51.19; H, 5.70; Cl, 11.62; N, 4.59. Found: C, 51.37; H, 5.49; Cl, 11.31; N, 4.54.

(+)-9-Amino-9-deoxydaunomycin (3). By the same procedure as described above, the hydrochloride of **3** was prepared in 92% yield: mp 197–200 °C; $[\alpha]^{20}_D$ +148.1° (*c* 0.1, methanol); IR 1725, 1620, 1580 cm^{-1}; MS, *m/e* 527 (M^+ + 1).

(+)-9-Amino-4-demethoxy-9-deoxy-1-methoxydaunomycin (37). By the same procedure as described for the preparation of **36**, the hydrochloride **37** was prepared in 76% yield: mp 198–202 °C; $[\alpha]^{20}_D$ +78.9° (*c* 0.1, methanol); IR 1730, 1620, 1585 cm^{-1}; MS, *m/e* 527 (M^+ + 1).

Acknowledgment. We are grateful to Mr. H. Sato for skillful technical assistance.

Synthesis of Halodimethoxy-1,2-benzoquinones

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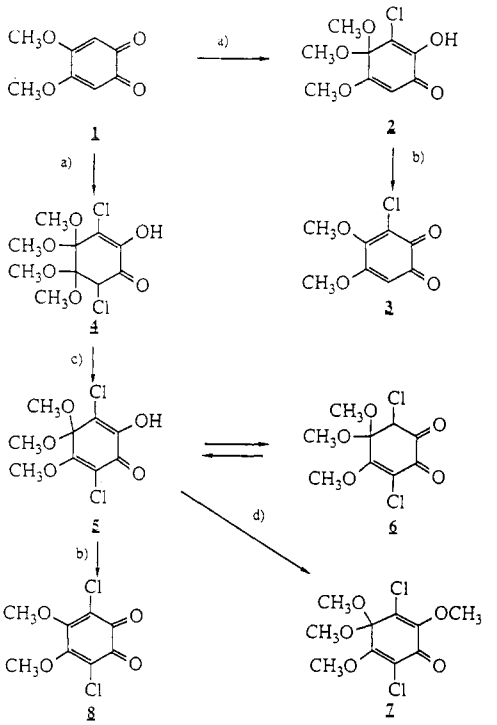
Syntheses of a large number of halodimethoxy-1,2-benzoquinones are described. A key reaction in these syntheses is the chlorination of methoxy-1,2-benzoquinones upon treatment with *tert*-butyl hypochlorite.

We have recently observed a number of interesting transformations associated with 1,2-benzoquinones. These include the conversion of 4,5-dimethoxy-1,2-benzoquinone to 2-alkynyl-5-methoxy-1,4-benzoquinones,[1] the generation of vinylketenes from the thermolysis of 3-azido-1,2-quinones,[2] and the rearrangement of 4-alkynyl-3-azido-1,2-benzoquinones to highly substituted cyanophenols.[3] Many of these transformations depend upon the availability of halodimethoxy-1,2-benzoquinones, compounds that until now have not been readily available.[4] Reported here are viable synthetic routes to such quinones. Specifically, syntheses of examples of nearly all possible regioisomeric mono- and dihalodimethoxy-1,2-benzoquinones are described in this paper (Schemes I–V).

A key reaction in many of these syntheses is the chlorination of methoxy-1,2-benzoquinones upon treatment with *tert*-butyl hypochlorite.[5] For example, treatment of 4,5-dimethoxy-1,2-benzoquinone (**1**)[6] with 1 equiv of *tert*-butyl hypochlorite in methanol gave a 46% yield of the quinone ketal **2** (Scheme I). This was converted to 3-chloro-4,5-dimethoxy-1,2-benzoquinone (**3**) in 91% yield upon treatment with a mixture of trifluoroacetic anhydride and trifluoroacetic acid followed by aqueous workup. When 2 equiv of the hypochlorite were employed, the quinone **1** gave **4** in 53% yield. This resulted in an equilibrium mixture of **5** and **6** when treated with $KHSO_4$ at 110 °C. Subsequent hydrolysis of this mixture gave 3,6-dichloro-4,5-dimethoxy-1,2-benzoquinone (**8**) in 91% yield (Scheme I). The structures of **5** and **6** are based upon their spectral properties as well as upon the observation that **5** gave the quinol **7** upon treatment with diazomethane.

The *tert*-butyl hypochlorite chlorination was also employed in the synthesis of 3-bromo-6-chloro-4,5-dimethoxy-1,2-benzoquinone (**13**) (Scheme II). Here, 2-hydroxy-4,5-dimethoxybenzaldehyde (**9**) was converted to

Scheme I[a]



[a] Key: (a) $(CH_3)_3COCl/CH_3OH$; (b) $(CF_3CO)_2O/CF_3CO_2H$; (c) $KHSO_4$; (d) CH_2N_2.

the catechol **11** in 72% overall yield via the bromo aldehyde **10**. Chloranil oxidation of **11** resulted in 3-bromo-4,5-dimethoxy-1,2-benzoquinone (**12**) (99%). Treatment of **11** with *tert*-butyl hypochlorite in dichloromethane gave **13** in 48% yield. It is noteworthy that the catechol **11** undergoes direct oxidative chlorination under these conditions. In an analogous fashion, 5-chloro- and 5,6-dichloro-3,4-dimethoxy-1,2-benzoquinone (**16** and **17**) were obtained from 5-chloro-1,2-dihydroxy-3,4-dimethoxybenzene (**15**), which, in turn, was prepared by SO_2Cl_2 chlorination of 1,2-dihydroxy-3,4-dimethoxybenzene (**14**) (Scheme III).

