**Acetophenone.** A mixture of bis(2,2,2-trifluoroethoxy)triphenylphosphorane (12 mmol), benzoic acid (10 mmol), and freshly dried diethyl ether (10 mL) was stirred for 10 min at −60 °C. Into the reaction mixture was added methylmagnesium bromide (31 mmol) in diethyl ether (20 mL), and then the reaction mixture was stirred at −60 °C for 2 h. The whole mixture was poured into water, and then the oily material was extracted with diethyl ether (100 mL). After removal of the solvent, distillation gave acetophenone in a 52% yield.

***trans*-Crotonyl Phenyl Sulfide.** *trans*-Crotonyl alcohol (10 mmol) and benzenethiol (10 mmol) were added to a solution of bis(2,2,2-trifluoroethoxy)triphenylphosphorane (12 mmol) in methylene chloride (20 mL)–diethyl ethher (20 mL). After being stirred for 20 h, the reaction mixture was poured into water, and the oily layer was extracted with diethyl ether (150 mL). The ethereal extract was washed with 5% aqueous sodium hydroxide solution and dried over magnesium sulfate. The solvent was removed, and the formed precipitates ($Ph_3P{=}O$) were removed by filtration. The residual oily material was distilled under vaccum, yielding *trans*-crotonyl phenyl sulfide in an 82% yield.

***N*-Benzylaniline.** A mixture of aniline (10 mmol) and bis-(2,2,2-trifluoroethoxy)triphenylphosphorane (12 mmol) in methylene chloride (20 mL)–diethyl ether (20 mL), which was prepared from triphenylphosphine dibromide (13 mmol) and sodium 2,2,2-trifluoroethoxide (26 mmol) in situ, was cooled at −60 °C. Into the solution was slowly added benzyl alcohol (10 mmol) in freshly dried diethyl ether (10 mL). After being stirred for 1.5 h at that temperature, the solution was allowed to warm to room temperature. The reaction mixture was poured into water, and the ethereal layer was separated and dried over magnesium sulfate. The solvent was then removed, and the residue was distilled in vacuo, giving *N*-benzylaniline in a 71% yield.

***N*-Phenylacetamide.** Acetic acid (10 mmol) was added to a solution of bis(2,2,2-trifluoroethoxy)triphenylphosphorane (12 mmol) at −60 °C, and then aniline (10 mmol) in freshly dried diethyl ether (10 mL) was added to the mixture. After being stirred for 1 h at that temperature, the reaction mixture was worked up as above, giving *N*-phenylacetamide in an 81% yield.

**Registry No.** $Ph_3P(OCH_2CF_3)_2$, 67696-25-7; $Bu_3P(OCH_2CF_3)_2$, 75399-87-0; $(NMe_2)_3P(OCH_2CF_3)_2$, 75399-88-1; *i*-PrCHO, 78-84-2; *n*-$C_5H_{11}CHO$, 66-25-1; *n*-$C_6H_{13}CHO$, 111-71-7; *i*-$PrCH(OCH_2CF_3)_2$, 75399-89-2; *n*-$C_5H_{11}CH(OCH_2CF_3)_2$, 75399-90-5; *n*-$C_6H_{13}CH(OCH_2CF_3)_2$, 75399-91-6; *n*-$C_5H_{11}OH$, 75-41-0; *n*-$C_8H_{17}OH$, 29063-28-3; $PhCH_2OH$, 100-51-6; $PhCH_2CH_2OH$, 60-12-8; $C_6H_{13}CH(Me)OH$, 25339-16-6; PhCH(Me)OH, 98-85-1; cyclohexanol, 108-93-0; borneol, 507-70-0; $PhCO_2H$, 65-85-0; *n*-$C_3H_7CO_2H$, 107-92-6; *n*-$C_4H_9CO_2H$, 109-52-4; *n*-$C_5H_{11}OCH_2CF_3$, 41029-58-7; *n*-$C_8H_{17}OCH_2CF_3$, 67696-27-9; $PhCH_2OCH_2CF_3$, 67696-28-0; $PhCH_2CH_2OCH_2CF_3$, 67696-29-1; $CH_2{=}CHPh$, 100-42-5; $C_6H_{13}CH(Me)OCH_2CF_3$, 67696-31-5; $PhCH(Me)OCH_2CF_3$, 67696-30-4; cyclohexene, 110-83-8; camphene, 79-92-5; $PhCO_2CH_2CF_3$, 1579-72-2; *n*-$C_3H_7CO_2CH_2CF_3$, 371-27-7; *n*-$C_4H_9CO_2CH_2CF_3$, 1651-34-9; $PhCH_2OH$, 100-51-6; *trans*-$CH_3CH{=}CHCH_2OH$, 504-61-0; *cis*-$CH_3CH{=}CHCH_2OH$, 4088-60-2; *trans*-$PhCH{=}CHCH_2OH$, 4407-36-7; $CH_2{=}CHCH(Me)OH$, 598-32-3; *trans*-$CH_3CH{=}CHCO_2H$, 107-93-7; $CH_3CO_2H$, 64-19-7; MeBr, 74-83-9; PhBr, 108-86-1; $PhC(OSiMe_3){=}CH_2$, 13735-81-4; 1-trimethylsiloxycyclohex-1-ene, 6651-36-1; $PhCH_2CH_3$, 100-41-4; $PhCH(CH_3)_2$, 98-82-8; *trans*-$CH_3CH{=}CHCH_2Ph$, 935-00-2; *trans*-$CH_3CH{=}CHCH_2CH_2COPh$, 57542-05-9; *cis*-$CH_3CH{=}CHCH_2CH_2COPh$, 38376-73-7; *trans*-$PhCH{=}CHCH_2Ph$, 3412-44-0; *trans*-$PhCH{=}CHCH_2CH_2COPh$, 28069-36-5; $CH_2{=}CHCH(Me)Ph$, 934-10-1; *trans*-$CH_3CH{=}CHCOPh$, 35845-66-0; PhCOMe, 122-78-1; $PhCOCH_2COPh$, 120-46-7; 2-acetylcyclohexanone, 847-23-7; EtOH, 64-17-5; *n*-PrOH, 71-23-8; PhSH, 108-98-5; $PhCH_2SH$, 100-53-8; BuSH, 109-79-5; EtSPh, 622-38-8; *n*-$PrSCH_2Ph$, 22336-59-0; $PhCH_2SPh$, 831-91-4; $PhCH_2CH_2SPh$, 13865-49-1; $PhCH_2SBu$, 5184-47-4; $PhCH_2CH_2SCH_2Ph$, 34372-24-2; *cis*-$CH_3CH{=}CHCH_2SPh$, 36195-55-8; *trans*-$CH_3CH{=}CHCH_2SPh$, 36195-56-9; *trans*-$CH_3CH{=}CHCH_2SCH_2Ph$, 71638-76-1; *trans*-$CH_3CH{=}CHCH_2SBu$, 3001-22-7; $CH_2{=}CHCH(Me)SPh$, 701-75-7; $CH_2{=}CHCH(Me)SEt$, 71638-77-2; *trans*-$PhCH{=}CHCH_2SPh$, 5848-60-2; *n*-$BuNH_2$, 109-73-9; *n*-$PrNH_2$, 107-10-8; $PhNH_2$, 62-53-3; *n*-$C_8H_{17}NHBu$, 4088-42-0; PhCH(Me)NHPr, 66896-60-4; $PhCH_2NHPh$, 103-32-2; *trans*-$CH_3CH{=}CHCH_2NHPh$, 35755-80-7; $CH_2{=}CHCH(Me)NHPh$, 15645-60-0; $CH_3CONHBu$, 1119-49-9; $CH_3CONHPh$, 103-84-4; PhCONHPr, 10546-70-0; PhCONHPh, 93-98-1; *trans*-$CH_3CH{=}CHCONHBu$, 75399-92-7; sodium 2,2,2-trifluoroethoxide, 420-87-1; 2,2,2-trifluoroethanol, 75-89-8; triphenylphosphine, 603-35-0; tri-*n*-butylphosphine, 998-40-3; tris(dimethylamino)phosphine, 1608-26-0.

# Synthesis of Substituted Quinones. 2,5-Disubstituted 1,4-Benzoquinones

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Synthetic methodology is presented which allows the facile synthesis of 2,5-disubstituted 1,4-benzoquinones. This involves the initial 1,2-addition of an alkynyllithium reagent to one of the carbonyl groups of 2,5-diethoxy- or 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone. This is followed by an analogous addition of an alkyl-, aryl-, or alkynyllithium to the remaining carbonyl to give a cyclohexa-2,5-diene-1,4-diol derivative. Acid hydrolysis of these adducts results in the 2,5-dialkylated 1,4-benzoquinones. This methodology was employed to prepare 7-chloro-6-methyl-1,2,5,8-tetrahydro-3*H*-pyrrolo[1,2-*a*]indole-5,8-dione (14), a compound having the basic ring system of the mitomycin antineoplastic antibiotics.

In a preliminary paper, we described new methodology which allowed the facile synthesis of 2,5-disubstituted quinones where one of the substituents is an alkynyl group and the other can be an alkynyl, alkenyl, alkyl, or aryl substituent.[1] In the present paper, we give the full details of this methodology and illustrate its utility in the synthesis of 7-chloro-6-methyl-1,2,5,8-tetrahydro-3*H*-pyrrolo[1,2-*a*]indole-5,8-dione (14), a compound having the basic ring system of the mitomycin antineoplastic antibiotics.

