benzene layers were combined, dried (Na_2SO_4), and evaporated to yield 0.9 g (90%) of a yellow oil which slowly crystallized. Recrystallization from EtOAc–cyclohexane afforded 8.0 g (80%) of white crystals: mp 71–75 °C; NMR ($CDCl_3$) δ 2.0 (m, 4 H), 4.3 (t, 2 H), 7.0–7.8 (m, 8 H). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55; S, 12.64. Found: C, 75.34; H, 5.51; S, 12.64.

9-Methoxy-9-(3-hydroxypropyl)thioxanthene (11). A solution of **9** (0.20 g, 0.6 mmol) in TFA (1 mL) was stirred at room temperature. The solution was deep red. After 2 h, MeOH (10 mL) was added and the resulting pale yellow solution was immediately added to vigorously stirred MeOH (30 mL) containing KOH (1.2 g). After 1 h of stirring, the volume of solution was evaporated to ca. 5 mL and Et_2O (20 mL) was added. The ether solution was washed twice with water, dried ($NaSO_4$), and evaporated to yield 0.15 g (88%) of a thick, yellow oil which by NMR was 85% of the desired **11**; NMR ($CDCl_3$) δ 1.4 (m, 2 H), 1.9 (m, 2 H), 2.4 (br exchangeable s, 1 H), 3.0 (s, 3 H), 3.3 (t, 2 H), 7.1–7.7 (m, 8 H). Addition of a small amount of *p*-TSA to the NMR tube converts the methyl ether to **12**.

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Registry No. 1a, 76583-73-8; **1b**, 76583-74-9; **3**, 76583-75-0; **4**, 76583-76-1; **5**, 76583-77-2; **6**, 76583-79-4; **8**, 492-22-8; **9**, 76583-80-7; **11**, 76583-81-8; **12**, 76583-82-9; **13**, 76583-87-4; 9-(3-chloropropyl)-thioxanthene, 25559-90-4; thioxanthene, 261-31-4; 3-bromopropanol, 627-18-9; 9-(2-methyl-3-chloropropyl)thioxanthene, 76583-83-0; 1-bromo-2-methyl-3-chloropropane, 6974-77-2; 9-cyano-9-(3-hydroxypropyl)thioxanthene, 76583-84-1; 9-cyanothioxanthene, 25559-83-5; 3-*tert*-butoxy-1-propyl bromide, 30418-76-9; 9-(3-*tert*-butoxy-1-propylene)thioxanthene, 76583-85-2.

Regiospecific Reactions of Some Vinylogous Ketene Acetals with Haloquinones and Their Regioselective Formation by Dienolization

Clément Brisson and Paul Brassard*

Département de chimie, Université Laval, Cité Universitaire, Québec, Canada G1K 7P4

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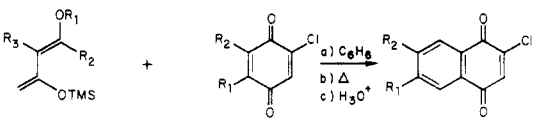
Regiospecific reactions of simple 1,3-bis(trimethylsiloxy)-1,3-butadienes with 2,5- and 2,6-dichlorobenzoquinones gave chloronaphthoquinones which, by applying the appropriate vinylketene acetal, provided various monomethyl ethers of isomeric polyhydroxyanthraquinones. The first total synthesis of macrosporin (**27**) was obtained in this way and the proposed structure for "cajaquinone" (**28**) found to be incorrect. Simple syntheses of 2-hydroxy-3-methylanthraquinone (**16**), phomarin (**19**), soranjidiol (**22**) and other naturally occurring quinones are also described. The dienolization of 1-methoxy-2,4-pentanedione in the presence of chlorotrimethylsilane gave either 1- or 5-methoxy-2,4-bis(trimethylsiloxy)-1,3-pentadiene, depending upon the reaction conditions. Both dienes react with haloquinones, giving regiospecific products, e.g., tetra-*O*-methylerythrolaccin (**35**).

Vinylogous ketene acetals (1,3-dioxygenated butadienes) have been shown to be useful partners in cycloaddition reactions with quinones[1a-m] and on occasion to provide effective regiochemical control of this process.[1d,f,i-k] Juglone (5-hydroxynaphthoquinone) and its derivatives in particular give regiospecific products,[1d,k] but the orientation of addition induced by halogen substituents has been observed only in the case of hindered reagents such as 2,4-dioxygenated pentadienes[1i] (**3**, **4**).

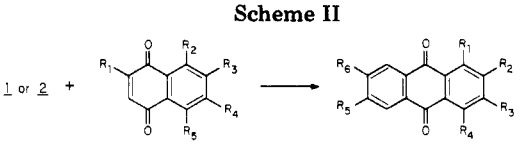
It has now been established that simple 1,3-bis(trimethylsiloxy)-1,3-butadienes (**1**, **2**) give analogous results with 2,5- and 2,6-dichlorobenzoquinones (**5**, **6**), providing chloronaphthoquinones as convenient intermediates for a second regiospecific annulation with other dienes such as vinylketene acetals (**23**, **26**). They also react directly with halonaphthoquinones to give various naturally occurring anthraquinones.

