rotary evaporator) or 0.05 Torr (vacuum pump, dry ice/acetone trap) as appropriate. Flash column chromatography was performed using E. Merck silica gel (230–400 mesh) or Fisher Scientific adsorption alumina (80–200 mesh) as indicated. Melting points were determined on a Buchi 510 capillary melting-point apparatus and are uncorrected. NMR spectroscopic studies were carried out on a General Electric QE-300 (or GN-500 where indicated) spectrophotometer, and chemical shifts are reported relative to tetramethylsilane (0.00 ppm, ^{1}H spectra) or the central peak in the deuteriochloroform signal (76.9 ppm, ^{13}C spectra) as internal standard. Infrared spectra were obtained on a Perkin-Elmer 281 sodium chloride spectrophotometer, and absorptions are reported relative to polystyrene (1601.8 cm^{-1}) as external standard. Ultraviolet spectra were recorded on a Perkin-Elmer Lambda 4A UV–vis spectrophotometer. Mass spectra were determined by using a medium-resolution Finnigan 4000 GC/MS quadrupole spectrometer interfaced to a Nova 312 data system. High-resolution mass spectra were obtained on a VG Analytical 7070E organic mass spectrophotometer interfaced to a VG Analytical LTD 11/250 data system. Elemental analyses were performed by Robertson Laboratory, Inc., Madison, NJ. Leucomethylene blue[17] was freshly prepared and used as a spot test for the quinone moiety.

4a,9a-Dichloro-4,9-dimethoxy-2-oxo-4,4a,9,9a-tetrahydro-4,9-[1′,2′]benzenonaphtho[2,3-*d*]-1,3-dioxole (2). A freeze-degassed solution of 3.72 g (15.6 mmol) of dimethoxyanthracene and 3.14 g (20.3 mmol) of dichlorovinylenecarbonate in 6 mL of

(14) Dupont, G.; Dulou, R.; Lefebvre, G. *Bull. Soc. Chim. Fr.* **1954**, 653.
(15) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; Chapter 5.
(16) Danheiser, R. L.; Gee, S. K. *J. Org. Chem.* **1984**, *49*, 1674. Danheiser, R. L.; Gee, S. K.; Perez, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 806. Kowalski, C. J.; Lal, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 3693.
(17) Lin, B.; Page, A.; Wong, E.; Ciale, P.; Shank, C.; Folkers, K. *J. Biol. Chem.* **1959**, *81*, 4007.

p-xylene was sealed in a glass vessel and heated to 225 °C for 25 h. The contents of the vessel were then taken up in 50 mL of hot toluene, and upon cooling 5.00 g (82%) of the product was deposited as a dark brown solid, mp 203–204 °C: ^{1}H NMR ($CDCl_3$) δ 4.16 (s, 6 H), 7.28–7.39 (m, 4 H), 7.58–7.66 (m, 4 H); IR ($CHCl_3$, cm^{-1}) 1850, 1460, 1090, 1080, 1060, 1010; MS (CI), *m/e* (rel intensity) 397 (11), 395 (78), 393 (100), 238 (9); exact mass (CI) calcd for $C_{19}H_{15}Cl_2O_5$ 393.0296, found 393.0277. The mother liquor was condensed to 10 mL and provided an additional 743 mg (12%) of the product, mp 199–202.5 °C.

Anal. Calcd for $C_{19}H_{14}Cl_2O_5$: C, 58.03; H, 3.59. Found: C, 57.79; H, 3.77.