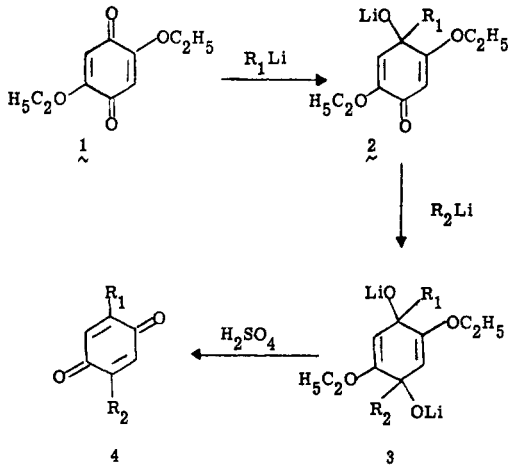
The rationale for developing a synthetic route to 2,5-disubstituted 1,4-benzoquinones stems from the fact that a wide variety of naturally occurring quinones exist[2] in which the nucleus is functionalized in this manner. However, no general methodology currently allows the facile construction of such structural features. Described here is a method which provides a simple solution to this problem. Specifically, we have observed that organolithium reagents undergo 1,2-addition to the carbonyl groups of 2,5-diethoxy-1,4-benzoquinone (1). Acid hy-

(1) H. W. Moore, Y. L. Sing, and R. S. Sidhu, *J. Org. Chem.*, **42**, 3321 (1977).

(2) R. H. Thomson, "Naturally Occurring Quinones", Academic Press, New York, 1977.

0022-3263/80/1945-5057$01.00/0 

Scheme I



| | $R_1$ | $R_2$ | Yield |
|---|---|---|---|
| a | $-C_6H_5$ | $-C_6H_5$ | 62 |
| b | $-CH_3$ | $-CH_3$ | 52 |
| c | $-\equiv-CH_2OCH_2C_6H_5$ | $-\equiv-CH_2OCH_2C_6H_5$ | 56 |
| d | $-\equiv-CH_2OCH_2C_6H_5$ | $-C_6H_5$ | 60 |

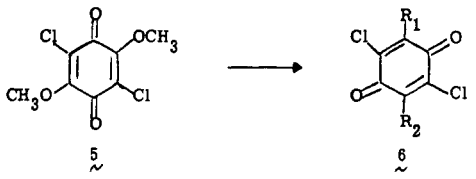
| | $R_1$ | $R_2$ | Yield |
|---|---|---|---|
| a | $-C_6H_5$ | $-C_6H_5$ | 62 |
| b | $-CH_3$ | $-CH_3$ | 52 |
| c | $-\equiv-CH_2OCH_2C_6H_5$ | $-\equiv-CH_2OCH_2C_6H_5$ | 56 |
| d | $-\equiv-CH_2OCH_2C_6H_5$ | $-C_6H_5$ | 60 |

drolysis of the resulting adducts, **3a–d**, gives the corresponding 2,5-disubstituted 1,4-benzoquinones **4a–d** in respectable yields. It is noteworthy that the total transformation can be accomplished without isolation of the intermediate products. Significantly, this technique can be employed to make unsymmetrically substituted quinones when the first organometallic used ($R_1Li$) is an alkynyllithium reagent. On the other hand, if $R_1Li$ is a more reactive alkyl or aryl reagent, the predominant product is the symmetrically substituted product.[3] However, the facts that an alkynyl group is easily introduced initially and that this can be followed by an alkyl or aryl group add synthetic versatility since alkynes are easily converted to a wide variety of other functionalities. Thus, a potentially general route to symmetrical as well as unsymmetrically substituted 1,4-benzoquinones is at hand.

The general procedure involves treatment of a diethyl ether/THF (1:1) solution of the quinone with the organolithium reagents (Scheme I). The reaction is accomplished at −22 to 0 °C, depending upon the specific example. After approximately 8 h the reaction mixture is quenched with ammonium chloride. The solvent is then reduced in volume and the residue dissolved in a mixture of glyme and concentrated $H_2SO_4$ which accomplishes the enol ether hydrolyses. The resulting quinones were then isolated by column chromatography on silica gel.

It was of interest to extend the scope of this reaction to include more highly substituted quinones, particularly those having halogens at the 3- and 6-positions. In certain situations quinones such as these provide a synthetic advantage, since halogen substituents on the quinone nucleus

Scheme II



| | $R_1$ | $R_2$ | Yield |
|---|---|---|---|
| a | $C_6H_5$ | $C_6H_5$ | 50 |
| b | $C_6H_4$-p-$OCH_3$ | $C_6H_4$-p-$OCH_3$ | 50 |
| c | $CH_3$ | $CH_3$ | 64 |
| d | $-\equiv-CH_2$-O-$CH_2C_6H_5$ | $CH_3$ | 55 |
| e | $-\equiv-C_6H_5$ | $CH_3$ | 61 |
| f | $-\equiv-CH_2OH$ | $CH_3$ | 65 |
| g | $-\equiv-(CH_2)_3OH$ | $CH_3$ | 60 |
| h | $-\equiv-CH_2$-O-$CH_2C_6H_5$ | $-\equiv-CH_2$-O-$CH_2C_6H_5$ | 50 |
| i | $-\equiv-C_6H_5$ | $-\equiv-C_6H_5$ | 63 |
| j | $-\equiv-CH_2$-$OCH_3$ | $-\equiv-CH_2$-$OCH_3$ | 46 |

| | $R_1$ | $R_2$ | Yield |
|---|---|---|---|
| a | $C_6H_5$ | $C_6H_5$ | 50 |
| b | $C_6H_4$-p-$OCH_3$ | $C_6H_4$-p-$OCH_3$ | 50 |
| c | $CH_3$ | $CH_3$ | 64 |
| d | $-\equiv-CH_2$-O-$CH_2C_6H_5$ | $CH_3$ | 55 |
| e | $-\equiv-CH_2$-O-$CH_2C_6H_5$ | $CH_3$ | 61 |
| f | $-\equiv-C_6H_5$ | $CH_3$ | 65 |
| g | $-\equiv-(CH_2)_3OH$ | $CH_3$ | 60 |
| h | $-\equiv-CH_2$-O-$CH_2C_6H_5$ | $-\equiv-CH_2$-O-$CH_2C_6H_5$ | 50 |
| i | $-\equiv-C_6H_5$ | $-\equiv-C_6H_5$ | 63 |
| j | $-\equiv-CH_2$-$OCH_3$ | $-\equiv-CH_2$-$OCH_3$ | 46 |

are easily replaced by a variety of nucleophiles. For example, hydroxyquinones can be obtained from the corresponding chloroquinones under hydrolytic conditions, and a number of natural products contain the 2,5-dialkyl- (or -aryl-) 3,6-dihydroxy-1,4-benzoquinone moiety. A specific example is polyporic acid, 2,5-dihydroxy-3,6-diphenyl-1,4-benzoquinone, which has been obtained by hydrolysis of the corresponding 2,5-dichloroquinone **6a**.[4] It was, in fact, found that when 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone (**5**) was subjected to the methodology outlined above, the corresponding 2,5-dichloro-3,6-disubstituted-1,4-benzoquinones (**6a–j**) were obtained (Scheme II), and the isolated yields range from 46% to 60%.

The methodology outlined here would appear to be superior in terms of experimental procedures and product yields as compared to other methods of accomplishing analogous transformations. As a comparison, 2,5-dichloro-3-(3-hydroxy-1-propenyl)-6-methyl-1,4-benzoquinone (**7**) was synthesized in 9% overall yield in seven steps by starting with 2,5-dichloro-3-methyl-1,4-benzoquinone (Scheme III) while construction of the analogous alkynyl derivative, **6f**, required no intermediate isolation steps and was obtained in 65% yield (Scheme II).

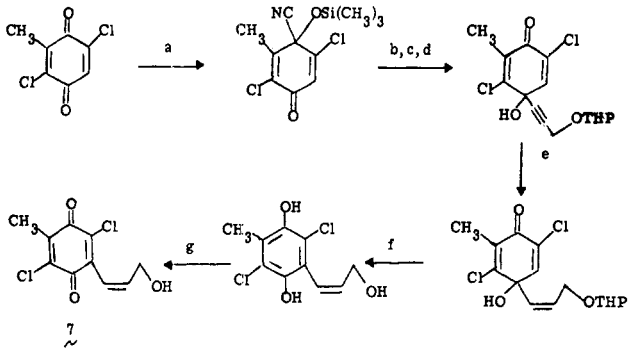
One of our fundamental objectives in initiating this project was to develop a new synthetic route to 2-azido-3-alkenyl-1,4-benzoquinones since we have previously shown that this class of azidoquinones undergoes facile thermolytic ring closure to an important class of heterocyclic quinones, indole-5,8-diones (indoloquinones).[5] The utilization of this indoloquinone synthesis has previously

(3) Mono-1,2-additions of organolithium reagents to quinones have recently been reported. See A. Fischer and G. N. Henderson, *Tetrahedron Lett.*, 701 (1980).

(4) R. J. Wikholm and H. W. Moore, *J. Am. Chem. Soc.*, **94**, 6152 (1972).