Scheme I



1 R_1 = TMS, R_2 = R_3 = H
2 R_1 = TMS, R_2 = H, R_3 = CH_3
3 R_1 = R_2 = CH_3, R_3 = H
4 R_1 = R_2 = CH_3, R_3 = CO_2CH_3
5 R_1 = Cl, R_2 = H
6 R_1 = H, R_2 = Cl
7 R_1 = H, R_2 = OH
8 R_1 = OH, R_2 = H
9 R_1 = CH_3, R_2 = OH
10 R_1 = OH, R_2 = CH_3

Scheme II



11 R_1 = Cl, R_2 = R_3 = R_4 = R_5 = H
12 R_1 = Cl, R_2 = OH, R_3 = R_4 = R_5 = H
13 R_1 = Cl, R_2 = OH, R_3 = R_5 = H, R_4 = CH_3
14 R_1 = Br, R_2 = OH, R_3 = CH_3, R_4 = H, R_5 = Cl
15 R_1 = R_2 = R_3 = R_4 = R_6 = H, R_5 = OH
16 R_1 = R_2 = R_3 = R_4 = H, R_5 = OH, R_6 = CH_3
17 R_1 = R_2 = R_3 = R_4 = H, R_5 = OCH_3, R_6 = CH_3
18 R_1 = R_5 = OH, R_2 = R_3 = R_4 = R_6 = H
19 R_1 = R_5 = OH, R_2 = R_4 = R_6 = H, R_3 = CH_3
20 R_1 = OH, R_2 = R_4 = R_6 = H, R_3 = CH_3, R_5 = OCH_3
21 R_1 = R_5 = OH, R_2 = CH_3, R_3 = R_6 = H, R_4 = Cl
22 R_1 = R_5 = OH, R_2 = CH_3, R_3 = R_4 = R_6 = H

The usual procedures used in combining ketene or vinylketene acetals with benzoquinones gave unsatisfactory results. An adduct formed in THF at −60 °C between diene **1** and quinone **6** was aromatized by being refluxed in methanol and gave a 14% yield of 2-chloro-6-meth-

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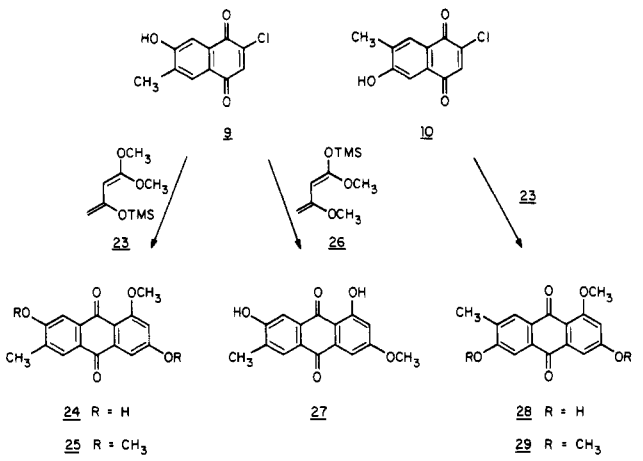
Scheme III



oxy-1,4-naphthoquinone (the methyl ether of **8**). A small amount of 2-chloro-5,6-dimethoxy-1,4-naphthoquinone was also isolated and undoubtedly resulted from a dienone–phenol-type of rearrangement involving an intermediate acetal.[2] Similar reaction mixtures treated with silica gel or formed in Me_2SO at room temperature gave the hydroxynaphthoquinone **8** with comparable efficiency (17–21%). It was eventually determined that the best results were obtained when the reactants were brought together in benzene at room temperature and the crude adduct was heated at 100–125 °C. Analogous conclusions were reached by using mixed ethers such 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene.

Under these conditions, (*E*)-1,3-bis(trimethylsiloxy)-1,3-butadiene[3] (**1**) and (*E*)-2-methyl-1,3-bis(trimethylsiloxy)-1,3-butadiene[4] (**2**) react regiospecifically with 2,5- and 2,6-dichlorobenzoquinones (**5**, **6**), giving only the corresponding naphthoquinone (**7**–**10**); thus diene **1** with benzoquinone **5** gives exclusively naphthoquinone **7** (Scheme I). The four compounds **7**–**10** appear to be new, and attempts to obtain one of them by other unambiguous means failed. The chlorination–dehydrochlorination of 6-hydroxy-1,4-naphthoquinone analogous to the sequence used previously for the preparation of 2-bromo-6-hydroxy-1,4-naphthoquinone[5] produced a mixture of isomers while the reaction of diene **1** with 2,6-dibromobenzoquinone gave only a small amount of 2,7-dihydroxyanthraquinone. Dienes **1** and **2**, however, combine regiospecifically with chloronaphthoquinones as is illustrated by the formation of natural products of established structure (Scheme II). The identity of quinone **9** (and consequently of **10**) was eventually confirmed by conversion to known substances (Scheme III).