Scheme IV outlines the synthesis of 3,5-dibromo-4,6-dimethoxy-1,2-benzoquinone (**21**) starting from 2,4-dimethoxy-6-hydroxybenzaldehyde (**18**). This aldehyde was converted to the catechol **20** via **19**; *o*-chloranil oxidation

(1) Moore, H. W.; West, K. F. *J. Org. Chem.* **1982**, *47*, 3591.
(2) Dorsey, D. A.; King, S.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 2814.
(3) Nguyen, N. V.; Chow, K.; Karlsson, J. O.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 419.
(4) For an excellent review on the chemistry of orthoquinones see: Grundmann, C. *Orthoquinones*, Houben-Weyl; Springer-Verlag: Berlin, 1952; band VII/3b, teil II, p 1.
(5) For a related example describing the chlorination of aminoquinones see: Moore, H. W.; Cajipe, G. *Synthesis* **1973**, 49.
(6) Itoh, Y.; Kakuta, T.; Hirano, M.; Morimoto, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2169.
(7) Loubinoux, B.; Coudert, G.; Guillaumet, G. *Synthesis* **1980**, 638.

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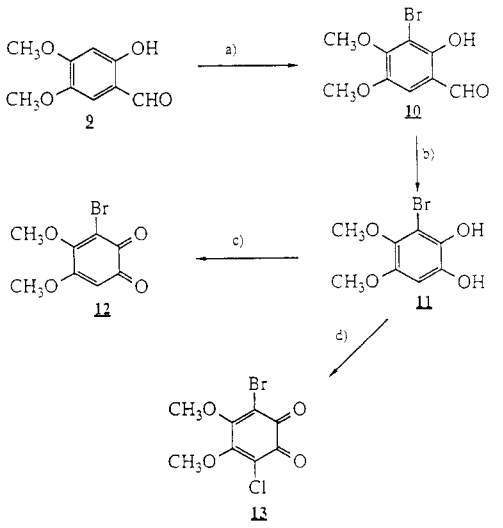
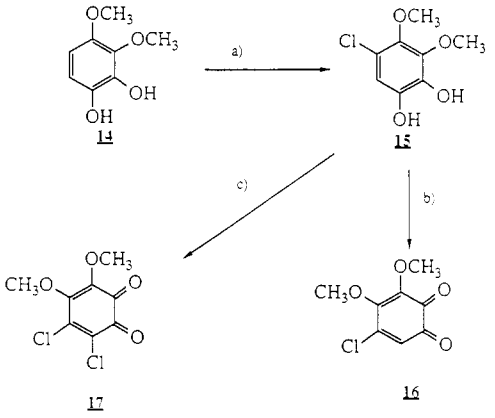
Scheme II[a]



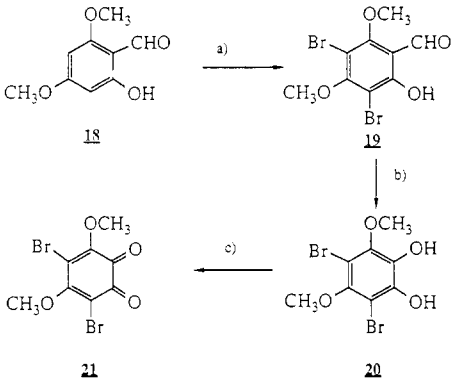
[a] Key: (a) Br_2/CH_3CO_2H (79%); (b) H_2O/OH^- (93%); (c) *o*-chloranil (99%); (d) $(CH_3)_3COCl/CH_2Cl_2$ (48%).

Scheme III[a]



[a] Key: (a) SO_2Cl_2 (92%); (b) *o*-chloranil (76%); (c) $(CH_3)_3COCl/CH_2Cl_2$ (93%).

Scheme IV[a]



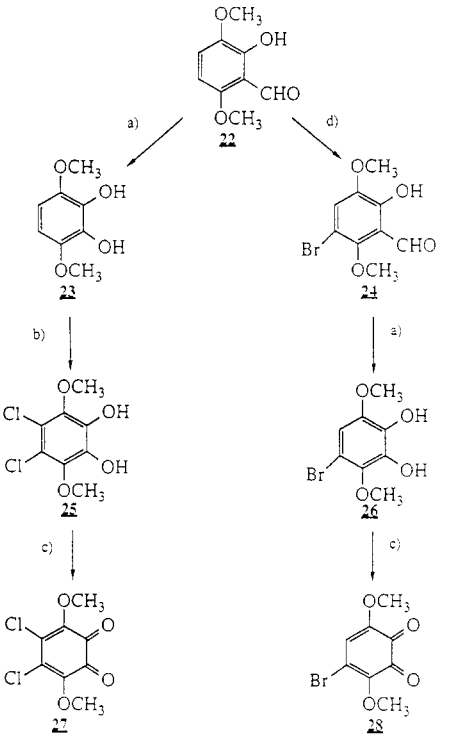
[a] Key: (a) Br_2/CH_3CO_2H (89%); (b) H_2O_2/OH^- (90%); (c) *o*-chloranil (71%).

of **20** gave the quinone **21** in 71% isolated yield.

4,5-Dichloro-3,6-dimethoxy-1,2-benzoquinone (**27**) and 4-bromo-3,6-dimethoxy-1,2-benzoquinone (**28**) were prepared from 2-hydroxy-3,6-dimethoxybenzaldehyde (**22**) as outlined in Scheme V.