9,10-Dihydro-9,10-dimethoxy-9,10-ethanoanthracene-11,12-dione (3). A solution of 7.82 g (19.9 mmol) of 4a,9a-dichloro-4,9-dimethoxy-2-oxo-4,4a,9,9a-tetrahydro-4,9[1′,2′]-benzenonaphtho[2,3-*d*]-1,3-dioxole in 200 mL THF was treated with 100 mL of 10% HCl(aq) at room temperature for 25 h. The resultant orange solution was poured into 250 mL of ether/250 mL of water, and the separated aqueous layer was washed with an additional 150 mL of ether. The combined organic layers were dried with $NaHCO_3$/brine and over $MgSO_4$ and stripped to give an orange oil which solidified upon standing. Recrystallization from CH_2Cl_2/hexane gave 5.16 g (88%) of the product as bright orange crystals, mp 134.5–136 °C: ^{1}H NMR ($CDCl_3$) δ 4.21 (s, 6 H), 7.40–7.47 (m, 4 H), 7.63–7.70 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 56.8, 87.8, 122.6, 129.0, 135.0, 183.4; IR ($CHCl_3$, cm^{-1}) 1760, 1470, 1460, 1250; UV ($CHCl_3$) λ 244 (max), 276, 305, 474 (br); MS (EI), *m/e* 294 (0.5), 239 (7.5), 238 (45), 224 (16), 223 (100), 165 (17), 163 (13), 152 (31), 151 (14), 119 (9), 91 (9), 82 (9), 76 (15), 50 (27); exact mass calcd for $C_{18}H_{14}O_4$ 294.0892, found 294.0880. Concentration and cooling of the mother liquod gave an additional 0.35 g of the product, mp 130–133 °C.

Anal. Calcd for: C, 73.46; H, 4.79. Found: C, 73.23; H, 4.81.

9,10-Dihydro-9,10-dimethoxy-11-oxo-12-(phenylethynyl)-12-(trimethylsiloxy)-9,10-ethanoanthracene (4). A solution of 1-lithio-2-phenylacetylene, prepared by addition of 1.425 mL (1.75 mmol) of 1.23 M *n*-butyllithium in hexane to 209 mg (2.05 mmol) of phenylacetylene in 5 mL of THF at −78 °C under argon, was cannulated into a solution of 344 mg (1.17 mmol) of 9,10-dihydro-9,10-dimethoxy-9,10-ethanoanthracene-11,12-dione in 10 mL of THF at −78 °C under argon. After 20 min the solution was quenched with 254 mg (2.34 mmol) of chlorotrimethylsilane, warmed to room temperature, and poured into 100 mL of ether/20 mL of 5% $NaHCO_3$(aq). The aqueous layer was washed with 20 mL of ether, and the combined organic layers were dried with brine and over K_2CO_3. Removal of the solvent gave an orange oil which was eluted through alumina with 1% ethyl acetate/hexane to give 449 mg (82%) of the desired product as a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 4.14 (s, 3 H), 4.19 (s, 3 H), 7.12–7.18 (m, 2 H), 7.18–7.38 (m, 7 H), 7.52–7.58 (m, 2 H), 7.61–7.66 (m, 1 H), 7.71–7.76 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.150, 55.7, 56.6, 84.3, 86.2, 87.5, 88.5, 121.3, 121.4, 122.0, 123.2, 123.5, 127.0, 127.1, 127.3, 128.0, 128.4, 131.3, 134.5, 135.2, 139.5, 140.0, 196.1; IR (neat, cm^{-1}) 2230, 1750, 1460, 1250 (br); MS (CI), *m/e* (rel intensity) 469 (13), 379 (100), 351 (68), 239 (12), 238 (9), 203 (4), 105 (4), 92 (5), 91 (46), 75 (5); exact mass calcd for $C_{29}H_{28}O_4Si$ 468.1757, found 468.1762.

Cycloaddition of (Trimethylsiloxy)(phenylethynyl)ketene to Diphenylacetylene: 4,5-Diphenyl-2-(phenyl[trimethylsilyl]methylene)-4-cyclopentene-1,3-dione (9). A freeze-degassed solution of 148 mg (0.316 mmol) of 9,10-dihydro-9,10-dimethoxy-11-oxo-12-(phenylethynyl)-12-(trimethylsiloxy)-9,10-ethanoanthracene (4) and 84.5 mg (0.474 mmol) of diphenylacetylene in 4 mL of *p*-xylene was heated to 220 °C in a sealed vessel for 48 h. Removal of the solvent and chromatography (1:1 benzene/hexane on SiO_2) gave 91 mg (70%) of the product as a yellow oil which partially solidified upon standing. Recrystallization of this material from methanol gave 63 mg of bright yellow needles (49%), mp 191–192 °C (lit. mp 196–197 °C[1]).