(*E*)-1,3-Bis(trimethylsiloxy)-1,3-butadiene (**1**) with 2-chloro-1,4-naphthoquinone (**11**) gave the natural product 2-hydroxyanthraquinone[6] (**15**) while a fungicide, 1,6-dihydroxyanthraquinone[7] (**18**), was obtained with 3-chlorojuglone (**12**) as substrate. 3-Chloro-7-methyljuglone (**13**), prepared earlier from 2,6-dichlorobenzoquinone (**6**) and 1-methoxy-3-methyl-1-(trimethylsiloxy)-1,3-butadiene,[8] reacted with the same diene **1**, providing a very simple synthesis of phomarin[6,9,10] (**19**). Similarly, soranjidiol[6,11] (**22**) could be obtained advantageously in a 39% yield from 3-bromo-8-chloro-6-methyljuglone (**14**) after reductive dechlorination. (*E*)-2-Methyl-1,3-bis(trimethylsiloxy)-1,3-butadiene (**2**) behaved similarly and by reaction with 2-chloro-1,4-naphthoquinone (**11**), in particular, afforded an efficient synthesis of the natural product 2-hydroxy-3-methylanthraquinone (**16**) (Scheme II).

2- and 3-chloro-6-hydroxy-7-methyl-1,4-naphthoquinones **9** and **10** were found to be convenient intermediates for the subsequent formation of anthraquinones using dienes known to react regiospecifically.[1i,8,12] This not only confirmed the proposed structures of the naphthoquinones but also rendered possible the direct and unambiguous synthesis of some partially methylated polyhydroxylated anthraquinones. Thus 3-chloro-6-hydroxy-7-methyl-1,4-naphthoquinone (**9**) and 1,1-dimethoxy-3-(trimethylsiloxy)-1,3-butadiene[12] (**23**) gave 1-methoxy-3,7-dihydroxy-6-methylanthraquinone (**24**), the dimethyl ether **25** of which was identical with the corresponding derivative[13] of macrosporin[6,14,15] (**27**). The latter could be obtained, for the first time by synthesis, from the same naphthoquinone (**9**) and 1,3-dimethoxy-1-(trimethylsiloxy)-1,3-butadiene[8] (**26**). On the other hand, 2-chloro-6-hydroxy-7-methyl-1,4-naphthoquinone (**10**) and diene **23** gave 1-methoxy-3,6-dihydroxy-7-methylanthraquinone (**28**), a structure recently proposed for "cajaquinone".[16] The physical and spectroscopic properties of synthetic **28** are at complete variance with those published for the natural product, the identity of which is therefore obviously in error. The dimethyl ether of this compound (**29**) is also quite different from the isomeric substance **25** (Scheme III).

There are many examples of useful dienes produced from β-keto aldehydes, 2,4-pentanediones, and 1,3-cyclohexanediones;[1] however, the dienolization of unsymmetrically functionalized diones does not seem to have been much considered. Under conditions favoring thermodynamically equilibrated silyl ethers,[17] 1-methoxy-2,4-pentanedione[18] (**30**) gave, after distillation, only the fully conjugated 5-methoxy-2,4-bis(trimethylsiloxy)-1,3-pentadiene (**31**). Reaction of this synthon with the usual dienophiles proceeds satisfactorily but is of limited use in the synthesis of naturally occurring quinones. Thus 3-chlorojuglone (**12**), for example, gives a 45% yield of 3,8-dimethoxy-1-(methoxymethyl)anthraquinone (**32**) after methylation of the crude product.

Kinetic deprotonation of the same dione **30** using LDA followed by silylation led to the formation of 1-methoxy-2,4-bis(trimethylsiloxy)-1,3-pentadiene (**33a,b**) as a mixture of unidentified stereoisomers. The nature of the reagent was confirmed by reaction with 3-chloro-5,7-dimethoxy-1,4-naphthoquinone (**34**) (or more rapidly with 3-chloro-5-hydroxy-7-methoxy-1,4-naphthoquinone) which provid-

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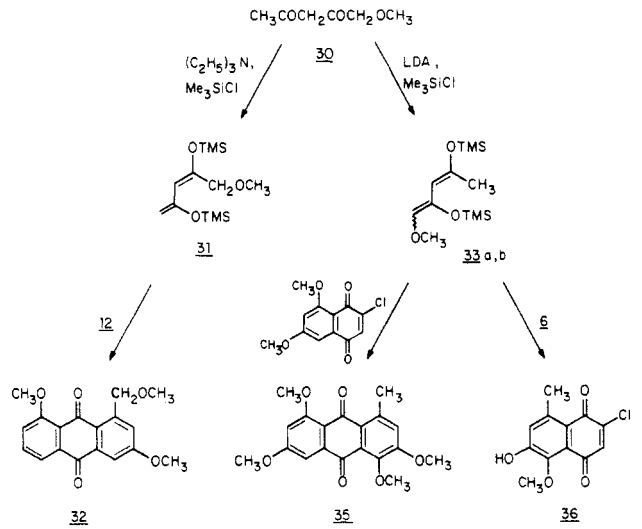
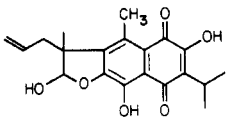
Scheme IV



ed, after methylation, the known tetramethyl ether[19] of erythrolaccin (**35**). The process is completely regiospecific in spite of the fact that the electronic effects of two oxygenated functions effectively are canceled out.

The principal objective in elaborating this compound was the synthesis of the basic structure of coleon A[20] (**37**).



In this perspective, dienes **33a,b** were combined with 2,6-dichlorobenzoquinone (**6**) in THF at −72 °C and afforded an 11% yield of the expected but somewhat labile 2-chloro-6-hydroxy-5-methoxy-8-methyl-1,4-naphthoquinone (**36**); however, when the process was conducted in ether at −120 °C, its efficiency could be increased to 43% (Scheme IV).