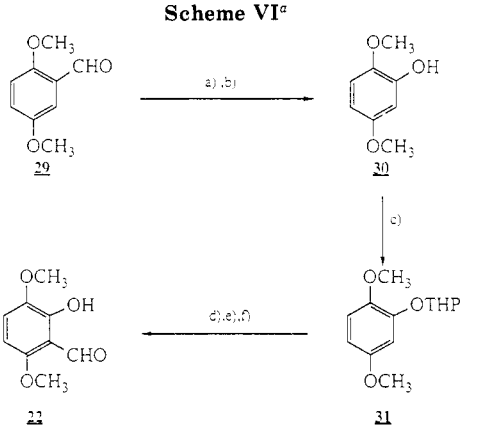
Even though 2-hydroxy-3,6-dimethoxybenzaldehyde is commercially available, its expense required the development of routes to this compound that would allow its large-scale preparation. One successful synthesis that gives

Scheme V[a]



[a] Key: (a) H_2O_2/OH^- (79%); (b) SO_2Cl_2 (81%); (c) *o*-chloranil (67%); (d) Br_2/CH_3CO_2H (78%).

Scheme VI[a]



[a] Key: (a) *m*-CPBA/CH_2Cl_2; (b) NaOH (92%); (c) DHP/H^+ (88%); (d) *n*-BuLi; (e) DMF; (f) H_3O^+ (79%).

22 in 64% overall yield is outlined in Scheme VI. Here, 2,5-dimethoxybenzaldehyde (**29**) was converted to the phenol **30** in 92% yield. The THP derivative **31** was prepared in 88% yield, and subsequent formylation and deprotection gave **22** in 79% yield. Still another route to **22** was achieved in 41% yield starting with the readily available *o*-vanillin (**32**) (Scheme VII).

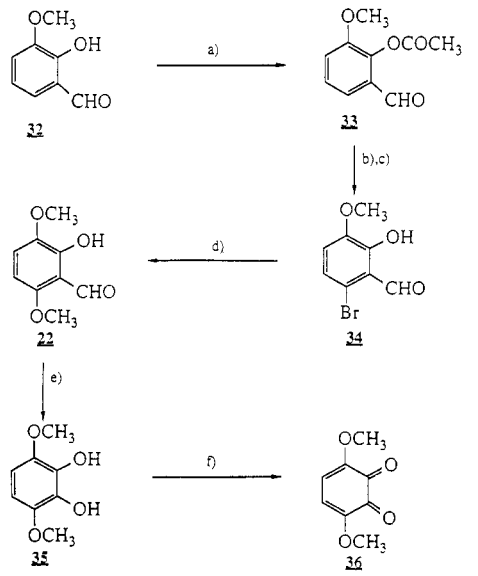
Finally, it is noted that Dakin oxidation of **22** gave the catechol **35** in 79% yield, and this was converted to 3,6-dimethoxy-1,2-benzoquinone (**36**) in 98% yield upon treatment with *o*-chloranil (Scheme VII).

The quinones described here are useful starting materials for the syntheses of a variety of other substituted quinones and aromatic compounds. Studies of this nature will be reported subsequently.

Experimental Section

3-Chloro-2-hydroxy-4,4,5-trimethoxy-2,5-cyclohexadien-1-one (2). To a solution of 5 g (30 mmol) of 4,5-dimethoxy-1,2-benzoquinone in 400 mL of methanol was added dropwise at

Scheme VII[a]



[a] Key: (a) $(CH_3CO)_2O$/Py (97%); (b) Br_2/H_2O (85%); (c) HCl (68%); (d) CH_3ONa/CH_3OH (73%); (e) H_2O_2/OH^- (79%); (f) *o*-chloranil (98%).

ambient temperatures 3.3 g (30 mmol) of *tert*-butyl hypochlorite in 20 mL of methanol. After an additional 1 h, the pale yellow solution was concentrated in vacuo at 35 °C. The resulting oil was crystallized from ether to yield 3.2 g (46%) of **2** as light orange crystals: mp 122–124 °C; IR (KBr, cm^{-1}) 3353, 1762, 1680, 1653; ^1H NMR ($CDCl_3$, δ) 3.31 (s, 3 H), 3.45 (s, 3 H), 3.94 (s, 3 H), 4.68 (s, 1 H); 5.91 (s, 1 H).

3-Chloro-4,5-dimethoxy-1,2-benzoquinone (3). This quinone was prepared from the crude cyclohexadien-1-one **2**. Specifically, the oil was dissolved in 250 mL of dry toluene, and 8.5 mL (60 mmol) of trifluoroacetic anhydride and 3.5 mL (45 mmol) of trifluoroacetic acid were added. After 1 h at 65 °C, the solvent was removed in vacuo and the orange solid was recrystallized from dichloromethane/ether to yield 2.53 g (42% from 3,4-dimethoxy-1,2-benzoquinone) of the quinone **2**: mp 118–119 °C; IR (Nujol, cm^{-1}) 1694, 1660, 1614; ^1H NMR ($CDCl_3$, δ) 3.92 (s, 3 H), 4.19 (s, 3 H), 5.75 (s, 1 H); MS (M + 1, CI), *m/z* 203/205. Anal. Calcd for $C_8H_7ClO_4$: C, 47.43; H, 3.48. Found: C, 47.32; H, 3.54.