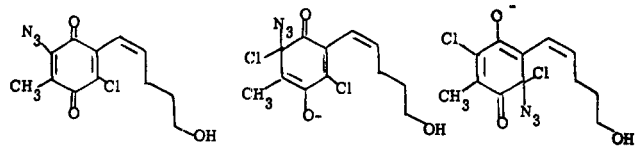
(5) P. Germeraad and H. W. Moore, *J. Org. Chem.*, **39**, 774 (1974).

Scheme III[a]



[a] (a) $(CH_3)_3SiCN$, $Ph_3P$, 0 °C; (b) Li—≡—$CH_2OTHP$, $(C_2H_5)_2O$, THF, −22 °C; (c) $(CH_3)_3SiCl$; (d) AgF, THF, $H_2O$; (e) $H_2$, $Pd/BaSO_4$, $C_5H_5N$, $CH_3CO_2C_2H_5$; (f) $BF_3 \cdot (C_2H_5)_2O$; (g) $FeCl_3$, $CHCl_3$, $H_2O$.

been limited by the fact that better and more versatile syntheses of alkenyl-1,4-benzoquinones were needed. We are now pleased to report that the alkynyl-1,4-benzoquinones described here are easily converted to alkenyl analogues by reductive methods. Furthermore, in the 2,5-dichloro series, **6**, the corresponding azidoquinones are easily prepared, and these in turn can be converted to the corresponding indoloquinones upon thermolysis. To specifically illustrate this methodology, 7-chloro-6-methyl-1,2,5,8-tetrahydro-3*H*-pyrrolo[1,2-*a*]indole-5,8-dione (**14**), an indoloquinone having the basic ring system of the mitomycins,[6] was prepared as outlined in Scheme IV. The most critical step in this sequence of reactions is the conversion of **11** to the azidoquinone **12**. This was conveniently accomplished in 70% yield when a toluene solution of **11** (−78 °C) was treated with potassium azide in the presence of dibenzo-18-crown-6. However, when more standard conditions are employed such as treatment of an ethanolic solution of **11** with sodium azide at 0 °C, an 80% yield of the regioisomer **8** was obtained. The



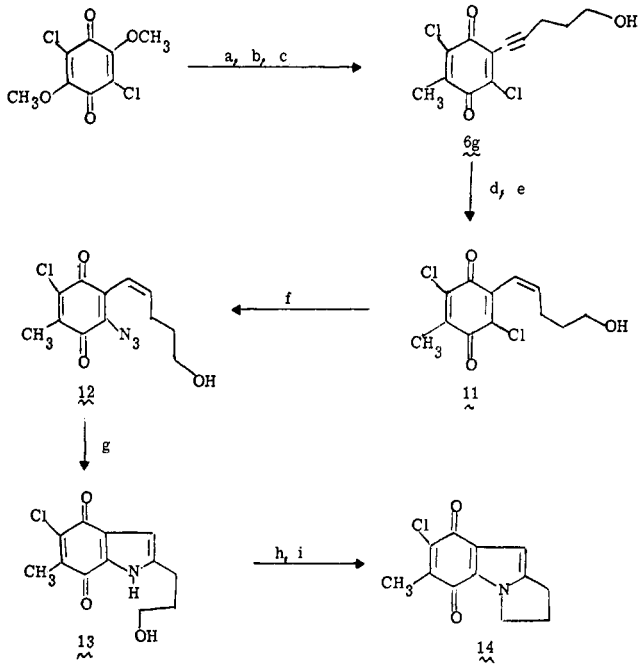
reason for this selectivity is not obvious. Indeed, we anticipated **12** to be formed under both reaction conditions described since the intermediate enolate **10** should be more stable than **9**. Presumably, ethanol solvation of the enolate center of **9** is more important than analogous interactions for **10**, and thus, the aprotic conditions favor **12**, while the protic conditions favor **8**.

The azidoquinone **12** smoothly ring closed to the indoloquinone **13** (80%) in refluxing benzene. This was converted to the mesylate (85%) which underwent intramolecular alkylation to give **14** (68%) upon treatment with potassium *tert*-butoxide in THF. This last reaction involves the highly colored (purple) ambident anion, and the reaction course is conveniently followed by the disappearance of this color. Only the product of N-alkylation, i.e., **14**, was isolated. However, it is possible that products of C-alkylation were also formed and were among the minor products of the reaction.

In summary, the synthetic methodology outlined in this paper provides one of the simplest routes to 2,5-dialkylated

(6) R. W. Franck, *Prog. Chem. of Nat. Prod.*, 1, 38 (1979).

Scheme IV[a]



[a] (a) Li-≡—$(CH_2)_3OTHP$/ether, −20 °C; (b) $CH_3Li$, −20 °C; (c) $H_2SO_4$; (d) $H_2$, $Pd/BaSO_4$ (81% yield); (e) $FeCl_3$ (67% yield); (f) $KN_3$, dibenzo-18-crown-6-toluene, −78 °C (70% yield); (g) Δ (81 °C), benzene (80 % yield); (h) MsCl/$Et_3N$, $CH_2Cl_2$, 0 °C, 1 h (85% yield); (i) *t*-BuOK/THF (68% yield).

1,4-benzoquinones and complements recent advances directed toward the monoalkylation and arylation of the quinone nucleus. Particularly noteworthy in this regard are the utilization of trimethylsilyl cyanide ($Me_3SiCN$) protected quinones,[7] the use of lithium salts of 1-bromo-3,3,6,6-tetramethoxy-1,4-cyclohexadiene (a latent quinone carbanion),[8] the reactions of quinones or protected bromoquinols with π-allylnickel complexes,[9] the utilization of monoketals of quinones,[10] the use of 1,4-dimethoxynaphthyllithium reagents,[11] and the reactions of quinone with alkylboranes.[12]

## Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer 137 sodium chloride spectrophotometer, a Beckman AccuLab 2, and a Perkin-Elmer 283. In the descriptions of the infrared spectra the following abbreviations were used: s, strong absorption; m, medium absorption; w, weak absorption. Infrared absorptions are reported in reciprocal centimeters with polystyrene as the external standard. Nuclear magnetic resonance spectra were obtained on a Varian Associates A 56/60 analytical spectrophotometer, a Varian EM-360 NMR spectrophotometer, and a Bruker WH-90 Fourier transform spectrophotometer. In the descriptions of the NMR spectra the following abbreviations were used: s, singlet; d,

(7) D. A. Evans, J. M. Hoffman, and L. K. Truesdale, *J. Am. Chem. Soc.*, **95**, 5822 (1973).
(8) M. J. Manning, R. W. Raynolds, and J. S. Swenton, *J. Am. Chem. Soc.*, **98**, 5008 (1976).
(9) L. S. Hegedus, E. L. Waterman, and J. Catlin, *J. Am. Chem. Soc.*, **94**, 7155 (1972); K. Sato, S. Inoue, and K. Saito, *J. Chem. Soc., Perkin Trans. 1*, 2289 (1973).
(10) A. McKillop, D. H. Perry, M. Edwards, S. Antus, L. Farkas, M. Nogradi, and E. C. Taylor, *J. Org. Chem.*, **41**, 282 (1976).
(11) C. D. Snyder, W. E. Bondinell, and H. Rapoport, *J. Org. Chem.*, **36**, 3951 (1971).
(12) M. F. Hawthorne and M. Reintjes, *J. Am. Chem. Soc.*, **87**, 4585 (1965); K. Marayama, K. Saimoto, and Y. Yamamoto, *J. Org. Chem.*, **43**, 4895 (1978).

doublet; t, triplet; q, quartet; m, multiplet; br, broad. Chemical shifts in $^1H$ NMR and $^{13}C$ NMR spectra were reported on the $\delta$ scale with tetramethylsilane as the internal standard. Mass spectra were obtained on a Du Pont 21-492B double-focussing spectrometer at Caltech Analytical Facility, Pasadena, CA. Elemental analyses were performed by Robertson Laboratory and Galbraith Laboratories, Inc.

Anhydrous solvents [tetrahydrofuran (THF), diethyl ether, benzene, hexane] were distilled over lithium aluminum hydride (ca. 2 g/L of solvent) under a nitrogen atmosphere. For moisture-sensitive reaction, flasks were flame dried with a Bunsen burner while being flushed with dry nitrogen to remove moisture.

Commercial organolithium reagents were titrated according to the double-titration method described by Whitesides, Casey, and Krieger.[13]

Air/moisture-sensitive solutions were transferred by using a double-tipped-needle technique which has been described by Brown, Kramer, Levey, and Midland.[14]

Emmerie–Engel reagent[15] (a solution of 0.125 g of $\alpha,\alpha$-bipyridine and 0.05 g of ferric chloride hexahydrate in 25 mL of 95% aqueous ethanol, kept below 0 °C) was used as a spot test for hydroquinones. This reagent will react with a hydroquinone and change from light yellow to pink. The sensitivity is very high, and it is thus particularly useful where a reaction is followed by thin-layer chromatography (TLC) in which a starting material or the expected product is a hydroquinone.

Leucomethylene Blue[16] (a very light blue solution of a mixture of methylene blue, acetic acid, and zinc dust prepared shortly before its use) was used as a spot test for quinones. This reagent is easily oxidized by most quinones and will turn from light blue to deep blue. The sensitivity is high for most quinones but is low or naught for hydroxy- or aminoquinones.