Experimental Section

All melting points were taken for samples in capillary tubes with a Thomas-Hoover apparatus and are not corrected. The IR and UV spectra were determined on Beckman Model IR-12 and Model DK-1A spectrophotometers, respectively. NMR spectra were recorded with a Bruker HX-90 spectrometer using tetramethylsilane as internal standard. Mass spectra were obtained with a Varian M-66 spectrometer. Woelm silica gel (activity III) for dry column chromatography was used throughout in a product to adsorbent ratio of 1:50. All UV spectra were recorded with solutions in redistilled 95% ethanol.

3-Chloro-6-hydroxy-1,4-naphthoquinone (7). To a well-agitated solution of 2,5-dichlorobenzoquinone (**5**; 354 mg, 2.00 mmol) in anhydrous benzene (5 mL) was added, at room temperature, (*E*)-1,3-bis(trimethylsiloxy)-1,3-butadiene[3] (**1**; 574 mg, 2.50 mmol) in the same solvent (5 mL). After the mixture was stirred for 1 h, xylene (10 mL) was added and solvent distilled off until the boiling point reached 125 °C. The reaction mixture was refluxed for 1.5 h, evaporated, dissolved in THF (10 mL) and 5% aqueous HCl (3 mL), refluxed again for 20 min, and finally taken up in chloroform (100 mL). Purification of the crude product by chromatography (benzene–ethyl acetate, 10:1) gave the expected quinone **7**: 368 mg (88%); mp 217–218 °C (1,2-dichloroethane); λ_{max} 218 nm (log ϵ 4.10), 268 (4.37), 407 (3.41); ν_{max} (KBr) 3395 and 3350 (OH), 1672 and 1648 (C=O), 1605 and 1582 (C=C) cm^{-1}; NMR [$(CD_3)_2SO$] δ 7.19 (1 H, dd, J = 8.0, 2.5 Hz, 7-H), 7.34 (1 H, s, 2-H), 7.36 (1 H, d, J = 2.5 Hz, 5-H), 7.87 (1 H, d, J = 8.0 Hz, 8-H), 11.09 (1 H, s, 6-OH); mass spectrum, m/e 210/208 (M^+). Anal. Calcd for $C_{10}H_5ClO_3$: C, 57.58; H, 2.42; Cl, 17.00. Found: C, 57.48; H, 2.69; Cl, 17.19.

2-Chloro-6-hydroxy-1,4-naphthoquinone (8). A similar reaction with 2,6-dichlorobenzoquinone (**6**) gave naphthoquinone **8**: 327 mg (79%); mp 229–230 °C (1,2-dichloroethane); λ_{max} 215 nm (log ϵ 3.99), 270 (4.32), 415 (3.29); ν_{max} (KBr) 3380 (OH), 1668 (C=O), 1588 and 1575 (C=C) cm^{-1}; NMR [$(CD_3)_2SO$] δ 7.17 (1 H, dd, J = 8.0, 2.5 Hz, 7-H), 7.27 (1 H, d, J = 2.5 Hz, 5-H), 7.38 (1 H, s, 3-H), 7.93 (1 H, d, J = 8.0 Hz, 8-H), 11.16 (1 H, s, 6-OH); mass spectrum, m/e 210/208 (M^+). Anal. Calcd for $C_{10}H_5ClO_3$: C, 57.58; H, 2.42; Cl, 17.00. Found: C, 57.53; H, 2.54; Cl, 16.63. For the 6-methyl ether: mp 167–168 °C; mass spectrum, m/e 224/222 (M^+).

3-Chloro-6-hydroxy-7-methyl-1,4-naphthoquinone (9). The residue of an analogous reaction between 2,5-dichlorobenzoquinone (**5**, 2.00 mmol) in dry benzene (5 mL) and (*E*)-2-methyl-1,3-bis(trimethylsiloxy)-1,3-butadiene[4] (**2**; 611 mg, 2.50 mmol) in the same solvent (10 mL) was pyrolyzed at 100 °C for 1–2 h, hydrolyzed, worked up in the usual way, and gave quinone **9**: 348 mg (78%); mp 236–237 °C (1,2-dichloroethane); λ_{max} 217 nm (log ϵ 4.80), 271 (4.51), 420 (3.42); ν_{max} (KBr) 3310 (OH), 1670 and 1643 (C=O), 1563 (C=C) cm^{-1}; NMR [$(CD_3)_2SO$] δ 2.22 (3 H, s, 7-CH_3), 7.27 (1 H, s, 2-H), 7.36 (1 H, s, 5-H), 7.68 (1 H, s, 8-H), 11.02 (1 H, br s, 6-OH); mass spectrum, m/e 224/222 (M^+). Anal. Calcd for $C_{11}H_7ClO_3$: C, 59.35; H, 3.17; Cl, 15.92. Found: C, 59.05; H, 3.20; Cl, 16.23.