2,5-Dichloro-6-hydroxy-3,3,4,4-tetramethoxy-5-cyclohexen-1-one (4). To a solution of 5 g (30 mmol) of **1** in 2.0 L of methanol was added dropwise 7 g (64 mmol) of *tert*-butyl hypochlorite in 40 mL of methanol. After 2 h, an additional 3.5 g of *tert*-butyl hypochlorite was added very slowly. The solvent was then removed in vacuo at 30 °C, and the resulting oil was subjected to flash chromatography (ethyl acetate/hexane 1:9) to yield 4.8 g (53%) of **3**: mp 132–133 °C; IR (KBr, cm^{-1}) 3436, 1689, 1647; ^1H NMR ($CDCl_3$, δ) 3.47, 3.54, 3.62, 3.64, 3.67, 3.68 (all s, 12 H), 5.06 (br s, 1 H), 6.51 (s, 1 H); MS (CI, M + 1), *m/z* 301/303/305 (3.7%/26.8%/26.1%). Anal. Calcd for $C_{10}H_{14}Cl_2O_6$: C, 39.89; H, 4.69. Found: C, 39.88; H, 4.70.

2,5-Dichloro-6-hydroxy-3,4,4-trimethoxy-2,5-cyclohexadien-1-one (5) and 3,6-Dichloro-4,4,5-trimethoxy-5-cyclohexene-1,2-dione (6). A solution of 3.83 g (12.7 mmol) of **4** in dry toluene was treated with 5 mg of potassium hydrogen sulfate, and the mixture was heated to 110 °C. The methanol released under these conditions was removed by distillation to give a deep red solution after 1 h. After filtration and removal of the solvent, the residue was recrystallized from ether/hexanes to yield 2.59 g (76%) of a mixture of **5** and **6** as red and yellow crystals. The spectral data on the manually separated samples are given below. Compound **5**: yellow crystals; mp 150–151 °C; IR (KBr, cm^{-1}) 3387, 1657, 1593; ^1H NMR ($CDCl_3$, δ) 3.29 (s, 6 H), 4.40 (s, 3 H), 7.01 (s, 1 H). Anal. Calcd for $C_9H_{10}Cl_2O_5$: C, 40.17; H, 3.75. Found: C, 40.21; H, 3.75. Compound **6**: red crystals; mp 102–103 °C; IR (KBr, cm^{-1}) 1763, 1573; ^1H NMR ($CDCl_3$, δ) 3.34 (s, 3 H), 3.45 (s, 3 H), 4.32 (s, 3 H), 4.71 (s, 1 H); MS (CI, M + 1), *m/z* 269/271/273 (100%/74.1%/8.3%). Anal. Calcd for $C_9H_{10}Cl_2O_5$: C, 40.17; H, 3.37. Found: C, 40.04; H, 3.65.

3,6-Dichloro-2,4,4,5-tetramethoxy-2,5-cyclohexadien-1-one (7). A solution of 300 mg (1.1 mmol) of **5** in 25 mL of ether was cooled to 0 °C, and an ethereal solution of diazomethane was added dropwise. The addition was stopped after the starting material could not be detected by TLC analysis. Removal of the solvent gave a residue that was purified by flash chromatography to yield 260 mg (84%) of **7** as colorless crystals: mp 70–71 °C; IR (KBr, cm^{-1}) 1685, 1599; ^1H NMR ($CDCl_3$, δ) 3.20 (s, 6 H), 3.91 (s, 3 H), 4.24 (s, 3 H). Anal. Calcd for $C_{10}H_{12}Cl_2O_5$: C, 42.43; H, 4.27. Found: C, 42.64; H, 4.19.

3,6-Dichloro-4,5-dimethoxy-3,5-cyclohexadiene-1,2-dione (8). A solution containing 1.35 g (5 mmol) of a mixture of **5** and **6** in 60 mL of dry toluene (under N_2) was treated with 2 mL of trifluoroacetic anhydride and 1 mL of trifluoroacetic acid at 65 °C. After 1 h the solution was cooled to ambient temperature, and the solvents were removed in vacuo. The residue was recrystallized from dichloromethane/hexane to yield 1.08 g (91%) of the quinone **8** as a red crystalline solid: mp 115–116 °C; IR (KBr, cm^{-1}) 1675, 1553; ^1H NMR ($CDCl_3$, δ) 4.21 (s, 6 H); MS (CI, M + 1), *m/z* 237/239/241 (86.3%/100%/41.8%). Anal. Calcd for $C_8H_6Cl_2O_4$: C, 40.54; H, 2.55. Found: C, 40.40; H, 2.44.

3-Bromo-2-hydroxy-4,5-dimethoxybenzaldehyde (10). To a solution of 14.6 g (80 mmol) of 2-hydroxy-4,5-dimethoxybenzaldehyde (**9**) and 10 g of anhydrous sodium acetate in 350 mL of glacial acetic acid was added dropwise 13 g (80 mmol) of bromine in 150 mL of glacial acetic acid. After 1 h the solvent was removed in vacuo at 40 °C. The residue was poured into water and then extracted with dichloromethane. This was then washed with 2% sodium bicarbonate and dried over magnesium sulfate. The solvent was removed, and the residue was recrystallized from dichloromethane/ether to give 16 g (77%) of **10** as yellow crystals: mp 111–112 °C; IR (KBr, cm^{-1}) 2950, 1647, 1620; ^1H NMR ($CDCl_3$, δ) 3.88 (s, 3 H), 3.99 (s, 3 H), 7.02 (s, 1 H), 9.75 (s, 1 H), 11.5 (s, 1 H). Anal. Calcd for $C_9H_9BrO_4$: C, 41.41; H, 3.47. Found: C, 41.35; H, 3.45.