**2,5-Diphenyl-1,4-benzoquinone (4a).** A 1-L, round-bottomed, one-necked flask was flamed with a Bunsen burner while being flushed with dry nitrogen to remove moisture. 2,5-Diethoxy-1,4-benzoquinone (1; 500 mg, 2.55 mmol) and 700 mL of anhydrous diethyl ether were placed in the reaction flask under an argon atmosphere, and the reaction flask was then equipped with a rubber septum. The mixture was cooled to 0 °C, and 7.1 mL (7.65 mmol) of phenyllithium (1.09 M in 70:30 benzene–ether) was added slowly. The color of the solution turned from yellow to green and then to light yellow and milky. Stirring was continued at 0 °C for 10 h. The reaction was quenched with aqueous ammonium chloride and then washed with water. Two-thirds of the solvent was removed by evaporation, and 1 mL of concentrated sulfuric acid was added to the residual solution. After being stirred at room temperature for 2 h, the solution became yellow. TLC (silica gel, benzene) showed that hydrolysis was complete. Water was added and the resulting mixture extracted with diethyl ether. The combined ethereal extracts were washed with water and saturated aqueous sodium bicarbonate and then dried over anhydrous magnesium sulfate. Removal of the solvent by evaporation gave yellow plates. After the product was washed with hexanes, 360 mg of **4a** as yellow plates was obtained, mp 211–213 °C. After the solvent was evaporated, column chromatography of the yellow residue gave an additional 50 mg of **4a** to bring the total yield to 62%. Further purification by recrystallizing from acetic acid gave **4a** as yellow plates: mp 217–218 °C (lit.[17] mp 214 °C); IR (Nujol) 1602 (m), 1640 $cm^{-1}$ (s); NMR ($CDCl_3$) $\delta$ 7.01 (s, 1 H), 7.52 (s, 5 H).

**2,5-Dimethyl-1,4-benzoquinone (4b).** To a solution of 2 g (10.2 mmol) of 2,5-diethoxy-1,4-benzoquinone (1) in 500 mL of anhydrous diethyl ether at 0 °C under an argon atmosphere was slowly added 16 mL (22.4 mmol) of methyllithium (1.4 M in hexane). After stirring for 8 h, the resulting white-gray mixture was quenched with aqueous ammonium chloride, washed with water, and then dried over magnesium sulfate. The solvent was evaporated at reduced pressure and replaced by 30 mL of glyme. Concentrated sulfuric acid (1 mL) was added to this solution to effect the hydrolysis of the enol ether. After being stirred at room temperature overnight, the solution became yellow-brown, and TLC (silica gel, 1:1 diethyl ether/hexanes) showed that reaction was complete. The reaction mixture was then diluted with 100 mL of chloroform and washed with water until the aqueous layer was neutral. The aqueous layer was extracted with chloroform. The combined organic layer was dried ($MgSO_4$) and the solvent removed to yield a yellow-brown solid. This was purified by column chromatography (silica gel, 1:1 diethyl ether/hexanes) to give 722 mg (52%) of **4b** as yellow crystals: mp 123–124 °C (authentic sample, mp 124–125 °C); IR (Nujol) 1662 (s), 1642 (s), 1613 $cm^{-1}$ (s); NMR ($CDCl_3$) $\delta$ 1.97 (d, $J$ = 1.6 Hz, 3 H), 6.67 (q, $J$ = 1.6 Hz, 1 H).

**2,5-Bis[3-(benzyloxy)-1-propynyl]-1,4-benzoquinone (4c).** To a solution of 12.28 g (84.08 mmol) of 3-(benzyloxy)-1-propyne in 400 mL of freshly distilled (from $LiAlH_4$) tetrahydrofuran at dry ice–acetone bath temperature was added 33 mL (75.9 mmol) of *n*-butyllithium (2.3 M in hexane). After the addition was finished, the mixture was stirred at −22 °C for 8 h. The reaction was quenched with aqueous ammonium chloride and then washed with water. Two-thirds of the solvent was removed by evaporation, and 1 mL of concentrated sulfuric acid was added. After being stirred at room temperature for 2 h, the solution became yellow and TLC (silica gel, benzene) showed that hydrolysis was complete. Water was added and the resulting mixture extracted with diethyl ether. The combined ethereal extracts were washed with water and saturated aqueous sodium bicarbonate and then dried over anhydrous magnesium sulfate. Removal of solvent gave a brown-yellow solid. Recrystallization from 95% aqueous ethanol gave 5.7 g (56%) of **4c** as golden plates: mp 70–72 °C; IR (Nujol) 2215 (w), 1650 (s), 1570 $cm^{-1}$ (m); NMR ($CDCl_3$) $\delta$ 4.33 (s, 2 H), 4.53 (s, 2 H), 6.97 (s, 1 H), 7.40 (s, 5 H).

Anal. Calcd for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.82; H, 5.20.

**2-[3-(Benzyloxy)-1-propynyl]-5-phenyl-1,4-benzoquinone (4d).** To a solution of 4.44 g (30.36 mmol) of 3-(benzyloxy)-1-propyne in 400 mL of freshly distilled (from $LiAlH_4$) tetrahydrofuran at dry ice–acetone bath temperature was added 12 mL (27.6 mmol) of *n*-butyllithium (2.3 M in hexane). After the addition was completed, stirring was continued at −78 °C for 2 h. By use of a double-tipped needle, this alkynyllithium solution was added over a 1-h period to a solution of 4.87 g (24.84 mmol) of 2,5-diethoxy-1,4-benzoquinone (1) in 450 mL of anhydrous diethyl ether which was cooled at −22 °C under an argon atmosphere. The solution became very light green-yellow and milky. The mixture was stirred at −22 °C for 8 h. To this reaction mixture was added slowly 40 mL (41.4 mmol) of phenyllithium (1.09 M in 70:30 benzene–diethyl ether). The solution changed to light brown with the formation of a white precipitate in 15 min. Further stirring at −22 °C was continued for an additional 8 h. The reaction was quenched with aqueous ammonium chloride and then washed with water. Two-thirds of the solvent was removed, and 1 mL of concentrated sulfuric acid was added to this reaction mixture. After being stirred at room temperature for 2 h, the solution became yellow, and TLC (silica gel, benzene) showed that hydrolysis was complete. Water was added, and the resulting mixture was extracted with diethyl ether. The combined ethereal extract was washed with water and saturated aqueous sodium bicarbonate and then dried over magnesium sulfate. Removal of solvent gave a brown-yellow solid, which was recrystallized from 95% aqueous ethanol to give 4.89 g (60%) of **4d** as golden plates: mp 96–97.5 °C; IR (Nujol) 2210 (w), 1657 (s), 1645 (s), 1597 (m), 1585 $cm^{-1}$ (m); NMR ($CDCl_3$) $\delta$ 4.37 (s, 2 H), 4.70 (s, 2 H), 6.97 (s, 1 H), 7.03 (s, 1 H), 7.43 (s, 5 H), 7.50 (s, 5 H).

Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.73; H, 4.95.

**2,5-Dichloro-3,6-diphenyl-1,4-benzoquinone (6a).** To a solution of 237 mg (1 mmol) of 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone (**5**) in 180 mL of anhydrous diethyl ether at 0 °C under an argon atmosphere was added 2.0 mL (2.18 mmol) of phenyllithium (1.09 M) over a 5-min period. After being stirred at −20 °C for 8 h, the resulting milky solution was quenched with aqueous ammonium chloride, washed with water, and then dried

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over anhydrous magnesium sulfate. The solvent was removed at reduced pressure and replaced by 10 mL of glyme. Concentrated sulfuric acid (1 mL) was added to this solution to effect the hydrolysis of the enol ether. After being stirred at room temperature overnight, the solution became brown-yellow, and TLC (silica gel, benzene) showed that hydrolysis was complete. The reaction mixture was then diluted with 100 mL of chloroform and washed with water until the aqueous layer was neutral. The combined aqueous layer was extracted with chloroform. The combined organic extract was dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a yellow solid, which was recrystallized from propanol to give 180 mg (50%) of **6a** as yellow crystals: mp 208–211 °C (lit.[18] mp 209–210 °C); NMR ($CDCl_3$) $\delta$ 7.35–7.67 (m).

**2,5-Dichloro-3,6-Bis(4-methoxyphenyl)-1,4-benzoquinone (6b).** To a solution of 561 mg (3 mmol) of 4-bromoanisole in 40 mL of anhydrous diethyl ether at 0 °C under an argon atmosphere was added 2 mL (4 mmol) of *n*-butyllithium (2.0 M in hexane). The solution was stirred at room temperature for 1 h. By means of a double-tipped needle, the aryllithium solution was added to a solution of 200 mg (0.84 mmol) of 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone (**5**) in 80 mL of anhydrous diethyl ether at 0 °C under an argon atmosphere. After being stirred at 0 °C for 5 h, the resulting pale green-yellow and milky solution was quenched with aqueous ammonium chloride, washed with water, and then dried over anhydrous magnesium sulfate. The solvent was evaporated at reduced pressure and replaced by 10 mL of glyme. Concentrated sulfuric acid (1 mL) was added to this solution to effect the hydrolysis of the enol ether. After being stirred at room temperature overnight, the solution became brown-yellow, and TLC (silica gel, benzene) showed that hydrolysis was complete. The reaction mixture was then diluted with 100 mL of chloroform and washed with water until the aqueous layer was neutral. The combined aqueous layer was extracted with chloroform. This chloroform extraction was combined with the organic layer and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a brown solid, which was purified by column chromatography (silica gel, chloroform) and recrystallized from ethanol–chloroform to give 164 mg (50%) of **6b** as brown crystals: mp 250–253 °C (lit.[19] mp 258–259 °C); NMR ($CDCl_3$) $\delta$ 3.77 (s, 3 H), 7.06 (d, $J$ = 8 Hz, 2 H), 7.44 (d, $J$ = 8 Hz, 2 H).