2-Chloro-6-hydroxy-7-methyl-1,4-naphthoquinone (10). The crude product obtained from a reaction similar to the foregoing, with 2,6-dichlorobenzoquinone (**6**; 2.00 mmol), was purified by chromatography (benzene–ethyl acetate, 20:1) and crystallization from methanol to give the expected quinone **10**: 252 mg (57%); mp 215 °C dec.; λ_{max} 217 nm (log ϵ 4.69), 273 (4.44), 407 (3.34); ν_{max} (KBr) 3380 (OH), 1662 (C=O), 1580 (C=C) cm^{-1}; NMR [$(CD_3)_2SO$] δ 2.22 (3 H, s, 7-CH_3), 7.26 (1 H, s, 5-H), 7.28 (1 H, s, 3-H), 7.71 (1 H, s, 8-H), 11.13 (1 H, br s, 6-OH); mass spectrum, m/e 224/222 (M^+). Anal. Calcd for $C_{11}H_7ClO_3$: C, 59.35; H, 3.17; Cl, 15.92. Found: C, 59.36; H, 3.20; Cl, 15.96.

2-Hydroxyanthraquinone (15). A solution of 2-chloro-1,4-naphthoquinone (**11**; 385 mg, 2.00 mmol) and diene **1** (2.50 mmol) in dry benzene (10 mL) was stirred at room temperature for 3 h and then refluxed for 14 h. Two additional portions of diene (0.50 mmol each) were introduced during this period. After the usual workup, quinone **15** was isolated by chromatography (benzene–ethyl acetate, 20:1) and crystallization from methanol: 265 mg (59%); mp 298–299 °C (lit.[6] mp 306 °C); NMR [$(CD_3)_2SO$] δ 7.21 (1 H, dd, J = 8.0, 3.0 Hz, 3-H), 7.47 (1 H, d, J = 3.0 Hz, 1-H), 7.81–8.20 (5 H, m, 4–8-H), 11.02 (1 H, br s, 2-OH); mass spectrum, m/e 224 (M^+). For the methyl ether [$(CH_3)_2SO_4$–K_2CO_3–$(CH_3)_2CO$], mp 196–197 °C (lit.[6] mp 195–196 °C).

2-Hydroxy-3-methylanthraquinone (16). A similar reaction mixture with diene **2** (2.50 mmol) was refluxed for 36 h. After the usual workup, quinone **16** was obtained by crystallization from ethanol: 382 mg (80%); mp 294–295 °C (lit.[6] mp 302 °C); mass spectrum, m/e 238 (M^+). Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.82; H, 3.97. Acetate, mp 181–182 °C (lit.[21] mp 177 °C). Methyl ether **17** [$(CH_3)_2SO_4$–K_2CO_3–$(CH_3)_2CO$], mp 197–198 °C (lit.[22] mp 197 °C).

1,6-Dihydroxyanthraquinone (18). A suspension of 3-chloro-5-hydroxy-1,4-naphthoquinone[23] (**12**; 312 mg, 1.50 mmol) and diene **1** (2.00 mmol) in dry benzene (15 mL) was stirred for 4.5 h. Another portion of diene (0.50 mmol) was added, and the mixture was refluxed for 6.5 h. After the usual workup, quinone **18** was obtained by crystallization from 1,2-dichloroethane and treatment of the mother liquor by chromatography (benzene–ethyl acetate): 332 mg (93%); mp 271.5–272.5 °C (lit.[24] mp 269 °C); ν_{max} (KBr) 3370 (OH), 1660 (C=O), 1628 (chelated C=O), 1593 and 1578 (C=C) cm^{-1}; NMR [$(CD_3)_2SO$] δ 7.13–7.82 (5 H, m,

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2-5,7-H), 8.03 (1 H, d, J = 9.0 Hz, 8-H), 12.67 (1 H, br s, 1-OH); mass spectrum, m/e 240 (M^+). Diacetate, mp 205–206 °C.

1,6-Dihydroxy-3-methylanthraquinone (Phomarin, 19). A similar reaction mixture with 3-chloro-5-hydroxy-7-methyl-1,4-naphthoquinone[8] (**13**, 1.50 mmol) and diene **1** (2.00 mmol) was refluxed for 2 h and evaporated, and the residue was heated at 170 °C for 4 h. The usual workup gave the crude quinone **19** which was purified by chromatography (benzene–ethyl acetate) and recrystallized from petroleum ether (bp 30–60 °C): 298 mg (78%); mp 263–264 °C (lit. mp 259.5–260.5 °C,[9] 264–266 °C[10]); NMR [$(CD_3)_2SO$] δ 2.37 (3 H, s, 3-CH_3), 7.07–7.44 (4 H, m, 2,4,5,7-H), 8.04 (1 H, d, J = 9.0 Hz, 8-H), 12.64 (1 H, br s, 1-OH); mass spectrum, m/e 254 (M^+). Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96. Found: C, 70.63; H, 4.29. This substance was found to be identical (mixture melting point, IR spectrum, and TLC in three solvent systems) with a sample of the authentic material. The 6-methyl ether **20** [$(CH_3)_2SO_4$–K_2CO_3–DME, 14 days] was purified by chromatography (benzene) and crystallization from ethanol: 81% yield; mp 187.0–187.5 °C (lit.[9] mp 193 °C); NMR ($CDCl_3$) δ 2.43 (3 H, s, 3-CH_3), 3.96 (3 H, s, 6-OCH_3), 7.02–7.66 (4 H, m, 2,4,5,7-H), 8.17 (1 H, d, J = 8.5 Hz, 8-H), 12.64 (1 H, s, 1-OH); mass spectrum, m/e 268 (M^+). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.93; H, 4.56.

