Friedel–Crafts Condensations with Maleic Anhydrides. III.[1] The Synthesis of Polyhydroxylated Naphthoquinones

RICHARD HUOT AND PAUL BRASSARD

Département de Chimie, Université Laval, Québec, Québec

Received August 10, 1973

The condensation of hydroquinone ethers with an excess of dihalomaleic anhydrides has been found to give particularly good yields of dihalonaphthazarins. The etherification of the latter and the nucleophilic substitution of 2,3-dichloronaphthoquinones have been examined. Finally the structures of the products obtained from the Fries rearrangement of polyacetoxynaphthalenes have been definitively established.

La condensation d'éthers d'hydroquinones avec un excès d'anhydrides dihalogénomaléiques donne des rendements particulièrement élevés en dihalogénonaphtazarines. La méthylation de ces substances et la substitution nucléophile de dichloro-2,3 naphtoquinones ont été étudiées. Enfin la structure des produits obtenus lors de la transposition de Fries de polyacétoxynaphtalènes a été établie de façon définitive.

Can. J. Chem., **52**, 838 (1974)

Few methods exist for the formation of naphthazarins and none of these are very satisfactory. The syntheses of substituted compounds of this type (whether natural or otherwise), in spite of their apparent simplicity, are therefore usually quite tedious processes. We have attempted to improve the preparation of the basic structure and in principle render its derivatives more readily accessible.

The Preparation and Structure of Dihalonaphthazarins and of the Corresponding Ethers

Since its discovery by Zahn and Ochwat (1), the preparation of naphthazarins by the condensation of hydroquinones (or their ethers) (2) and maleic anhydrides in a molten mixture of aluminum and sodium chlorides has been frequently used. This method remains the most simple way of obtaining many naphthazarins but it suffers the serious inconvenience of giving rather low yields. We have found that the use of excess dichloromaleic anhydride can increase the yield quite spectacularly, in one case to 97%. Stoichiometric amounts of anhydride, dibromomaleic anhydride, and substituted hydroquinones give lower yields. Since the halogens can readily be removed (3), this modification also constitutes a convenient synthesis of some halogen-free naphthazarins.

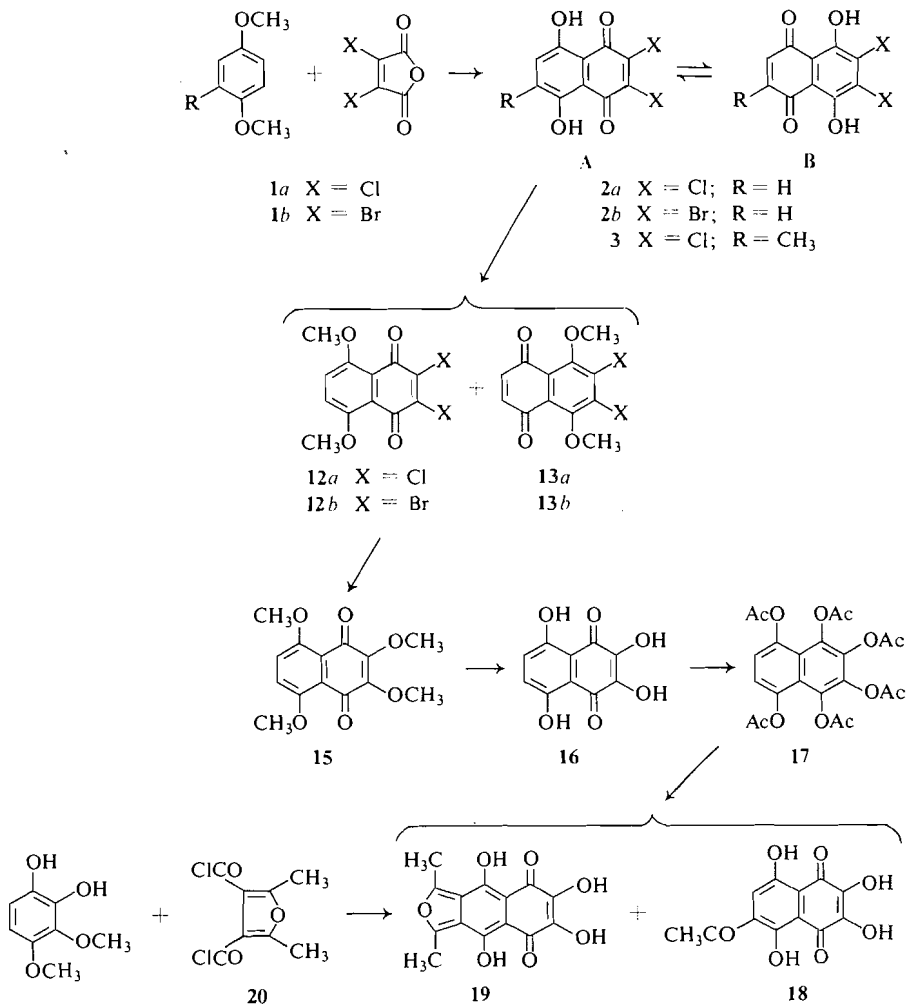
The determination of oxidation–reduction potentials of quinones (4) and the analysis of the n.m.r. spectra of naphthazarins (5)[2] have shown that the latter exist mainly in the tautomeric form with the electron-withdrawing groups in the aromatic ring. These results suggest that the predominant tautomer of 2,3-dihalonaphthazarins should be **B** (Scheme 1). However the n.m.r. spectra of **2***a*, **2***b*, and **3** show only one signal at δ 7.33, 7.31, an 7.12, respectively, for ring protons and indicate that these compounds exist mainly with the halogens in the quinoid ring. (The spectrum of **3** could seem ambiguous but is in good agreement with other well established structures such as 6-ethyl-2-hydroxynaphthazarin, δ 7.13 (7-CH) (5).) The resonance effects which seem to predominate over other considerations in these cases apparently were not taken into account in earlier works.