**2,5-Dichloro-3,6-dimethyl-1,4-benzoquinone (6c).** To a solution of 1 g (4.22 mmol) of 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone (**5**) in 800 mL of anhydrous diethyl ether at 0 °C was added 9 mL (12.6 mmol) of methyllithium (1.4 M in hexane). The solution turned light yellow-white and milky in appearance. After the addition was complete, stirring was continued, and the reaction mixture was maintained at 0 °C for 10 h. The reaction was then quenched with aqueous ammonium chloride and the organic layer washed with water. The solvent was removed by evaporation to give a crude material, which was dissolved in a mixture of 50 mL of glyme and 2 mL of sulfuric acid. After being stirred at room temperature for 2 h, the solution became brown-yellow, and TLC (silica gel, benzene) showed hydrolysis was complete. Water was added and the resulting mixture extracted with ether. The combined ethereal extracts were washed with water and saturated aqueous sodium bicarbonate and then dried over magnesium sulfate. Removal of solvent gave a yellow solid, which was purified by column chromatography (silica gel, 1:1 benzene/hexanes) and recrystallized from 95% aqueous ethanol to give 550 mg (64%) of **6c** as yellow plates: mp 178–179 °C (lit.[20] 176–177 °C); IR (Nujol) 1664 (s), 1605 $cm^{-1}$ (m); NMR ($CDCl_3$) $\delta$ 2.18 (s).

**3-[3-(Benzyloxy)-1-propynyl]-2,5-dichloro-6-methyl-1,4-benzoquinone (6d).** To a solution of 7.45 g (51 mmol) of 3-(benzyloxy)-1-propyne in 850 mL of anhydrous THF (distilled over $LiAlH_4$) at −78 °C under an argon atmosphere was added 36.4 mL (51 mmol) of methyllithium (1.4 M in hexane) in 10 min. The solution was stirred at −78 °C for 2 h. By means of a double-tipped needle, the alkynyllithium solution was added over a 1-h period to a solution of 12 g (51 mmol) of 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone (**5**) in 1000 mL of anhydrous diethyl ether at 0 °C under an argon atmosphere. After being stirred at −20 °C for 5 h, the solution became brown. To this solution was added 38.6 mL (54 mmol) of methyllithium (1.4 M in hexane) in 10 min, and a white precipitate was observed immediately. After further stirring at −20 °C for 8 h, the resulting brown and milky solution was quenched with aqueous ammonium chloride, washed with water, and then dried over anhydrous magnesium sulfate. The solvent was removed at reduced pressure and replaced by 100 mL of glyme. Concentrated sulfuric acid (4 mL) was added to this solution to effect the hydrolysis of the enol ether. After being stirred at room temperature overnight, the solution became brown-yellow, and TLC (silica gel, 1:2 benzene/hexanes) showed that hydrolysis was complete. The reaction mixture was then diluted with 200 mL of chloroform and washed with water until the aqueous layer was neutral. The combined aqueous layer was extracted with chloroform. This combined organic layer was dried over anhydrous magnesium sulfate. Removal of the solvent at reduced pressure gave 11.11 g (65%) of **6d** as a yellow-brown solid which was purified by column chromatography (silica gel, 1:2 benzene/hexanes) and recrystallized from ethanol to give 9.4 g (55%) of **6d** as yellow leaflets: mp 93–94 °C; IR (Nujol) 2270 (w), 1680 (s), 1670 (s), 1570 $cm^{-1}$ (m); NMR ($CDCl_3$) $\delta$ 2.18 (s, 3 H), 4.40 (s, 2 H), 4.60 (s, 2 H), 7.45 (s, 5 H).

Anal. Calcd for $C_{17}H_{12}Cl_2O_3$: C, 60.91; H, 3.61; Cl, 21.16. Found: C, 60.95; H, 3.74; Cl, 21.19.

**2,5-Dichloro-3-methyl-6-(phenylethynyl)-1,4-benzoquinone (6e).** To a solution of 0.86 g (8.44 mmol) of phenylacetylene in 350 mL of anhydrous tetrahydrofuran (distilled over $LiAlH_4$) at −78 °C under an argon atmosphere was added 5.3 mL (8.44 mmol) of methyllithium (1.6 M in hexane) in 5 min. The reaction was stirred at −78 °C for 3 h. By means of a double-tipped needle, the alkynyllithium solution was added over a 5-h period to a solution of 2.0 g (8.44 mmol) of 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone (**5**) in 600 mL of anhydrous diethyl ether at 0 °C under an argon atmosphere. After being stirred at −20 °C for 5 h, the solution became red-brown and homogeneous. To this solution, 7.9 mL (12.66 mmol) of methyllithium (1.6 M in hexane) was added in 5 min, and a bright yellow precipitate was observed immediately. After being stirred further at −20 °C for 8 h, the resulting light yellow and milky solution was quenched with aqueous ammonium chloride, washed with water, and then dried over anhydrous magnesium sulfate. The solvent was evaporated at reduced pressure and replaced by 60 mL of glyme. Concentrated sulfuric acid (6 mL) was added to this solution to effect the hydrolysis of the enol ether. After being stirred at room temperature overnight, the solution became brown-yellow, and TLC (silica gel, benzene) showed that hydrolysis was complete. The reaction mixture was diluted with 200 mL of chloroform and then washed with water until the aqueous layer was neutral. The aqueous layer was extracted with chloroform. The combined organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave 2.08 g of a yellow solid which was recrystallized from ethanol to give **6e** as yellow powder-like crystals (61%): mp 153–154 °C dec; IR (Nujol) 2208 (m), 1688 (s), 1680 (s), 1676 (s), 1667 (s), 1598 (m), 1583 $cm^{-1}$ (s); $^1H$ NMR ($CDCl_3$) $\delta$ 2.22 (s, 3 H), 7.37–7.87 (m, 5 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 75.69, 81.78, 110.58, 121.50, 128.74, 129.36, 130.26, 132.65, 140.69, 143.04, 143.17, 173.93, 177.12.

Anal. Calcd for $C_{15}H_8Cl_2O_2$: C, 61.88; H, 2.77; Cl, 24.36. Found: C, 62.14; H, 2.87.

**2,5-Dichloro-3-(3-dihydroxy-1-propynyl)-6-methyl-1,4-benzoquinone (6f).** To a solution of 1.77 g (12.66 mmol) of 3-(2-tetrahydropyranyloxy)-1-propyne in 30 mL of anhydrous THF (distilled over $LiAlH_4$) at −78 °C under an argon atmosphere was added 8.5 mL (12.66 mmol) of methyllithium (1.4 M in hexane) in 5 min. The solution was stirred at −78 °C for 3 h. By means of a double-tipped needle, the alkynyllithium solution was added over 0.5 h to a solution of 3 g (12.66 mmol) of 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone (**5**) in 600 mL anhydrous diethyl ether at 0 °C under an argon atmosphere. After being stirred at 0 °C for 3 h, the solution became light yellow-brown and milky. To this solution was added 8.5 mL (12.66 mmol) of methyllithium (1.4 M in hexane) in 5 min. After further stirring of the mixture at −20 °C for 8 h, the resulting yellow and milky solution was quenched with aqueous ammonium chloride, washed

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(19) B. F. Cain, *J. Chem. Soc.*, 356 (1963).
(20) H. Muller and H. Linde, *J. Prakt. Chem.*, 4(4), 69 (1956).

with water, and then dried over anhydrous magnesium sulfate. The solvent was evaporated at reduced pressure and replaced by 60 mL of glyme. Concentrated sulfuric acid (6 mL) was added to this solution to effect the hydrolysis of the enol ether. After the mixture was stirred at room temperature for 1 h, TLC (silica gel, 5:1 chloroform/ethyl acetate) showed that hydrolysis was completed. The reaction mixture was then diluted with 200 mL of chloroform and washed with water until the aqueous layer was neutral. The combined aqueous layer was extracted with chloroform. This chloroform extraction was combined with the organic layer and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a brown-yellow solid, which was purified by preparative TLC (silica gel, 1:5 ethyl acetate/chloroform) to give 2.01 g (65%) of **6f** as yellow crystals: mp 122–123 °C dec; IR (Nujol) 3330 (m, br), 2227 (w), 1690 (s), 1682 (s), 1679 (s), 1670 (s), 1588 $cm^{-1}$ (m); NMR ($CDCl_3$) $\delta$ 2.20 (s, 3 H), 4.54 (s, 2 H); mol wt calcd for $C_{16}H_6Cl_2O_3$ 243.9695, found 243.972.