4-Chloro-1,6-dihydroxy-2-methylanthraquinone (21). To a solution of 3-bromo-8-chloro-5-hydroxy-6-methyl-1,4-naphthoquinone[25] (**14**; 302 mg, 1.00 mmol) in dry benzene (5 mL) was added rapidly diene **1** (460 mg, 2.00 mmol) in the same solvent (2 mL). The mixture was stirred for 1 h at room temperature, refluxed for 4 h, and evaporated, and the residue was pyrolyzed at 110 °C for 2 h. Purification of the crude product by chromatography (benzene–ethyl acetate, 20:1) and crystallization from ethanol gave quinone **21**: 211 mg (73%); mp 301–303 °C; λ_{max} 223 nm (log ϵ 4.50), 273 (4.45), 280 (sh, 4.40), 410 (sh, 3.93), 420 (3.93), 430 (sh, 3.92); ν_{max} (KBr) 3390 (OH), 1675 (C=O), 1638 (chelated C=O), 1604 and 1583 (C=C) cm^{-1}; NMR [$(CD_3)_2SO$] δ 2.13 (3 H, s, 2-CH_3), 7.06 (1 H, dd, J = 8.5, 2.5 Hz, 7-H), 7.23 (1 H, d, J = 2.5 Hz, 5-H), 7.39 (1 H, s, 3-H), 7.83 (1 H, d, J = 8.5 Hz, 8-H), 13.59 (1 H, s, 1-OH); mass spectrum, m/e 290/288 (M^+). Anal. Calcd for $C_{15}H_9ClO_4$: C, 62.41; H, 3.14; Cl, 12.28. Found: C, 62.14; H, 2.99; Cl, 12.04.

1,6-Dihydroxy-2-methylanthraquinone (Soranjidiol, 22). The foregoing quinone **21** was dehalogenated according to the method of Yosioka et al.[26] A mixture of **21** (360 mg, 1.25 mmol), NaOH (1.1 g), ethanol (40 mL), and water (40 mL) was stirred under nitrogen for 24 h while sodium hydrosulfite (6.0 g) was added in four portions. Oxygen was bubbled through the mixture (4 h) which was then poured into water (200 mL), acidified, and extracted with ether (2 × 200 mL). Purification of the crude material by chromatography (benzene–ethyl acetate, 20:1) and crystallization from aqueous ethanol give soranjidiol (**22**): 170 mg (53%); mp 274–275 °C (lit. mp 275,[6] 283,[11] 287–288 °C[27]). The substance was indistinguishable from an authentic sample (mixture melting point, IR spectrum and TLC in several solvent systems): NMR [$(CD_3)_2SO$] δ 2.27 (3 H, s, 2-CH_3), 7.13–8.11 (5 H, m, 3–5,7,8-H), 13.06 (1 H, s, 1-OH); mass spectrum, m/e 254 (M^+). Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96. Found: C, 70.60; H, 4.15.

3,7-Dihydroxy-1-methoxy-6-methylanthraquinone (24). To a suspension of 3-chloro-6-hydroxy-7-methyl-1,4-naphthoquinone (**9**; 334 mg, 1.50 mmol) in dry benzene (10 mL) was added at room temperature 1,1-dimethoxy-3-(trimethylsiloxy)-1,3-butadiene[12] (**23**; 808 mg, 4.00 mmol) in the same solvent (2 mL). The reaction mixture was stirred for 40 min (another 0.50-mmol portion of diene being added during this interval), evaporated, dissolved in absolute methanol (10 mL), refluxed for 1 h, evaporated again, and pyrrolyzed at 100 °C. Quinone **24** was then washed with methanol and crystallized from pyridine: 315 mg (74%); mp >330 °C; λ_{max} 225 nm (log ϵ 4.36), 283 (4.54), 303 (sh, 4.20), 370 (3.86); ν_{max} (KBr) 3250 (OH), 1660 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 67.45; H, 3.92. Diacetate: mp 226–227 °C; NMR ($CDCl_3$) δ 2.33, 2.36, and 2.38 (3 × 3 H, 3 s, 6-CH_3 and 3,7-OAc), 4.02 (3 H, s, 1-OCH_3), 7.11 (1 H, d, J = 2.5 Hz, 2-H), 7.68 (1 H, d, J = 2.5 Hz, 4-H), 7.89 (1 H, s, 8-H), 8.12 (1 H, s, 5-H).

1,3,7-Trimethoxy-6-methylanthraquinone (macrosporin 1,7-dimethyl ether) (**25**) [$(CH_3)_2SO_4$–K_2CO_3–$(CH_3)_2CO$]: mp 269–270 °C (lit.[28] mp 270–271 °C); NMR (CF_3CO_2D) δ 2.41 (3 H, s, 6-CH_3), 4.11, 4.19, and 4.34 (3 × 3 H, 3 s, 1,3,7-OCH_3), 6.95 (1 H, d, J = 2.0 Hz, 2-H), 7.62 (1 H, d, J = 2.0 Hz, 4-H), 7.71 (1 H, s, 8-H), 8.01 (1 H, s, 5-H); mass spectrum, m/e 312 (M^+). Anal. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16. Found: C, 69.02; H, 5.26.