Cycloaddition of (Trimethylsiloxy)(phenylethynyl)ketene to Di-*n*-butylacetylene: 4,5-Di-*n*-butyl-2-(phenyl[trimethylsilyl]methylene)-4-cyclopentene-1,3-dione (15) and 2,3-Di-*n*-butyl-5-phenyl-6-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione (14). A freeze-degassed solution of 33 mg (0.0704 mmol) of 9,10-dihydro-9,10-dimethoxy-11-oxo-12-(phenylethynyl)-12-(trimethylsiloxy)-9,10-ethanoanthracene and 49 mg (0.352 mmol) of di-*n*-butylacetylene in 3 mL of *p*-xylene was heated to 220 °C for 48 h. Removal of the solvent gave an orange semisolid that showed trimethylsilane peaks in the ^{1}H NMR spectrum at −0.09 and 0.15 ppm in a ratio of 1:7 and that was purified by preparative TLC (2% EtOAc/hexane followed by 25% benzene/hexane, each on silica gel) to give 3 mg (12%) of the quinone 14 as a yellow oil: ^{1}H NMR ($CDCl_3$) δ −0.09 (s, 9 H), 0.9–1.0 (m, 6 H), 1.35–1.50 (m, 8 H), 2.40–2.55 (m, 4 H), 7.10–7.16 (m, 2 H), 7.35–7.41 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 0.3, 13.7, 13.8, 23.1 (br), 26.3, 26.4, 31.5, 31.6, 127.6, 128.5, 129.5, 135.4, 144.0, 146.0, 148.3, 154.3, 186.4, 192.5; IR (neat, cm^{-1}) 1640, 1250, 850; MS (EI), *m/e* (rel intensity) 368 (10), 354 (12), 353 (43), 352 (45), 311 (13), 297 (19), 283 (10), 270 (11), 269 (53), 267 (13), 255 (10), 195 (10), 165 (12), 159 (19), 149 (13), 129 (18), 85 (10), 81 (11), 75 (49), 73 (100), 67 (12), 59 (11), 58 (15), 57 (20), 55 (16), 54 (11); exact mass calcd for $C_{23}H_{32}O_2Si$ 368.21715, found 368.267. Also produced was 14 mg (54%) of the alkylidenecyclopentenedione 15 as a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.145 (s, 9 H), 0.87 (t, *J* = 7 Hz, 3 H), 0.96 (t, 3 H, *J* = 7 Hz), 1.25–1.60 (m, 8 H), 2.36 (t, 2 H, *J* = 7 Hz), 2.48 (t, 2 H, *J* = 7 Hz), 6.85–6.90 (m, 2 H), 7.23–7.38 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ −0.7, 13.6, 13.7, 23.0 (br), 23.7, 23.75, 30.1, 30.3, 124.2, 126.1, 127.6, 133.9, 141.8, 156.4, 158.3, 166.2, 191.4, 194.6; IR (neat, cm^{-1}) 1690, 1250, 850; MS (EI), *m/e* (rel intensity) 368 (4), 353 (17), 297 (10), 283 (5), 165 (6), 129 (15), 105 (6), 91 (9), 81 (6), 75 (27), 74 (9), 73 (100), 71 (5), 69 (6), 67 (8), 57 (12), 55 (12), 53 (6); exact mass calcd for $C_{23}H_{32}O_2Si$ 368.21715, found 368.2161.