The etherification of naphthazarins has not been studied extensively. Brass *et al.* (6) were not able to determine which isomer was isolated after the etherification of 2,3-dibromonaphthazarin. Bruce and Thomson (3) obtained two products by the methylation of chloronaphthazarin but the structure of only one was established. All other etherifications of naphthazarins yielded only one isomer. Hardegger *et al.* (7) however obtained both from javanicin but in this case the electronic effects of the substituents compete effectively.

We have methylated two 2,3-dihalonaphtha-

[1]For parts I and II see refs. 23 and 24, respectively.

[2]Halogenated naphthazarins are not specifically mentioned here.



SCHEME I

zarins using methyl iodide and silver oxide and found that both isomers are formed. The main product invariably corresponds to the only discernible tautomer of the starting material. Furthermore these experiments established that a rapid etherification of the less stable tautomer plays an important role in this process.

Acetylation of a number of naphthazarins gives quite different results. This reaction with 2,3-dimethyl-, 2,3-dichloro-, 2,3-dibromo-, and 2,3-dibromo-6-methylnaphthazarins yields only the isomer corresponding to the most stable tautomer as shown by n.m.r. spectroscopy. Substrates with competing electronic effects such as 2-methyl-6- and 7-chloronaphthazarin give mixtures of isomers.

The Nucleophilic Substitution of Polyhalogenated Quinones

Since the main purpose in preparing the foregoing compounds was the synthesis of polyhydroxylated naphthoquinones, we have attempted, with various substrates, to find methods of improving the substitution of vicinal halogens.

The nucleophilic substitution of chloranil (**4**) even with strong bases (alkoxides and hydroxides) gives a mixture of the 2,5- and 2,6-disubstituted products (8). Although these undergo subsequent displacement to the completely substituted compound, the direct formation of tetramethoxybenzoquinone (**9**) using methoxide does not seem to have been recorded. The substitution of chloranil by methanol using potassium fluoride

as catalyst is claimed to yield only the 2,5-disubstituted product (9); we have repeated this procedure and found three products: trichloromethoxy- (**5**) (10%), 2,5-dichloro-3,6-dimethoxy- (**6**) (60%), and 2,6-dichloro-3,5-dimethoxybenzoquinone (**7**) (30%). When this reaction is carried out in a sealed tube at 110°, mixtures of chlorotrimethoxybenzoquinone (**8**) and tetramethoxybenzoquinone (**9**) are obtained. All of the foregoing substitution products are readily separated by column chromatography on silica gel (Table 1).

Although 2,3-dimethoxynaphthoquinone (**11**) is available from the dichloro compound **10** with sodium methoxide (10), a milder substitution was attempted. A direct displacement by methanol and potassium carbonate gave only 50% of the expected quinone **11** but when 2,3-dichloronaphthoquinone was converted to the diazido compound (11) (in a nearly quantitative yield) and the latter treated with potassium carbonate in boiling methanol, an 83% yield of **11** was obtained. The method is not applicable to chloranil as the substrate decomposes completely. Many attempts at direct substitution on dichloronaphthazarins confirmed the earlier findings as to the difficulty of this operation (12, 13). However the corresponding ether **12***a* was found to undergo efficient substitution in the presence of methoxide.