1,7-Dihydroxy-3-methoxy-6-methylanthraquinone (Macrosporin, 27). An analogous reaction mixture with 1,3-dimethoxy-1-(trimethylsiloxy)-1,3-butadiene[8] (**26**; 4.0 mmol, in two portions) was stirred for 105 min and evaporated, and the residue was heated at 100 °C overnight, hydrolyzed in the usual way, and washed with methanol. Crystallization of the crude product from pyridine gave macrosporin (**27**): 365 mg (83%); mp 304–306 °C dec (lit.[28] mp 301–305 °C). This substance was indistinguishable from an authentic sample (mixture melting point, IR spectrum, and TLC in five solvent systems). Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 67.38; H, 4.29. Diacetate, mp 215–217 °C (lit.[28] mp 213–216 °C).

3,6-Dihydroxy-1-methoxy-7-methylanthraquinone ("Cajaquinone",[16] 28). A similar reaction with 2-chloro-6-hydroxy-7-methyl-1,4-naphthoquinone (**10**, 1.00 mmol) and 1,1-dimethoxy-3-(trimethylsiloxy)-1,3-butadiene (**23**, 3.00 mmol) gave anthraquinone **28** after crystallization from pyridine: 234 mg (82%); mp >330 °C; λ_{max} 218 nm (log ϵ 4.38), 285 (4.63), 298 (4.11), 405 (3.59); ν_{max} (KBr) 3380 and 3185 (OH), 1665 (C=O), 1598 (C=C) cm^{-1}; NMR (CF_3CO_2D) δ 2.47 (3 H, s, 7-CH_3), 4.42 (3 H, s, 1-OCH_3), 7.11 (1 H, d, J = 2.0 Hz, 2-H), 7.77 (1 H, d, J = 2.0 Hz, 4-H), 7.84 (1 H, s, 5-H), 8.31 (1 H, s, 8-H). Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 67.47; H, 4.18.

1,3,6-Trimethoxy-7-methylanthraquinone (**29**) [$(CH_3)_2SO_4$–K_2CO_3–$(CH_3)_2CO$]: mp 227.5–228.5 °C; mass spectrum, m/e 312 (M^+).

5-Methoxy-2,4-bis(trimethylsiloxy)-1,3-pentadiene (31). Pentadiene **31** (21.9 g, 80%) was obtained from 1-methoxy-2,4-pentanedione[18] (**30**; 13.0 g, 0.100 mol), chlorotrimethylsilane (43.2 g, 0.400 mol), triethylamine (44.0 g, 0.440 mol), and zinc chloride (0.80 g) according to the method of Danishefsky and Kitahara:[1e] bp 82–86 °C (0.8 mm); ν_{max} (film) 1650 (diene), 840 (Si–C, str) cm^{-1}; NMR ($CDCl_3$) δ 0.20 and 0.23 (2 × 9 H, 2 s, 2,4-OSi $(CH_3)_3$), 3.28 (3 H, s, 5-OCH_3), 3.75 (2 H, s, 5-H_2), 4.36 and 4.95 (2 × 1 H, 2 d, J = 1.5 Hz, 1-H_2), 4.79 (1 H, s, 3-H); mass spectrum, m/e 276/275/274 (M^+). Anal. Calcd for $C_{12}H_{26}O_3Si_2$: C, 52.51; H, 9.55. Found: C, 52.50; H, 9.25.

3,8-Dimethoxy-1-(methoxymethyl)anthraquinone (32). To a solution of 3-chloro-5-hydroxy-1,4-naphthoquinone (**12**; 312 mg, 1.50 mmol) in dry benzene (5 mL) was added pentadiene **31** (686 mg, 2.50 mmol) in the same solvent (2 mL). The mixture was stirred at room temperature for 3 h, evaporated, filtered on silica gel and methylated in the usual way. The crude material was purified by chromatography (benzene–ethyl acetate, 10:1) and crystallization from CCl_4 and gave quinone **32**: 212 mg (45%); mp 198.0–198.5 °C; λ_{max} 216 nm (log ϵ 4.50), 270 (4.49), 385 (3.79); ν_{max} (KBr) 1657 and 1648 (C=O), 1595 and 1585 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 3.56 (3 H, s, 1-CH_2OCH_3), 3.95 and 4.02 (2 × 3 H, 2 s, 3,8-OCH_3), 5.07 (2 H, s, 1-CH_2OCH_3), 7.24–7.92 (5 H, m, 2,4-7-H); mass spectrum, m/e 312 (M^+). Anal. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16. Found: C, 68.96; H, 5.20.

1-Methoxy-2,4-bis(trimethylsiloxy)-1,3-pentadienes (33a,b). Pentadienes **33a,b** were obtained as a mixture of stereoisomers (32–54%) from 1-methoxy-2,4-pentanedione (**30**; 6.5 g, 0.050 mol) in dry THF (20 mL), lithium diisopropylamide (0.100 mol), and chlorotrimethylsilane (13.0 g, 0.120 mol) according to Ainsworth et al.[29] (method 2): bp 70–77 °C (0.3 mm); ν_{max} (film) 1659 and 1620 (diene), 830 (Si–C, str) cm^{-1}; NMR ($CDCl_3$) δ 0.15, 0.20, and 0.16, 0.23 (18 H, 4 s, 2,4-OSi$(CH_3)_3$), 1.83 and 1.84 (3 H, 2 s, 5-H_3), 3.53 and 3.56 (3 H, 2 s, 1-OCH_3), 5.22, 5.83, 4.67, and 6.22 (2 H, 4 s, 1,3-H); mass spectrum, m/e 276/275/274 (M^+). Anal. Calcd

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for $C_{12}H_{26}O_3Si_2$: C, 52.51; H, 9.55. Found: C, 52.28; H, 9.63.