3,4-Di-*n*-butyl-3-cyclobutene-1,2-dione. To a stirred solution of 152 mg (1.07 mmol) of dimethyl squarate in 15 mL of THF at −78 °C under argon was added 2.61 mL (3.21 mmol) of 1.23 M *n*-BuLi in hexane. After 1.5 h the resultant dianion was treated with 741 mg (3.53 mmol) of trifluoroacetic anhydride, and after an additional 20 min with 5 mL of 10% NH_4Cl(aq). After warming to room temperature, the heterogeneous mixture was poured into 20 mL of 5% $NaHCO_3$(aq)/30 mL of ether. The aqueous layer was washed with an additional 20 mL of ether, and the combined organic layers were dried with brine and over $MgSO_4$. Removal of the solvent gave a yellow oil which was eluted through silica gel with 10% EtOAc/hexane to give 154 mg (74%) of the product as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 6 H, *J* = 7.5 Hz), 1.40 (m, app hex, 4 H), 1.70 (m, app quin, 4 H), 2.72 (t, 4 H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.4, 22.7, 26.2, 28.0, 199.4, 202.6; IR (neat, cm^{-1}) 1780 (br), 1600, 1470; MS (EI), *m/e* (rel intensity) 194 (38), 169 (8), 137 (37), 109 (24), 98 (12), 95 (37), 82 (12), 81 (71), 79 (12), 68 (20), 67 (68), 55 (33), 54 (100), 53 (23); exact mass calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1308.

Preparation and Thermolysis of 2,3-Di-*n*-butyl-4-(phenylethynyl)-4-(trimethylsiloxy)-2-cyclobuten-1-one (11), 4,5-Di-*n*-butyl-2-(phenyl[trimethylsilyl]methylene)-4-cyclopentene-1,3-dione (15), and 2,3-Di-*n*-butyl-5-phenyl-6-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione (14). A solution of 1-lithio-2-phenylacetylene (prepared as above from 144 mg (1.41 mmol) of phenylacetylene and 1.04 mL (1.28 mmol) of 1.23 M *n*-BuLi in hexane) in 10 mL of THF was added via a cannula to 208 mg (1.07 mmol) of 3,4-di-*n*-butyl-3-cyclobutene-1,2-dione in 15 mL of THF at −78 °C under argon. After 30 min the solution was quenched with 175 mg of chlorotrimethylsilane, stirred for 10 min, warmed to room temperature, and poured into 50 mL of 5% $NaHCO_3$(aq)/50 mL of ether. The aqueous layer was washed with 20 mL of ether, and the combined organic layers were dried with brine/5% $NaHCO_3$(aq) and over K_2CO_3. Removal of the solvent gave a light orange oil: ^{1}H NMR ($CDCl_3$) δ 0.269 (s, 9 H), 2.7–0.9 (m, 18 H), 7.28–7.35 (m, 3 H), 7.39–7.44 (m, 2 H); IR (neat, cm^{-1}) 1770, 1260. Attempted chromatographic purification of a similar sample of the crude product gave only a mixture of 4,5-di-*n*-butyl-2-(phenyl[trimethylsilyl]-methylene)-4-cyclopentene-1,3-dione (11) and 2,3-di-*n*-butyl-5-phenyl-6-(trimethylsilyl)-2,5-cyclohexadiene-1,4-dione (14), so the crude material was taken up in 75 mL of ether and refluxed for 1 h. Removal of the solvent and examination of the residue by ^{1}H NMR indicated that a 3:1 mixture of the alkylidenecyclopentenedione 15 and quinone 14 had formed, which were isolated by preparative TLC (2% EtOAc/hexane on silica gel) in 35% (140 mg) and 12% (49 mg) yields, respectively.