3-Bromo-1,2-dihydroxy-4,5-dimethoxybenzene (11). A solution containing 5 g (19 mmol) of **10** in 49 mL of 2% aqueous sodium hydroxide was treated dropwise with 2.5 g of 30% hydrogen peroxide in 50 mL of water. After 1 h, the solution was acidified (HCl) and extracted with dichloromethane. After the mixture was washed with water and dried over magnesium sulfate, the solvent was removed in vacuo and the residue was recrystallized from dichloromethane/hexane to give 4.49 g (93%) of **11**: mp 121–122 °C; IR (KBr, cm^{-1}) 3463, 3195, 1608; ^1H NMR ($CDCl_3$, δ) 3.80 (s, 6 H), 5.12 (br s, 2 H), 6.58 (s, 1 H). Anal. Calcd for $C_8H_9BrO_4$: C, 38.58; H, 3.65. Found: C, 38.54; H, 3.66.

3-Bromo-4,5-dimethoxy-3,5-cyclohexadiene-1,2-dione (12). To a solution of 2 g (8.1 mmol) of **11** in 70 mL of dry ether at −25 °C under N_2 was added 1.99 g (8.1 mmol) of *o*-chloranil. After 1 h at −25 °C, the reaction mixture was filtered to give 1.98 g (99%) of **12** as an orange crystalline solid: mp 181–182 °C; IR (KBr, cm^{-1}) 1695, 1664, 1658, 1609, 1569, 1559, 1260; ^1H NMR ($CDCl_3$, δ) 3.94 (s, 3 H), 4.12 (s, 3 H), 5.77 (s, 1 H); MS (CI, M + 1), *m/z* 247/249 (44.6%/100%). Anal. Calcd for $C_8H_7BrO_4$: C, 38.89; H, 2.86. Found: C, 38.80; H, 3.01.

3-Bromo-6-chloro-4,5-dimethoxy-3,5-cyclohexadiene-1,2-dione (13). A solution containing 2 g (8.1 mmol) of **11** in 200 mL of dichloromethane was treated dropwise with 1.6 g (16.5 mmol) of *tert*-butyl hypochlorite in 20 mL of dichloromethane. After 1 h, the solvent was removed and the residue was recrystallized from dichloromethane/hexane to yield 1.1 g (48%) of **13** as red-purple crystals: mp 101–102 °C; IR (KBr, cm^{-1}) 1703, 1680, 1570, 1555; ^1H NMR ($CDCl_3$, δ) 4.14 (s, 3 H), 4.24 (s, 3 H); MS (CI, M + 1), *m/z* 281/283/285 (12.1%/28.1%/23.2%). Anal. Calcd for $C_8H_6BrClO_4$: C, 34.13; H, 2.15. Found: C, 34.28; H, 2.13.

5-Chloro-1,2-dihydroxy-3,4-dimethoxybenzene (15). A solution composed of 1.02 g (5.9 mmol) of 1,2-dihydroxy-3,4-dimethoxybenzene (**14**) in 30 mL of anhydrous diethyl ether was treated with 1 g (7.4 mmol) of sulfuryl chloride in 5 mL of ether at −25 °C under N_2. During the addition, the solution became yellow and was allowed to warm to ambient temperature over a period of 3 h. The solution was then washed with saturated sodium carbonate solution and dried over $MgSO_4$. Removal of the solvent in vacuo gave 1.13 g (92%) of **15** as orange crystals: mp 91–92 °C; IR (KBr, cm^{-1}) 3500, 3460; ^1H NMR ($CDCl_3$, δ) 3.83

(s, 3 H), 3.93 (s, 3 H), 5.81 (s, 2 H), 6.69 (s, 1 H). Anal. Calcd for $C_8H_9ClO_4$: C, 46.96; H, 4.43. Found: C, 46.87; H, 4.60.

5-Chloro-3,4-dimethoxy-3,5-cyclohexadiene-1,2-dione (16). *o*-Chloranil (1.7 g, 5.5 mmol) was added in one portion to a solution of 1.13 g (5.5 mmol) of **15** in 50 mL of anhydrous diethyl ether at −20 °C. After 1 h at −20 °C, the precipitate was collected and the mother liquor was concentrated. The residue was chromatographed through a short silica gel column (ethyl acetate/hexane, 2:8) to yield 0.859 g (76%) of **16** as purple crystals: mp 76–77 °C; IR (KBr, cm^{-1}) 1700, 1670; ^1H NMR ($CDCl_3$, δ) 3.87 (s, 3 H), 4.23 (s, 3 H), 6.50 (s, 1 H); MS (CI, M + 1), m/z 205/207 (100/30.4). This compound was unstable and showed some decomposition after a few days when it was stored in the dark under argon at −20 °C. Thus, no satisfactory CH analysis was obtained.

3,4-Dichloro-5,6-dimethoxy-3,5-cyclohexadiene-1,2-dione (17). A solution of 190 mg of **15** in 200 mL of dichloromethane was treated dropwise with 1.6 g (16.5 mmol) of *tert*-butyl hypochlorite in 20 mL of dichloromethane. The resulting deep red-purple solution was concentrated and the residue recrystallized from ether/hexane to yield 180 mg (93%) of **17** as dark purple crystals: mp 112–114 °C; IR (KBr, cm^{-1}) 1720, 1675; ^1H NMR ($CDCl_3$, δ) 3.87 (s, 3 H), 4.25 (s, 3 H); MS (CI, M + 1), m/z 237/239/241 (85.8%/100%/38.5%).