1,3,5,6-Tetramethoxy-8-methylanthraquinone (Erythrolaccin Tetramethyl Ether, 35). A suspension of 3-chloro-5,7-dimethoxy-1,4-naphthoquinone[30] (**34**; 379 mg, 1.50 mmol) and pentadienes (**33a,b**; 549 mg, 2.00 mmol) in dry benzene (12 mL) was refluxed for 21 days (an extra portion of diene (1.00 mmol) was added after 6 days). The residue was heated at 110 °C for 4 h, hydrolyzed, and methylated in the usual way. Purification of the crude product by chromatography (chloroform) and crystallization from methanol gave the tetramethyl ether **35**: 243 mg (47%); mp 155–156 °C (lit.[19] mp 159 °C); mass spectrum, *m/e* 342 (M^+). This substance had physical and spectroscopic characteristics very close to the published data.

2-Chloro-6-hydroxy-5-methoxy-8-methyl-1,4-naphthoquinone (36). Pentadienes **33a,b** (686 mg, 2.50 mmol) were added to a suspension of 2,6-dichlorobenzoquinone (**6**; 354 mg, 2.00 mmol) in ether (30 mL) at −120 °C. After being stirred for 15 min, the mixture was allowed to warm to room temperature (2 h). The solvent was evaporated and the residue refluxed in methanol (20 mL) for 30 min. Naphthoquinone **36** was isolated by chromatography (benzene) and crystallization from CCl_4: 217 mg (43%); mp 154.0–155.5 °C; λ_{max} 218 nm (log ϵ 4.27), 275 (3.82), 298 (sh, 3.65), 420 (3.16); ν_{max} (KBr) 3300 (OH), 1650 (C=O), 1618 and 1587 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 2.69 (3 H, s, 8-CH_3), 3.91 (3 H, s, 5-OCH_3), 6.60 (1 H, br s, 6-OH), 6.81 (1 H, s, 7-H), 7.07 (1 H, s, 3-H); mass spectrum, *m/e* 254/252 (M^+). This substance is somewhat unstable and correct analyses could not be obtained.

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Registry No. **1**, 61838-70-8; **2**, 63446-78-6; **5**, 615-93-0; **6**, 697-91-6; **7**, 69119-29-5; **8**, 76665-65-1; **8** methyl ether, 76665-66-2; **9**, 76665-67-3; **10**, 76665-68-4; **11**, 1010-60-2; **12**, 18855-92-0; **13**, 62993-89-9; **14**, 52431-62-6; **15**, 605-32-3; **15** methyl ether, 3274-20-2; **16**, 17241-40-6; **16** acetate, 17241-41-7; **17**, 17241-42-8; **18**, 569-10-8; **18** diacetate, 75312-34-4; **19**, 6866-87-1; **20**, 34425-59-7; **21**, 76665-69-5; **22**, 518-73-0; **23**, 61539-61-5; **24**, 71241-94-6; **24** diacetate, 76665-70-8; **25**, 71241-95-7; **26**, 74272-66-5; **27**, 22225-67-8; **27** diacetate, 22225-68-9; **28**, 76665-71-9; **29**, 76665-72-0; **30**, 6290-50-2; **31**, 76665-73-1; **32**, 76665-74-2; **33a,b**, 76665-75-3; **34**, 57165-99-8; **35**, 801-96-7; **36**, 76665-76-7.

Oxidation of 1,5-Naphthalenediol and Its Methyl Ether: Preparation of Juglone Methyl Ether Monoacetal[1]

David J. Crouse, Margaret M. Wheeler, Marti Goemann, Paul S. Tobin, Swapan K. Basu, and Desmond M. S. Wheeler*

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588

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Thallium trinitrate (TTN) oxidizes 1,5-naphthalenediol (**1a**) and its monomethyl ether (**1b**) in good yield to juglone (**2a**) and its methyl ether (**2b**), respectively. Oxidation of **1b** with TTN in a mixture of ethylene glycol and trimethyl orthoformate gave **2c** (the 4-monoacetal of **2b**), which is a promising intermediate in the synthesis of daunomycinone (**3a**) and some of its analogues. This is the first direct oxidation of a para-unsubstituted phenol to a monoacetal of a quinone.

For some years the synthesis of daunomycinone (**3a**; see Chart I), which is convertible into the important anticancer (and cardiotoxic) antibiotic adriamycin (**3b**), has been studied by many research groups.[2] We have been interested in devising a DCAB regioselective route to **3a** and some of its analogues, e.g., **3c** and the tricyclic compound **4**.[3] A logical starting point is the readily available diol **1a**. Two approaches are being examined: in the first the methyl ether **1b**[4,5] is acylated at C_2 via a photo-Fries rearrangement, and then the oxygen at C_4 is introduced;[6] in the second, which is described in this paper, the oxygen at C_4 is introduced in **1** to give a compound in which further substituents on the quinone ring can be introduced regioselectively.

As **2b**, the methyl ether of juglone, does not undergo addition at the double bond regioselectively,[7] we originally planned to reduce β-dihydrojuglone (**5**) regioselectively at C_4[8] and later acylate at C_2. However, in our hands the reduction of **5** was not selective and the route was aban-

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