Photolysis of 9,10-Dihydro-9,10-dimethoxy-11-oxo-12-(phenylethynyl)-12-(trimethylsiloxy)-9,10-ethanoanthracene

(4) and 9,10-Dihydro-9,10-dimethoxy-11-(phenylethynyl)-11-(trimethylsiloxy)-9,10-methanoanthracene (18). A solution of 148 mg (0.316 mmol) of 9,10-dihydro-9,10-dimethoxy-11-oxo-12-(phenylethynyl)-12-(trimethylsiloxy)-9,10-ethanoanthracene (**4**) and 1.0 mL (5.56 mmol) of 5-decyne in 200 mL of THF at room temperature under argon was irradiated through a Pyrex filter with a 450-W Hanovia lamp for 7 h. Removal of the solvent gave a yellow oil which was chromatographed (preparative TLC on silica gel with 20% benzene/hexane followed by column chromatography on silica gel with 5% EtOAc/hexane) to give 94 mg (68%) of the product **4** as a colorless oil which partially solidified upon standing, mp 104–107.5 °C: ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 4.03 (s, 6 H), 7.03–7.07 (m, app dd, 2 H), 7.09–7.13 (m, app dd, 2 H), 7.12–7.15 (m, 2 H), 7.20–7.26 (m, 3 H), 7.28–7.33 (m, app dd, 2 H), 7.35–7.40 (m, app dd, 2 H); IR (neat, cm^{-1}) 1490, 1470, 1450, 1290, 1250, 850, 750; MS (EI), *m/e* (rel intensity) 440 (0.31), 409 (16), 336 (23), 293 (14), 235 (21), 223 (18), 159 (39), 152 (12), 129 (25), 73 (100); exact mass calcd for $C_{28}H_{28}O_3Si$ 440.1808, found 44.1806. Recrystallization of the material from CH_2Cl_2/hexanes gave 61 mg of **18** as a white solid, mp 109.5–110.5 °C.

Anal. Calcd for $C_{28}H_{28}O_3Si$: C, 76.33; H, 6.41. Found: C, 76.24; H, 6.52.

12-Cyano-9,10-dihydro-9,10-dimethoxy-11-oxo-12-(trimethylsiloxy)-9,10-ethanoanthracene (19). Trimethylsilyl cyanide (0.325 mL, 2.43 mmol) was added to a stirred solution of 651 mg (2.21 mmol) of 9,10-dihydro-9,10-dimethoxy-9,10-ethanoanthracene-11,12-dione (**3**) in 5 mL of CH_3CN at 0 °C under argon. Following dissipation of the orange color (approximately 5 min.) the solution was poured into 50 mL of CH_2Cl_2/40 mL 5% $NaHCO_3$(aq). The aqueous layer was washed with 20 mL of CH_2Cl_2, and the combined organic layers were dried with brine/5% $NaHCO_3$(aq) and over anhydrous K_2CO_3. Attempted chromatography of similar samples of the crude material caused hydrolysis to the starting dione, so the solvent was removed in vacuo to give a light orange oil which was recrystallized from ether/hexanes to give 796 mg (91% yield) of the product as a white solid, mp 125.5–126.5 °C: ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9 H), 4.14 (s, 3 H), 4.17 (s, 3 H), 7.45–7.30 (m, 4 H), 7.65–7.54 (m, 3 H), 7.79–7.74 (m, 1 H); IR ($CHCl_3$, cm^{-1}) 1770, 1460, 1250 (br), 1080, 850 (br); UV ($CHCl_3$) λ 242 (max), 270, 276, 328; MS (CI), *m/e* (rel intensity) 394 (17), 340 (22), 339 (100), 239 (10), 238 (11), 212 (32), 156 (57); exact mass calcd for $C_{22}H_{23}O_4Si$ 393.1396, found 393.1411.

Anal. Calcd for $C_{22}H_{23}O_4Si$: C, 67.15; H, 5.89. Found: C, 66.95; H, 5.83.