3,5-Dibromo-2-hydroxy-4,6-dimethoxybenzaldehyde (19). To a reaction mixture containing 10 g (55 mmol) of 2,4-dimethoxy-6-hydroxybenzaldehyde (**18**) and 14 g of sodium acetate in 300 mL of glacial acetic acid was added 17.6 g (110 mmol) of bromine in 200 mL of acetic acid. After 1 h, the solvent was removed in vacuo (40 °C) and water was added to the residue. This was then extracted with dichloromethane. The organic extract was then washed with 2% Na_2CO_3 and H_2O and then dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography (ethyl acetate/hexane, 4:6) to give 16.6 g (89%) of **19** as yellow crystals: mp 102–103 °C; IR (KBr, cm^{-1}) 3500, 2500, 1650, 1610; ^1H NMR ($CDCl_3$, δ) 3.96 (s, 3 H), 4.00 (s, 3 H), 10.12 (s, 1 H), 12.47 (s, 1 H). Anal. Calcd for $C_9H_8Br_2O_4$: C, 31.80; H, 2.37. Found: C, 31.72; H, 2.48.

3,5-Dibromo-1,2-dihydroxy-4,6-dimethoxybenzene (20). A suspension of 3 g (8.8 mmol) of **19** and 0.38 g of NaOH in 20 mL of water was treated with 1.1 g of 30% H_2O_2 in 25 mL of water. The reaction mixture was acidified and extracted with dichloromethane. After the organic extract was dried, the solvent was removed in vacuo to give 2.86 g of **20** as a brownish oil. This was used without further purification for the synthesis of **21**: IR (neat, cm^{-1}) 3340, 1660, 1600; ^1H NMR ($CDCl_3$, δ) 3.82 (s, 3 H), 3.88 (s, 3 H), 6.52 (s, 2 H).

3,5-Dibromo-4,6-dimethoxy-3,5-cyclohexadiene-1,2-dione (21). A solution of 2.86 g (9 mmol) of **20** in 50 mL of anhydrous ether was treated with 2.21 g (9 mmol) of *o*-chloranil and 10 mL of hexane. After 1 h, the precipitate was collected and recrystallized from ether/hexane to yield 2.09 g (71%) of **21** as purple crystals: mp 93–95 °C; IR (KBr, cm^{-1}) 1690, 1600, 1550; ^1H NMR ($CDCl_3$, δ) 4.06 (s, 3 H), 4.09 (s, 3 H); MS (CI, M + 1), m/z 324/326/328 (8.4%/22.4%/21.6%). Anal. Calcd for $C_8H_6Br_2O_4$: C, 29.48; H, 1.86. Found: C, 29.23; H, 1.69.

3,6-Dimethoxy-1,2-benzenediol (23). A solution of 3,6-dimethoxy-2-hydroxybenzaldehyde (**22**) (3.60 g, 19.8 mmol) in 2% NaOH (0.83 g of NaOH, 20.75 mmol) was stirred while 2.46 g (21.75 mmol) of 30% hydrogen peroxide in 30 mL of water was added dropwise. The mixture darkened after the addition of about 1 mL, and the remainder of the starting material went into solution. The temperature began to rise and was allowed to return to room temperature before more peroxide was added. After the addition was complete, the mixture was stirred for 1 h, at which time TLC showed no starting material. The mixture was acidified with HCl and ice was added, followed by extraction with dichloromethane. The crude product was absorbed onto silica and passed through a flash column (6:4 hexane/ethyl acetate). This should be done as quickly as possible, since the compound decomposes slowly on silica. The solvent was removed to give 2.66 g (79%) of a cream-colored solid: mp 105–106 °C [lit.[11] mp 106 °C]; ^1H NMR ($CDCl_3$, δ) 3.83 (s, 3 H), 5.65 (br, 1 H), 6.37 (s, 1 H).

3,6-Dimethoxy-4,5-dichlorocatechol (25). To an ice-cooled solution of 2.2 g (0.013 mol) of 3,6-dimethoxycatechol in 25 mL of anhydrous ether, maintained under nitrogen, was added dropwise with stirring 2.25 mL (0.026 mol) of sulfuryl chloride in 10 mL of ether. The solution was allowed to warm to room temperature. The ethereal solution was washed 3 × 20 mL with saturated sodium bicarbonate. The organic layer was dried with $MgSO_4$ and the solvent evaporated to give 2.5 g (81%) of dichlorinated product that was recrystallized from carbon tetrachloride: mp 138–140 °C; ^1H NMR ($CDCl_3$, δ) 3.92 (s, 3 H), 5.58 (br, 1 H).

3,6-Dimethoxy-4,5-dichloro-1,2-benzoquinone (27). In a 250-mL round-bottomed flask at −22 °C under argon, 7.76 g (0.0325 mol) of 3,6-dimethoxy-4,5-dichlorocatechol and 7.90 g (0.0325 mol) of *o*-chloranil were dissolved in 75 mL of anhydrous ether, and the resultant mixture was stirred at this temperature for 2 h. Most of the product precipitated out of solution; dark solids were recrystallized twice with boiling diethyl ether to yield 5.2 g (67%) of dark purple shiny crystals: mp 125–126 °C; ^1H NMR ($CDCl_3$, δ) 3.80 (s); IR (KBr, cm^{-1}) 2940 (w), 1670 (s), 1450 (w), 1428 (w), 1295 (m), 1285 (s); MS, m/z 237.0 (CI, EI). Anal. Calcd for $C_8H_6Cl_2O_4$: C, 40.53; H, 2.55. Found: C, 40.31; H, 2.44.