The Fries Rearrangement of Polyacetoxynaphthalenes

By diverse combinations of processes (reduction, nucleophilic and electrophilic substitution, etc.), a large number of polyhydroxynaphthoquinones are in principle readily accessible by the use of the foregoing intermediates. We have chosen the synthesis of 6-acetyl-2,3-dihydroxynaphthazarin (**18**) to illustrate the versatility of the method since this compound was once claimed to be a natural product (14) but was never adequately described (widely divergent m.p.'s have been attributed to the starting material, 1,2,3,4,5,8-hexaacetoxynaphthalene (15, 16); the end product gave an ambiguous analysis (16) and its m.p. was eventually found to indicate a mixture).

TABLE 1. The substitution of chloranil

Substrate	Conditions	Yield (%) 6 and 7	8	9
4	5 h at 95°	53	27	0
4	7 h at 110°	7	47	27
4	24 h at 110°	0	27	23
6	6 h at 105°	0	41	21
7	6 h at 105°	0	43	55

The hexaacetate of leucospinazarin (**17**) was subjected to various modifications of the Fries rearrangement and gave two products, one of which is undoubtedly the expected acetylspinazarin (**18**). The other appeared to be the furan resulting from a cyclization of the intermediate diacetyl derivative. An analogous structure has been proposed by Cort and Rodriguez (17) for a product obtained from 1,4,5,8-tetraacetoxynaphthalene. We have established both structures are correct by unambiguous syntheses. 1,3-Dimethylnaphtho[2,3-*c*]furan-4,9-quinone is prepared readily by the method of Nightingale and Sukornick (18) but the 5,8-dihydroxy derivative could be obtained only by condensing the substrates in a molten mixture of aluminum and sodium chlorides (Scheme 1).

Experimental

Dihalonaphthazarins

2,3-Dichloronaphthazarin (2a)

To a molten mass of $AlCl_3$ (142 g) and NaCl (28.3 g) at 140–150°, was added in portions a mixture of *p*-dimethoxybenzene (16.6 g) and dichloromaleic anhydride (**1***a*) (40.1 g). The temperature was then raised to 170–175° for 1–2 min and the dark red melt was allowed to cool, hydrolyzed with water (1.5 l) and concentrated HCl (100 ml), and allowed to stand overnight. 2,3-Dichloronaphthazarin (**2***a*) was then recovered by filtration and recrystallized from petroleum ether (b.p. 90–120°), m.p. 198–199° (97%) (lit. (19) m.p. 195°); ν_{max} (KBr) 1627, 1595 (sh), 1573 cm^{-1}; δ ($CDCl_3$) 7.33 s (6,7-CH), 12.36 s (5,8-OH).

Diacetate, m.p. 232–233° (lit. (3) m.p. 233°).

2,3-Dibromonaphthazarin (2b)

This compound was prepared as for the foregoing quinone using $AlCl_3$ (19.5 g), NaCl (3.90 g), *p*-dimethoxy benzene (1.60 g), and dibromomaleic anhydride (**1***b*) (6.16 g); m.p. 219–220° (petroleum ether) (77%) (lit. (19) m.p. 216.5°); ν_{max} (KBr) 1623, 1579, 1555 cm^{-1}; δ ($CDCl_3$) 7.31 s (6,7-CH), 12.43 s (5,8-OH).

2,3-Dichloro-6-methylnaphthazarin (3)

This quinone was obtained by the foregoing method using $AlCl_3$ (50 g), NaCl (10.0 g), 2,5-dimethoxytoluene (6.1 g), and dichloromaleic anhydride (13.4 g); m.p. 148–150° (petroleum ether) (75%); ν_{max} (KBr) 1630, 1573 cm^{-1}; δ ($CDCl_3$) 2.33 d (J = 1.3 Hz) (6-CH_3), 7.12 q (J = 1.3 Hz) (7-CH), 12.58 and 12.91 2 s (5,8-OH).

Anal. Calcd. for $C_{11}H_6O_4Cl_2$: C, 48.35; H, 2.21; Cl, 25.96. Found: C, 48.56; H, 2.29; Cl, 26.01.

Methylation of 2,3-Dichloronaphthazarin

A mixture of 2,3-dichloronaphthazarin (**2***a*) (5.2 g),

iodomethane (8 ml), freshly prepared silver oxide (8.0 g), and chloroform (100 ml) was stirred for 22 h at room temperature. The same amounts of iodomethane and silver oxide were added after 6 and 16 h. The residue after filtration and evaporation of the solvent was crystallized from a mixture of chloroform and carbon tetrachloride and gave 2,3-dichloro-5,8-dimethoxynaphthoquinone (**12***a*) (red needles), m.p. 237–238° (56%) (lit. (20) m.p. 237°; ν_{max} (KBr) 1671, 1646 (sh), 1600 cm^{-1}; δ ($CDCl_3$) 3.97 s (5,8-OCH_3), 7.37 s (6,7-CH).