**2,5-Dichloro-3-(5-hydroxy-1-pentynyl)-6-methyl-1,4-benzoquinone (6g).** To a solution of 2.34 g (13.93 mmol) of 5-(2-tetrahydropyranyloxy)-1-pentyne in 50 mL of anhydrous diethyl ether at −78 °C under an argon atmosphere was added 9 mL (13.29 mmol) of methyllithium (1.5 M in hexane) in 5 min. The solution was stirred at 0 °C for 0.5 h. By means of a double-tipped needle, the alkynyllithium solution was added over 0.5 h to a solution of 3 g (12.66 mmol) of 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone (**5**) in 900 mL of anhydrous diethyl ether at 0 °C under an argon atmosphere. After this milky solution was stirred at −20 °C for 8 h, 9 mL (13.29 mmol) of methyllithium (1.5 M in hexane) was added in 5 min. After further stirring of the mixture at −20 °C for 8 h, the resulting pale yellow and milky solution was quenched with aqueous ammonium chloride, washed with water, and then dried over anhydrous magnesium sulfate. The solvent was removed and replaced by 60 mL of glyme. Concentrated sulfuric acid (3 mL) was added to this solution to effect the hydrolysis of the enol ether. After being stirred at room temperature overnight, the solution became brown-yellow, and TLC (silica gel, 7:1 chloroform/ethyl acetate) showed that hydrolysis was complete. Methanol (40 mL) was added to this solution to effect the hydrolysis of the THP ether. After being stirred for an additional 5 h, the reaction mixture was diluted with 200 mL of chloroform and washed with water until the aqueous layer was neutral. The combined aqueous layer was extracted with chloroform. This chloroform extraction was combined with the organic layer and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a brown oil, which was purified by column chromatography (silica gel, chloroform) and recrystallized from aqueous ethanol to give 2.08 g (60%) of **6g** as yellow crystals: mp 77–79 °C; IR (Nujol) 3200–3320 (s, br), 2225 (m), 1690 (s), 1680 (s), 1675 (s), 1668 (s), 1585 (s), 1198 $cm^{-1}$ (s); NMR ($CDCl_3$) $\delta$ 1.84 (m, 2 H), 2.20 (s, 3 H), 2.68 (t, $J$ = 6.4 Hz, 2 H), 3.82 (t, $J$ = 6.4 Hz, 2 H).

Anal. Calcd for $C_{12}H_{10}Cl_2O_3$: C, 52.77; H, 3.69; Cl, 25.96. Found: C, 52.65; H, 3.79; Cl, 25.69.

**3,6-Bis[3-(benzyloxy)-1-propynyl]-2,5-dichloro-1,4-benzoquinone (6h).** To a solution of 1.85 g (12.66 mmol) of 3-(benzyloxy)-1-propyne in 300 mL of anhydrous tetrahydrofuran at −78 °C under an argon atmosphere was added 5.2 mL (11.96 mmol) of *n*-butyllithium (2.3 M in hexane) in 5 min. The solution was stirred at −78 °C for 2 h. By means of a double-tipped needle, the alkynyllithium solution was added over 1 h to a solution of 1 g (4.22 mmol) of 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone (**5**) in 500 mL of anhydrous diethyl ether at 0 °C under an argon atmosphere. After being stirred at −20 °C for 8 h, the resulting green-yellow and milky solution was quenched with aqueous ammonium chloride, washed with water, and then dried over anhydrous magnesium sulfate. The solvent was evaporated at reduced pressure and replaced by 50 mL of glyme. Concentrated sulfuric acid (2 mL) was added to this solution to effect the hydrolysis of the enol ether. After being stirred at room temperature overnight, the solution became brown-yellow, and TLC (silica gel, benzene) showed that hydrolysis was complete. The reaction mixture was then diluted with 200 mL of chloroform and washed with water until the aqueous layer was neutral. The combined aqueous layer was extracted with chloroform. This chloroform extraction was combined with the organic layer and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave 1.18 g (60%) of **6h** as a brown-yellow solid which was purified by column chromatography (silica gel, 1:1 benzene/hexane) and recrystallized from hexanes to give 982 mg (50%) of **6h** as golden plates: mp 115.5–117 °C dec; IR (Nujol) 2224 (w), 1680 (s), 1673 (s), 1578 $cm^{-1}$ (m); NMR ($CDCl_3$) $\delta$ 4.40 (s, 2 H), 4.60 (s, 2 H), 7.42 (s, 5 H).

Anal. Calcd for $C_{26}H_{18}Cl_2O_4$: C, 67.11; H, 3.90; Cl, 15.24. Found: C, 67.24; H, 4.03; Cl, 15.51.

**2,5-Dichloro-3,6-(diphenylethynyl)-1,4-benzoquinone (6i).** To a solution of 3.88 g (37.97 mmol) of phenylacetylene in 400 mL of anhydrous tetrahydrofuran at −78 °C under an argon atmosphere was added 20 mL (31.64 mmol) of methyllithium (1.6 M in hexane) in 5 min. The solution was stirred at −78 °C for 3 h. By means of a double-tipped needle, the alkynyllithium solution was added in 10 min to a solution of 3.0 g (12.66 mmol) of 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone (**5**) in 600 mL of anhydrous diethyl ether at 0 °C under an argon atmosphere. After being stirred at −20 °C for 8 h, the resulting light brown and milky solution was quenched with aqueous ammonium chloride, washed with water, and then dried over anhydrous magnesium sulfate. The solvent was removed at reduced pressure and replaced by 60 mL of glyme. Concentrated sulfuric acid (18 mL) was added to this solution to effect the hydrolysis of the enol ether. After being stirred at room temperature for 5 h, the solution became brown-red, and TLC (silica gel, benzene) showed that hydrolysis was complete. The reaction mixture was then diluted with 200 mL of chloroform and washed with water until the aqueous layer was neutral. The combined aqueous layer was extracted with chloroform. This chloroform extraction was combined with the organic layer and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave 4.7 g of **6i** which was recrystallized from ethanol to give 3 g (63%) of **6i** as red needles: mp 225–226 °C dec; IR (Nujol) 2195 (s), 1677 (s), 1548 $cm^{-1}$ (s); $^1H$ NMR ($CDCl_3$) $\delta$ 7.38–7.77 (m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 81.92, 111.55, 121.42, 128.76, 130.06, 130.76, 132.73, 142.82, 173.69.

Anal. Calcd for $C_{22}H_{10}Cl_2O_2$: C, 70.05; H, 2.67. Found: C, 70.21; H, 2.79.

**2,5-Dichloro-3,6-bis(3-methoxy-1-propynyl)-1,4-benzoquinone (6j).** To a solution of 2.0 g (28.5 mmol) of 3-methoxy-1-propyne in 350 mL of anhydrous tetrahydrofuran at −78 °C under an argon atmosphere was added 16.6 mL (24.7 mmol) of methyllithium (1.48 M in hexane) during a 5-min period. The solution was stirred at −78 °C for 3 h. By means of a double-tipped needle, the alkynyllithium solution was added over 1 h to a solution of 2.25 g (9.5 mmol) of 2,5-dichloro-3,6-dimethoxy-1,4-benzoquinone (**5**) in 600 mL of anhydrous diethyl ether at 0 °C under an argon atmosphere. After being stirred further at −20 °C for 8 h, the resulting green-yellow and milky solution was quenched with aqueous ammonium chloride, washed with water, and then dried over anhydrous magnesium sulfate. The solvent was evaporated at reduced pressure and replaced by 50 mL of glyme. Concentrated sulfuric acid (2 mL) was added to this solution to effect the hydrolysis of the enol ether. After being stirred at room temperature overnight, the solution became brown-yellow, and TLC (silica gel, benzene) showed that hydrolysis was completed. The reaction mixture was then diluted with 200 mL of chloroform and washed with water until the aqueous layer was neutral. The combined aqueous layer was extracted with chloroform. This chloroform extraction was combined with the organic layer and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a yellow solid, which was purified by dry-column chromatography (silica gel, 1:1 benzene/hexanes) and recrystallized from aqueous ethanol to give 1.24 g (46%) of **6j** as yellow crystals: mp 124–125 °C dec; IR (Nujol) 2218 (m), 1678 (s), 1095 $cm^{-1}$ (s); NMR ($CDCl_3$) $\delta$ 3.43 (s, 3 H), 4.41 (s, 2 H).

Anal. Calcd for $C_{14}H_{10}Cl_2O_4$: C, 53.70; H, 3.22; Cl, 22.65. Found: C, 53.75; H, 3.38; Cl, 22.49.

**4-Cyano-2,5-dichloro-3-methyl-4-[(trimethylsilyl)oxy]-2,5-cyclohexadienone.** A mixture of 25 g (129 mmol) of 2,5-dichloro-3-methyl-1,4-benzoquinone, 23 mL (176.33 mmol) of trimethylsilyl cyanide, and 5 mg of triphenylphosphine was stirred at 0 °C for 2 h. The crude product, a light yellow liquid containing 97% of the title compound and 3% of the regioisomer, was used without purification. The site of cyanosilylation was assigned on

the basis of $^1H$ NMR chemical shifts: NMR ($CDCl_3$) for 4-cyano-2,5-dichloro-3-methyl-4-[(trimethylsilyl)oxy]-2,5-cyclohexadienone $\delta$ 0.20 (s, 9 H), 2.35 (s, 3 H), 6.73 (s, 1 H); NMR ($CDCl_3$) for 4-cyano-2,5-dichloro-6-methyl-4-[(trimethylsilyl)-oxy]-2,5-cyclohexadienone $\delta$ 0.21 (s, 9 H), 2.09 (s, 3 H), 7.12 (s, 1 H).