4-Bromo-3,6-dimethoxysalicylaldehyde (24). After dropwise addition of 4.4 g (0.027 mol) of bromine in 40 mL of acetic acid to a solution of 5.0 g (0.027 mol) of 3,6-dimethoxybenzaldehyde in 100 mL of 80% acetic acid at 70 °C and after stirring for 1 h, the temperature was lowered to room temperature and the product was precipitated by adding an equal volume of water. The product was recrystallized from methanol to give 5.6 g (78%) of **24**: mp 73–74 °C; ^1H NMR ($CDCl_3$, δ) 3.75 (s, 3 H), 3.81 (s, 3 H), 7.18 (s, 1 H), 9.71 (s, 1 H), 11.2 (s, 1 H).

4-Bromo-3,6-dimethoxycatechol (26). A 1.60-g (0.00613-mol) sample of 4-bromo-3,6-dimethoxysalicylaldehyde was dissolved in 75 mL of 2% aqueous solution of NaOH. To this solution was added dropwise an excess of 30% hydrogen peroxide in 25 mL of distilled water. The mixture was stirred at room temperature for 90 min. The reaction was quenched by transferring the mixture to an Erlenmeyer flask containing 300 mL of distilled water plus 50 mL of concentrated HCl. The product was extracted from the aqueous solution with 3 × 150 mL of dichloromethane, the organic layers were combined and dried with $MgSO_4$. The organic solvent was flashed off, and the residue was passed through a flash column (silica gel; hexane/ethyl acetate, 1:1) to give 0.95 g (75%) of a light yellow oil: ^1H NMR ($CDCl_3$, δ) 3.71 (s, 3 H), 5.65 (br, 1 H), 6.6 (s, 1 H).

3,6-Dimethoxy-4-bromo-1,2-benzoquinone (28). A 0.41-g (0.0017-mol) sample of 3,6-dimethoxy-4-bromocatechol was dissolved in 35 mL of anhydrous ether and the mixture cooled to −22 °C under argon. Then, *o*-chloranil (0.40 g (0.0017 mol)) was added and the mixture stirred at this temperature for 2 h. Most of the quinone, which precipitated out of solution, was collected by suction filtration and was washed with very cold ether to yield 0.20 g (70%) of black crystals: mp 115–116 °C dec; ^1H NMR ($CDCl_3$, δ) 3.71 (s, 3 H), 3.85 (s, 3 H), 6.1 (s, 1 H); IR (KBr, cm^{-1}) 2930 (m), 1650 (s), 1625 (s), 1430 (m), 1270 (s), 1060 (s); exact mass calcd for $C_8H_7BrO_4$ 246.9300, found 247.9551.

2,5-Dimethoxyphenol (30). A solution of 50 g (0.30 mol) of 2,5-dimethoxybenzaldehyde (**29**) in 100 mL of dichloromethane was added dropwise (1 h) to an ice-cold solution of 70 g (0.325 mol) of *m*-chloroperbenzoic acid in 400 mL of dichloromethane. After the addition was complete, the ice bath was removed and the mixture allowed to come to room temperature and then refluxed for 14 h. After cooling to room temperature, the organic solution was extracted with aqueous saturated sodium bicarbonate (12 × 200 mL) and then with 250 mL of 10% sodium thiosulfate to remove excess peroxide. The dichloromethane was removed, giving a dark yellow oil that was dissolved in methanol, and stirred with excess 10% aqueous sodium hydroxide for 3 h. The mixture was acidified to pH 1 with 6 N hydrochloric acid and extracted with dichloromethane (3 × 250 mL). The organic layers were combined and dried and the solvent was removed. Vacuum distillation gave 40 g (86%) of **30**: bp 131–133 °C (12 mm) [lit.[6] bp 131 °C (12 mm)]; ^1H NMR ($CDCl_3$, δ) 6.53 (m, 3 H), 6.11 (br s, 1 H), 3.79 (s, 3 H), 3.72 (s, 3 H).

2,5-Dimethoxyphenol Tetrahydropyranyl Ether (31). A solution of 40 g (0.26 mol) of 2,5-dimethoxyphenol (**30**) was stirred (14 h) with 87 g (1.04 mol) of dihydropyran (freshly distilled from sodium) and four drops of concentrated hydrochloric acid under nitrogen. Dichloromethane (300 mL) was added, and then the

resultant solution was extracted with 10% NaOH (2 × 100 mL). The organic layer was dried with $MgSO_4$ and the solvent removed. Vacuum distillation gave 55 g (88%) of a colorless oil: bp 115 °C (0.25 mm); ^1H NMR ($CDCl_3$, δ) 6.65 (m, 3 H), 5.35 (br, 1 H), 3.78 (s, 3 H), 3.70 (s, 3 H), 1.65 (m, 9 H).

3,6-Dimethoxy-2-hydroxybenzaldehyde (22). 2,5-Dimethoxyphenol tetrahydropyranyl ether (**31**) (10.3 g, 43.09 mmol) was stirred in 500 mL of dry THF under argon for 10 min. The solution was then cooled to 0 °C, and 23.4 mL of *n*-butyllithium (2.03 M in hexane) was slowly added. The mixture was brought to room temperature, stirred for 2 h, and then cooled to −78 °C prior to addition of dry *N,N*-dimethylformamide (12.6 g, 172.4 mmol). The stirring was continued for 2 h while the solution was allowed to come to room temperature. Then, 40 mL of 6 N hydrochloric acid was carefully added and the mixture stirred vigorously for 1 h. The organic layer was removed to give a yellow oil that was passed through a flash column (fluorisil; hexane/ethyl acetate, 1:1) to give 6.0 g (79%) of the desired product as yellow needles: mp 67–69 °C; ^1H NMR ($CDCl_3$, δ) 12.18 (s, 1 H), 10.22 (s, 1 H), 7.01 (d, 1 H), 6.25 (d, 1 H), 3.83 (s, 6 H).