2,5-Dihydro-3,4-diphenyl-5-oxo-2-furancarbonitrile (20a). A freeze-degassed solution of 90 mg (0.229 mmol) 12-cyano-9,10-dihydro-9,10-dimethoxy-11-oxo-12-(trimethylsiloxy)-9,10-ethanoanthracene (**19**) and 204 mg (1.14 mmol) of diphenylacetylene in 3 mL of *o*-dichlorobenzene was sealed under vacuum and heated to 220 °C in an oil bath for 72 h. Removal of the solvent gave an orange slurry that provided an NMR spectrum containing a singlet at 0.327 ppm and no singlets at approximately 6 ppm. The crude product mixture was eluted through silica gel with 20% EtOAc/hexanes to give 40 mg (67% yield) of the product as a white solid, mp 164–166.5 °C: ^{1}H NMR ($CDCl_3$) δ 5.995 (s, 1 H), 7.38–7.44 (m, 10 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 67.1, 113.1, 127.7, 127.8, 128.1, 128.4, 128.8, 129.0, 129.3, 129.7, 131.5, 151.2, 169.7; IR ($CHCl_3$, cm^{-1}) 1780, 1450, 1350, 1145, 1070, 690; MS (EI), *m/e* (rel intensity) 262 (12), 261 (73), 249 (16), 233 (14), 216 (17), 215 (13), 207 (27), 204 (39), 189 (15), 180 (15), 179 (100), 177 (32), 105 (91), 94 (26), 89 (13), 77 (45), 51 (30); exact mass calcd for $C_{17}H_{11}NO_2$ 261.0790, found 261.0788. Recrystallization of the product from ether/hexanes gave 33 mg of a white solid, mp 166.5–167.5 °C.

Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.25. Found: C, 77.94; H, 4.33.

2,5-Dihydro-3-phenyl-4-methyl-5-oxo-2-furancarbonitrile (20b). A freeze-degassed solution of 107 mg (0.272 mmol) of 12-cyano-9,10-dihydro-9,10-dimethoxy-11-oxo-12-(trimethylsiloxy)-9,10-ethanoanthracene (**19**) and 0.170 mL (1.36 mmol) of 1-phenyl-1-propyne in 2 mL of chlorobenzene was sealed under vacuum and heated to 220 °C in an oil bath for 48 h. Removal of the solvent gave an orange slurry which was taken up in 0.5 mL of CCl_4 and eluted through silica gel with 20% EtOAc/hexanes to give 40 mg of the product as a colorless oil which partially solidified upon standing (74% yield): ^{1}H NMR ($CDCl_3$) δ 2.19 (d, 3 H, J = 1.8 Hz), 5.88 (q, 2 H, J = 1.8 Hz), 7.50–7.59 (m, 5 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.6, 67.0, 113.3, 125.5, 127.5, 128.7, 129.4, 131.2, 150.7, 171.5; IR ($CHCl_3$, cm^{-1}) 3025, 1780, 1335, 1215, 1055, 690; MS (EI), *m/e* (rel intensity) 200 (8), 199 (57), 154 (15), 145 (55), 117 (47), 116 (78), 115 (100), 89 (16), 77 (21), 75 (12), 65 (13), 64 (15), 63 (37), 62 (13), 58 (28), 52 (13), 51 (92); exact mass calcd for $C_{12}H_9NO_2$ 199.0633, found 199.0623. Recrystallization from ether/hexanes gave 28.5 mg of the product as a white solid, mp 95–95.5 °C, with spectroscopic properties identical with those reported above.

Anal. Calcd for $C_{12}H_9NO_2$: C, 72.35; H, 4.55. Found: C, 72.13; H, 4.48.