**1-Cyano-3,6-dichloro-2-methyl-1,4-bis[(trimethylsilyl)-oxy]-4-[3-(2-tetrahydropyranyloxy)-1-propynyl]-2,5-cyclohexadiene.** To a solution of 18.97 g (135.3 mmol) of 3-(2-tetrahydropyranyloxy)-1-propyne in 100 mL of anhydrous tetrahydrofuran at −78 °C under an argon atmosphere was added 62.9 mL (128.86 mmol) of *n*-butyllithium (2.05 M in hexane). The mixture was stirred at −22 °C for 1 h. By means of a double-tipped needle, the alkynyllithium solution was added over 1 h to a solution of 4-cyano-2,5-dichloro-3-methyl-4-[(trimethylsilyl)oxy]-2,5-cyclohexadienone. After the mixture was stirred for 1 h at −22 °C, 15.4 g (141.75 mmol) of trimethylsilyl chloride was added slowly to this solution. The solution was allowed to warm to room temperature and stirred overnight. The solvent was distilled at reduced pressure and replaced by 600 mL of dry hexanes. The resulting solution was treated with 50 g of silica gel and filtered, and after removal of the solvent by distillation at reduced pressure, 52 g of a brown oil was obtained which was further purified by column chromatography (silica gel, benzene) to give 42 g (64%) of the title compound as an orange-brown oil. A small portion of this oil was further purified by molecular distillation (105 °C, 2 $\mu$m) to give an amorphous solid: IR (neat) 2280 (w), 1650 (w), 1250 $cm^{-1}$ (s); NMR ($CDCl_3$) $\delta$ 0.18 (s, 9 H), 0.28 (s, 9 H), 1.36–1.93 (br, 6 H), 2.12 (s, 3 H), 3.30–4.00 (m, 2 H), 4.30 (s, 1 H), 4.76 (br s, 1 H), 6.30 (s, 1 H).

This compound was hydrolyzed to 3,6-dichloro-4-hydroxy-2-methyl-4-[3-(2-tetrahydropyranyloxy)-1-propenyl]-2,5-cyclohexadienone without further purification.

**3,6-Dichloro-4-hydroxy-2-methyl-4-[3-(2-tetrahydropyranyloxy)-1-propynyl]-2,5-cyclohexadienone.** A mixture of 42 g (83.6 mmol) of 1-cyano-3,6-dichloro-2-methyl-1,4-bis-[(trimethylsilyl)oxy]-4-[3-(2-tetrahydropyranyloxy)-1-propynyl]-2,5-cyclohexadienone, 14.04 g (334 mmol) of sodium fluoride, 33.38 g (167 mmol) of cupric acetate, and 100 mL of 1,2-dimethoxyethane was stirred at room temperature for 3 h. After filtration of the inorganic salts, the solvent was removed at reduced pressure. The residue was extracted with ether, which was washed with water, aqueous sodium bicarbonate, and brine and then dried over anhydrous magnesium sulfate to give 25 g of a brown oil. The resulting brown oil was purified by column chromatography (silica gel, 1:1 hexanes/diethyl ether) to give 10 g (36%) of the title compound as a light brown oil. Further purification by preparative TLC (silica gel, 2:1 hexanes/ether) gave the product as a gray-white oily solid: NMR ($CDCl_3$) $\delta$ 1.33–1.87 (br, 6 H), 2.03 (s, 3 H), 3.26–3.90 (m, 2 H), 4.25 (s, 2 H), 4.73 (br s, 1 H), 5.18 (s, 1 H), 7.21 (s, 1 H).

Anal. Calcd for $C_{15}H_{16}Cl_2O_4$: C, 54.39; H, 4.87. Found: C, 54.27; H, 4.92.

**2,6-Dichloro-4-hydroxy-2-methyl-4-[3-(2-tetrahydropyranyloxy)-1-propenyl]-2,5-cyclohexadienone.** A mixture of 3 g (9.06 mmol) of 3,6-dichloro-4-hydroxy-2-methyl-4-[3-(2-tetrahydropyranyloxy)-1-propynyl]-2,5-cyclohexadienone and 90 mg of Pd(5%)–$BaSO_4$ in 6 mL of ethyl acetate and 3 mL of pyridine was exposed to hydrogen at atmospheric pressure for 2 h. The mixture was filtered and the solvent removed to leave a brown oil which was purified by column chromatography (silica gel, 1:1 hexane/diethyl ether) to give 2.6 g (86%) of the title compound which was used without further purification: NMR ($CDCl_3$) $\delta$ 1.30–1.73 (br s, 6 H), 1.95 (s, 3 H), 3.20–3.93 (m, 2 H), 4.33 (d, 2 H, $J$ = 6 Hz), 4.55 (s, 1 H), 5.25 (d, 1 H, $J$ = 12 Hz), 5.6–6.2 (m, 1 H), 7.12 (s, 1 H).

**2,5-Dichloro-3-(3-hydroxy-1-propenyl)-6-methyl-1,4-benzoquinone (7).** A solution of 2.6 g (7.8 mmol) of 3,6-dichloro-4-hydroxy-2-methyl-4-[3-(2-tetrahydropyranyloxy)-1-propenyl]-2,5-cyclohexadienone and 2 mL of boron trifluoride etherate (distilled from calcium hydride) in 100 mL of anhydrous diethyl ether was refluxed overnight. TLC (silica gel, 2:1 hexanes/diethyl ether) showed the reaction to be complete, and the product showed a positive Emmerie–Angel spot test for hydroquinone. Without isolation of the hydroquinone, the reaction mixture was poured into 50 mL of 50% aqueous methanol solution saturated with ferric chloride. After the mixture was shaken for 10 min, the product was extracted with diethyl ether, washed with water, and then dried over magnesium sulfate. Evaporation of the solvent at reduced pressure gave a yellow oil, which was purified by column chromatography (silica gel, benzene) to give 811 mg of the title compound as a light yellow oil: IR (neat) 3300 (s), 1650 (s), 1620 (s), 1590 $cm^{-1}$ (s); NMR ($CDCl_3$) $\delta$ 2.05 (s, 3 H), 3.53 (s, 1 H), 4.40–4.63 (m, 2 H), 6.33–6.63 (m, 1 H), 6.75–7.10 (m, 1 H).

**2,5-Dichloro-3-(5-hydroxy-1-pentenyl)-6-methylhydroquinone.** A solution of 30.3 mg (0.11 mmol) of 2,5-dichloro-3-(5-hydroxy-1-pentynyl)-6-methyl-1,4-benzoquinone (**6g**) in 50 mL of ethyl acetate and 10 mL of pyridine was placed in an atmospheric pressure hydrogenator. After addition of 5 mg of Pd-(5%)–$BaSO_4$, hydrogenation was conducted at room temperature at a slightly positive pressure. The reaction was completed in 2 h, and the solution was filtered by using ethyl acetate to wash the residue. After removal of the solvent by distillation at reduced pressure, a white solid was obtained. This white solid was recrystallized from chloroform–hexanes to give 24.6 mg (81%) of the title compound as white crystals: mp 108–109 °C; IR (Nujol) 3430 (s), 1610 $cm^{-1}$ (w); NMR (acetone-$d_6$) $\delta$ 1.4–1.95 (m, 4 H), 2.28 (s, 3 H), 3.48 (t, $J$ = 6 Hz, 2 H), 5.7–6.4 (m, 2 H), 5.0–6.7 (v br, OH).

Anal. Calcd for $C_{12}H_{14}Cl_2O_3$: C, 52.00; H, 5.09. Found: C, 51.77; H, 5.05.

**2,5-Dichloro-3-(5-hydroxy-1-pentenyl)-6-methyl-1,4-benzoquinone (11).** A solution of 30 mL of saturated aqueous ferric chloride was added to a solution of 24.6 mg of 2,5-dichloro-3-(5-hydroxy-1-pentenyl)-6-methylhydroquinone in 50 mL of chloroform and 20 mL of methanol. The mixture was stirred at room temperature for 2 h, and the resulting solution was washed with water and then dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residual yellow solid was recrystallized from chloroform–hexanes to give 16.3 mg (67%) of **9** as yellow needles: mp 107–109 °C; IR (Nujol) 3450 (m), 1682 (s), 1679 (s), 1670 (s), 1664 (s), 1600 $cm^{-1}$ (s); NMR ($CDCl_3$) $\delta$ 1.3–2.1 (m, 4 H), 2.20 (s, 3 H), 3.60 (t, $J$ = 6 Hz, 2 H), 6.10 (m, 2 H).

Anal. Calcd for $C_{12}H_{12}Cl_2O_3$: C, 52.38; H, 4.40; Cl, 25.77. Found: C, 52.28; H, 4.51; Cl, 25.86.

**Reaction of Sodium Azide and 2,5-Dichloro-3-(5-hydroxy-1-pentenyl)-6-methyl-1,4-benzoquinone (11) in Ethanol: 5-Azido-2-chloro-3-(5-hydroxy-1-pentenyl)-6-methyl-1,4-benzoquinone (8).** To a solution of 178 mg (0.65 mmol) of 2,5-dichloro-3-(5-hydroxy-1-pentyl)-6-methyl-1,4-benzoquinone (**9**) in 200 mL of ethanol at −22 °C was added dropwise 42 mg (0.65 mmol) of sodium azide in 1 mL of water. After the mixture was stirred at −22 °C for 6 h, the solvent of the resulting red solution was removed at reduced pressure to give a red oily solid, which was purified by preparative TLC (silica gel, 1:7 ethyl acetate/chloroform) to give 146 mg (80%) of **8** as a red oily solid: NMR ($CDCl_3$) $\delta$ 1.6–2.0 (m, 4 H), 1.98 (s, 3 H), 3.62 (t, $J$ = 6 Hz, 2 H), 6.0 (m, 2 H).