2-Acetoxy-3-methoxybenzaldehyde (33). A solution of 50 g (0.329 mol) of *o*-vanillin (**32**) in 50 mL of pyridine and 35 mL (0.340 mol) of acetic anhydride was stirred at room temperature for 24 h to give a white precipitate. The mixture was transferred to a flask containing 300 mL of 6 N HCl solution. The solids were collected by filtration, and the product was washed with additional (400 mL) 6 N HCl followed by distilled water. White crystals were obtained after recrystallization from methanol: 62 g (97%); mp 68–70 °C [lit.[8] mp 72–73 °C]; ^1H NMR ($CDCl_3$, δ) 10.12 (s, 1 H), 7.28 (m, 3 H), 3.86 (s, 3 H), 2.39 (s, 3 H).

2-Hydroxy-3-methoxy-6-bromobenzaldehyde (34). The aldehyde **33** (2.0 g, 10.3 mmol) was added in small portions to a solution of 4.0 g of KBr and 0.60 mL of bromine in 40 mL of distilled water. The mixture was stirred for 1 h and the resulting precipitate collected by filtration. The crude product (pinkish solid) was suspended in 50 mL of 6 N HCl and stirred for 3 h at room temperature. The yellow precipitate obtained was collected by filtration and recrystallized from methanol to give 1.9 g (68%) of yellow crystals: mp 116–117 °C [lit.[9] mp 105–108 °C]; ^1H NMR ($CDCl_3$, δ) 12.16 (s, 1 H), 10.29 (s, 1 H), 7.21 (d, J = 8.4 Hz, 1 H), 7.0 (d, J = 8.5 Hz, 1 H), 3.88 (s, 3 H).

3,6-Dimethoxy-2-hydroxybenzaldehyde (22). In a 500-mL three-necked flask, fitted with a condenser and an addition funnel, was added 38.4 g (0.713 mol) of sodium very slowly to 250 mL of absolute methanol. After all of the sodium was added, the mixture was stirred until hydrogen evolution ceased (15 min). Then, 25.0 g (0.108 mol) of **34** dissolved in 100 mL of dry DMF was added along with 2.0 g of copper(I) iodide. The mixture was refluxed for 4 h. After it was cooled to room temperature and filtered, the filtrate was transferred to an Erlenmeyer flask containing 300 g of ice and 100 mL of concentrated HCl. The yellow precipitate that formed was separated by filtration and recrystallized from boiling methanol to afford 14.2 g (72%) of fine yellow needles: mp 68–69 °C [lit.[10] mp 68–69 °C]; ^1H NMR ($CDCl_3$, δ) 12.16 (s, 1 H), 10.32 (s, 1 H), 7.0 (d, J = 8.8 Hz, 1 H), 6.25 (d, J = 9.4 Hz, 1 H), 3.80 (s, 3 H), 3.76 (s, 3 H).

3,6-Dimethoxy-1,2-benzenediol (35). A solution containing 3.60 g (19.8 mmol) of **22** in 100 mL of 2% NaOH was stirred at room temperature while 2.46 g (21.77 mmol) of 30% hydrogen peroxide in 30 mL of distilled water was added dropwise. After the addition was complete, the mixture was stirred for 90 min. The mixture was then transferred to an Erlenmeyer flask containing 250 mL of distilled water and 50 mL of concentrated HCl. The aqueous solution was extracted with dichloromethane (3 × 150 mL), and the organic layers were combined and dried with $MgSO_4$. Evaporation of the solvent gave a residue that was immediately filtered through silica gel (hexanes/ethyl acetate). Evaporation of the eluent afforded 2.6 g (79%) of a yellow solid: mp 105–106 °C [lit.[10] mp 105–106 °C]; ^1H NMR ($CDCl_3$, δ) 6.37 (s, 1 H), 5.65 (br, 1 H), 3.83 (s, 3 H).

3,6-Dimethoxy-1,2-benzoquinone (36). A mixture containing 2.65 g (15.6 mmol) of **35** and 3.91 g (12.3 mmol) of *o*-chloranil was stirred in 100 mL of anhydrous ether under argon at −22 °C for 2 h. The product was filtered and washed several times with cold ether to give 2.55 g (98%) of orthoquinone **36** as a dark purple solid: mp 120–122 °C; ^1H NMR ($CDCl_3$, δ) 5.87 (s, 1 H), 3.73 (s, 3 H); IR (KBr, cm^{-1}) 3070 (m), 2840 (m), 1670 (s), 1380 (s), 1340 (s), 1140 (s); MS, m/z 169 (Cl); exact mass calcd for $C_8H_8O_4$ 168.04220, found 168.04000.

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Metalation Reactions of 1-Silacyclo-3-pentenes

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The metalation of a series of 1-silacyclo-3-pentenes was studied. The reaction depends critically on the substituent at the silicon. 1,1-Bis(4-*tert*-butylphenyl)-1-silacyclo-3-pentene was metalated cleanly to give the anion derived from proton abstraction on the cyclopentenyl ring. The regioselectivity of the reaction of the 1-silacyclopentenyl anion with electrophiles was examined and found to be influenced by the steric size of the electrophile.

The α-silylallyl anion, derived from the metalation of allylsilanes, has found considerable application[1] in organic synthesis; however, the corresponding anion **2** derived from the metalation of 1-silacyclo-3-pentene **1** so far has not been studied. The anion **2** is potentially useful in synthesis since it is a polymetallic reagent with multiple reactive sites at carbons 1, 3, and 4. Reaction of these sites with electrophiles can give variously substituted siloles that may serve as functionalized masked dienes.[2] Another point

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