2,5-Dihydro-3,4-bis(phenylmethyl)-5-oxo-2-furancarbonitrile (20c). A freeze-degassed solution of 101 mg (0.254 mmol) of 12-cyano-9,10-dihydro-9,10-dimethoxy-11-oxo-12-(trimethylsiloxy)-9,10-ethanoanthracene (**19**) and 0.250 mL (1.27 mmol) of 1,4-diphenyl-2-butyne in 3.5 mL of *p*-xylene was sealed under vacuum and heated to 220 °C in an oil bath for 72 h. Removal of the solvent gave an orange oil which was taken up in 0.5 mL of CCl_4 and eluted through silica gel with 30% Et_2O/hexanes to give 54 mg (73% yield) of the product as a yellow oil: ^{1}H NMR ($CDCl_3$) d 3.65 (d, 1 H, J = 16 Hz), 3.73 (d, 1 H, J = 15 Hz), 3.81 (d, 1 H, J = 15 Hz), 4.12 (d, 1 H, J = 16 Hz), 5.13 (s, 1 H), 7.01–7.08 (m, 2 H), 7.23–7.38 (m, 8 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.8, 32.7, 67.2, 112.8, 127.2, 128.0, 128.6, 128.7, 129.0, 129.2, 129.4, 134.1, 136.4, 155.0, 171.0; IR (neat, cm^{-1}) 1780 (br), 1675, 1600, 1495, 1455, 1035, 750, 700; MS (EI), *m/e* (rel intensity) 289 (8), 244 (8), 217 (9), 205 (11), 128 (11), 115 (12), 108 (15), 92 (10), 91 (100), 78 (13), 77 (18), 65 (35), 63 (11), 51 (32); exact mass calcd for $C_{19}H_{15}NO_2$ 289.1103, found 289.1093.

Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H. 5.23. Found: C, 78.64; H, 5.45.

2-Hydroxy-4,6-diphenylbenzonitrile (31). A freeze-degassed solution of 100 mg (0.254 mmol) of 12-cyano-9,10-dihydro-9,10-dimethoxy-11-oxo-12-(trimethylsiloxy)-9,10-ethanoanthracene (**19**) and 0.139 mL (1.270 mmol) of phenylacetylene in 2.5 mL of *o*-dichlorobenzene was sealed under vacuum and heated to 220 °C for 48 h. Removal of the solvent gave a dark red slurry which was eluted through silica gel with 30% EtOAc/hexanes to give 19 mg (27% yield) of essentially pure product as a red oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.20 (d, 1 H, J = 1.5 Hz), 7.27 (d, 1 H, J = 1.5 Hz), 7.40–7.51 (m, 7 H), 7.58–7.62 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (carbon number, calcd value[16]) 97.4 (C_1, 98.1), 113.2, 116.1, 120.8, 127.1, 128.5, 128.6, 128.7, 128.75, 128.9, 138.0, 138.9, 146.5 (C_6, 146.9), 147.2 (C_4, 147.3), 159.6 (C_2, 159.8); IR ($CHCl_3$, cm^{-1}) 3600 (br), 3250 (br), 2220 (str), 1610, 1410, 910, 700; MS (EI), *m/e* (rel intensity) 272 (17), 271 (100), 243 (26), 242 (37), 241 (17), 215 (22), 122 (32), 121 (29), 120 (13), 113 (11), 109 (15), 108 (33), 106 (42), 95 (18), 94 (28), 81 (13), 77 (19), 75 (11), 63 (22), 51 (46); exact mass calcd for $C_{19}H_{13}NO$ 271.0997, found 271.0992.

Acknowledgment. We thank the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for financial support of this work.

Registry No. **1**, 2395-97-3; **2**, 122949-70-6; **3**, 122949-71-7; **4**, 122949-72-8; **5**, 119622-68-3; **9**, 119622-72-9; **10**, 122967-65-1; **11**, 122967-66-2; **14**, 122949-73-9; **15**, 122967-67-3; **18**, 122949-74-0; **19**, 122949-75-1; **20a**, 122949-76-2; **20b**, 122949-77-3; **20c**, 122949-78-4; **31**, 55249-87-1; dichlorovinylene carbonate, 17994-23-9; 1-lithio-2-phenylacetylene, 4440-01-1; diphenylacetylene, 501-65-5; di-*n*-butylacetylene, 1942-46-7; dimethyl squarate, 5222-73-1; 5-decyne, 1942-46-7; trimethylsilyl cyanide, 7677-24-9; 1-phenyl-1-propyne, 673-32-5; 1,4-diphenyl-2-butyne, 33598-23-1; phenylacetylene, 536-74-3.

Supplementary Material Available: ^{13}C NMR analysis for compounds for which no C,H analysis was obtained (**4**, **10**, **14**, **15**, and **31**) (15 pages). Ordering information is given on any current masthead page.