**Reaction of Potassium Azide and 2,5-Dichloro-3-(5-hydroxy-1-pentenyl)-6-methyl-1,4-benzoquinone (11) with Dibenzo-18-crown-6 as Catalyst in Toluene: 2-Azido-5-chloro-3-(5-hydroxy-1-pentenyl)-6-methyl-1,4-benzoquinone (12).** To a solution of 136.9 mg (0.5 mmol) of 2,5-dichloro-3-(5-hydroxy-1-pentenyl)-6-methyl-1,4-benzoquinone (**9**) in 50 mL of toluene at −78 °C was added 40.3 mg (0.5 mmol) of potassium azide and 5 mg of dibenzo-18-crown-6. The reaction mixture was protected from atmospheric moisture. After being stirred at −78 °C for 4 h, at −22 °C overnight, and then at room temperature for 3 h, the resulting red solution was filtered, and the solvent was then removed at reduced pressure to give a red oily solid, which was purified by preparative TLC (silica gel, 1:7 ethyl acetate/chloroform) to give 99 mg (70%) of the title compound as a red solid: mp 77–78 °C; IR (neat) 3450 (s), 2100 (s), 1670 (s), 1660 $cm^{-1}$ (s); NMR ($CDCl_3$) $\delta$ 1.6–2.0 (m, 4 H), 2.18 (s, 3 H), 3.57 (t, $J$ = 6 Hz, 2 H), 5.98 (m, 2 H).

**5-Chloro-2-(3-hydroxypropyl)-6-methylindoloquinone (13).** A solution of 50 mg (0.18 mmol) of 2-azido-5-chloro-3-(5-hydroxy-1-pentenyl)-6-methyl-1,4-benzoquinone (**10**) in 50 mL of anhydrous benzene was refluxed for 8 h. After removal of the solvent at reduced pressure, the reaction mixture was purified

by preparative TLC (silica gel, 1:2 ethyl acetate/chloroform) to give a red solid, which was recrystallized from aqueous ethanol to give 36.5 mg (80%) of the title compound as red needles: mp 196–197 °C dec; IR (Nujol) 3230 (s), 3130 (m), 1680 (m), 1675 (m), 1670 (m), 1660 (m), 1645 (s), 1635 $cm^{-1}$ (s); NMR (acetone-$d_6$) $\delta$ 1.89 (m, 2 H), 2.15 (s, 3 H), 2.83 (t, $J$ = 7.5 Hz, 2 H), 3.61 (t, $J$ = 6.2 Hz, 2 H), 6.39 (s, 1 H); mol wt calcd for $C_{12}H_{12}ClNO_3$ 253.0506, found 253.0512.

Anal. Calcd for $C_{12}H_{12}ClNO_3$: C, 56.81; H, 4.77; Cl, 13.98; N, 5.52. Found: C, 56.58; H, 4.89; Cl, 14.19; N, 5.29.

**5-Chloro-6-methyl-2-[3-(mesyloxy)propyl]indoloquinone.** A general procedure of Crossland and Servis[21] for the preparation of mesylates was adapted as follows. To a solution of 13.5 mg (0.053 mmol) of 5-chloro-2-(3-hydroxypropyl)-6-methylindoloquinone in 2 mL of dichloromethane containing 8.1 mg (0.08 mmol) of triethylamine at 0 °C was added slowly 6.7 mg (0.058 mmol) of methanesulfonyl chloride. The red indoloquinone suspension became an orange suspension. Stirring for an additional 1 h completed the reaction. The reaction mixture was transferred to a separatory funnel with the aid of chloroform. The mixture was first extracted with water, followed by 5% hydrochloric acid, saturated sodium bicarbonate solution, and brine. Drying of the chloroform solution followed by solvent removal gave a red solid. The red solid was purified by preparative TLC (silica gel, 1:5 ethyl acetate/chloroform) to give 13.5 mg (85%) of the title compound as red crystals: mp 124–126 °C; IR (film) 3220 (m), 3130 (w), 1665 (m), 1635 $cm^{-1}$ (s); NMR ($CDCl_3$) $\delta$ 2.1 (m, 2 H), 2.15 (s, 3 H), 2.85 (t, $J$ = 8 Hz, 2 H), 3.00 (s, 3 H), 4.25 (t, $J$ = 6 Hz, 2 H), 6.53 (s, 1 H).

**7-Chloro-6-methyl-1,2,5,8-tetrahydro-3*H*-pyrrolo[1,2-*a*]indole-5,8-dione (14).** To a solution of 13 mg (0.043 mmol) of 5-chloro-2-[[3-(mesyloxy)propyl]methyl]indoloquinone in 20 mL of anhydrous tetrahydrofuran was added 4.9 mg (0.043 mmol) of potassium *tert*-butoxide. The reaction mixture turned purple immediately and became purple-brown in 10 min. Stirring for an additional 2 h completed the reaction. The solvent of the resulting green-yellow solution was removed under reduced pressure. The residue was purified by preparative TLC (silica gel, 1:5 ethyl acetate/chloroform) to give 7 mg (68%) of **12** as a red solid. This solid was further purified by recrystallization from chloroform–hexanes to give red crystals: mp 156–157 °C; IR (Nujol) 1670 (s), 1665 (s), 1653 (s), 1645 (s), 1595 $cm^{-1}$ (m); NMR ($CDCl_3$) $\delta$ 2.21 (s, 3 H), 2.5–2.9 (m, 4 H), 4.26 (t, $J$ = 5.2 Hz, 2 H), 6.36 (s, 1 H); mol wt calcd for $C_{12}H_{10}ClNO_2$ 235.0401, found 235.038.

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**Registry No.** 1, 20765-04-2; **4a**, 844-51-9; **4b**, 137-18-8; **4c**, 64080-64-4; **4d**, 64080-65-5; **5**, 7210-71-1; **6a**, 24909-17-9; **6b**, 64080-66-6; **6c**, 46010-98-4; **6d**, 64080-67-7; **6e**, 75347-51-2; **6f**, 75347-52-3; **6g**, 75347-53-4; **6h**, 75347-54-5; **6i**, 75347-55-6; **6j**, 75347-56-7; **7**, 75347-57-8; **8**, 75347-58-9; 11, 75347-59-0; **12**, 75347-60-3; **13**, 75347-61-4; **14**, 75347-62-5; 3-(benzyloxy)-1-propyne, 4039-82-1; 4-bromoanisole, 104-92-7; phenylacetylene, 536-74-3; 3-(2-tetrahydropyranyloxy)-1-propyne, 6089-04-9; 5-(2-tetrahydropyranyloxy)-1-pentyne, 62992-46-5; 3-methoxy-1-propyne, 627-41-8; 4-cyano-2,5-dichloro-3-methyl-4-(trimethylsiloxy)-2,5-cyclohexadienone, 75365-45-6; 2,5-dichloro-3-methyl-1,4-benzoquinone, 40100-99-0; trimethylsilyl cyanide, 7677-24-9; triphenyl phosphine, 603-35-0; 1-cyano-3,6-dichloro-2-methyl-1,4-bis(trimethylsiloxy)-4-[3-(2-tetrahydropyranyloxy)-1-propynyl]-2,5-cyclohexadiene, 75347-63-6; 3-(2-tetrahydropyranyloxy)-1-propyne, 6089-04-9; 3,6-dichloro-4-hydroxy-2-methyl-4-[3-(2-tetrahydropyranyloxy)-1-propynyl]-2,5-cyclohexadienone, 75347-64-7; 1,2-dimethoxyethane, 110-71-4; 2,6-dichloro-4-hydroxy-2-methyl-4-[3-(2-tetrahydropyranyloxy)-1-propenyl]-2,5-cyclohexadienone, 75347-65-8; 2,5-dichloro-3-(5-hydroxy-1-pentenyl)-6-methylhydroquinone, 75365-46-7; 5-chloro-6-methyl-2-[3-(mesyloxy)propyl]indoloquinone, 75347-66-9; 5-chloro-2-(3-hydroxypropyl)-6-methylindoloquinone, 75347-67-0.

# Formation of the 5-Benzo[*d*]naphtho[2,3-*b*]pyran System during an Attempted Benzophenanthridine Synthesis

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The condensation of the Schiff base **6** with the homophthalic anhydride **7** was used during elaboration of a compound, **9**, suitable for closure of the B ring of the benzophenanthridine system. However, treatment of **9** with sodium hydride in THF resulted in formation of 3,4-dimethoxy-5-oxo-7-cyano-9,10-(methylenedioxy)-5-benzo[*d*]naphtho[2,3-*b*]pyran (**10**) instead of the Dieckmann–Thorpe cyclization product **2**.

The benzophenanthridine alkaloids constitute a large group of metabolites which occur in the Fumariaceae, Papaveraceae, and Rutaceae.[1] We have recently been attempting to utilize a condensation reaction between Schiff bases and homophthalic anhydrides as an approach to the synthesis of these compounds.[2] The present work was directed toward homochelidonine (**1**),[3] and the strategy in this case was to employ the condensation of the Schiff base **6** with the homophthalic anhydride **7**[4] for the elaboration of the isoquinolone **8**. The corresponding ester **9** was expected to undergo a base-catalyzed Dieckmann–Thorpe cyclization, yielding the tetracyclic system **2**.

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