Anal. Calcd. for $C_{12}H_8O_4Cl_2$: C, 50.20; H, 2.81; Cl, 24.70. Found: C, 50.16; H, 2.73; Cl, 24.59.

Chromatography on deactivated silica gel (21) (benzene–chloroform 1:1) of the mother liquor of the preceding crystallization gave 6,7-dichloro-5,8-dimethoxynaphthoquinone (**13***a*) (yellow needles), m.p. 203–203.5° (chloroform) (22%); ν_{max} (KBr) 1669, 1622 cm^{-1}; δ ($CDCl_3$) 3.96 s (5,8-OCH_3), 6.88 s (2,3-CH).

Anal. Found: C, 50.62; H, 2.89; Cl, 24.61.

Methylation of 2,3-Dibromonaphthazarin

The etherification was carried out as for 2,3-dichloronaphthazarin and gave two isomers.

2,3-Dibromo-5,8-dimethoxynaphthoquinone (**12***b*) (red needles), m.p. 212–213° (chloroform – carbon tetrachloride) (55%); ν_{max} (KBr) 1672, 1596 cm^{-1}; δ ($CDCl_3$) 3.96 s (5,8-OCH_3), 7.35 s (6,7-CH).

Anal. Calcd. for $C_{12}H_8O_4Br_2$: C, 38.32; H, 2.14. Found: C, 38.34; H, 2.06.

6,7-Dibromo-5,8-dimethoxynaphthoquinone (**13***b*) (yellow needles), m.p. 209–210° (benzene – petroleum ether) (17%); ν_{max} (KBr) 1668, 1622 cm^{-1}; δ ($CDCl_3$) 3.94 s (5,8-OCH_3), 6.87 s (2,3-CH).

Anal. Found: C, 38.34; H, 2.01.

The Nucleophilic Substitution of Haloquinones

Nucleophilic Substitution of Chloranil

Method A. A mixture of chloranil (**4**) (0.01 mol), anhydrous potassium fluoride (0.06 mol), and absolute methanol (50 ml) was heated in a sealed tube (Table 1). The cooled reaction mixture was filtered, evaporated under vacuum, diluted with water (200 ml), and extracted with benzene. After evaporation of the solvent, the residue was chromatographed on silica gel using a mixture of benzene and petroleum ether as eluant and gave two products.

Chlorotrimethoxybenzoquinone (**8**), m.p. 82–83° (methanol); ν_{max} (KBr) 1675, 1665, 1640, 1600 cm^{-1}; λ_{max} (ethanol) 298 nm (log ε 3.85); δ ($CDCl_3$) 4.04, 4.09 and 4.23 3 s (OCH_3).

Anal. Calcd. for $C_9H_9O_3Cl$: C, 46.67; H, 3.90; Cl, 15.24. Found: C, 46.59; H, 3.97; Cl, 15.18.

Tetramethoxybenzoquinone (**9**), m.p. 134.5–135.5° (methanol) (lit. (22) m.p. 135–136°); ν_{max} (KBr) 1670, 1610 cm^{-1}; λ_{max} (ethanol) 298 nm (log ε 3.86); δ ($CDCl_3$) 4.05 s (OCH_3).

Method B. Chloranil (0.01 mol) was added in small portions to a cooled solution of sodium methoxide (0.04 mol) in methanol (50 ml). The reaction mixture was then refluxed for 30 min and filtered hot. Tetramethoxybenzoquinone (**9**) crystallized on cooling, m.p. 134-135° (46%). 2,5-Dichloro-3,6-dimethoxybenzoquinone (**6**) could be recovered from the insoluble material (bishemiacetal salt) in the reaction mixture, m.p. 141–142° (methanol) (35%) (lit. (9) m.p. 141°).

*2,3-Dimethoxynaphthoquinone (**11**)*

A mixture of 2,3-diazidonaphthoquinone (0.6 g) (prepared in nearly quantitative yield from 2,3-dichloronaphthoquinone (**10**)) (11), anhydrous potassium carbonate (1.7 g), and absolute methanol (25 ml) was stirred at room temperature for 1.5 h and filtered. The residue was washed with methanol and the filtrates when concentrated and cooled in ice yielded 2,3-dimethoxynaphthoquinone (**11**), m.p. 116–117° (methanol) (83%) (lit. (10) m.p. 114–115°).

*2-Chloro-3,5,8-trimethoxynaphthoquinone (**14**)*

A mixture of 2,3-dichloro-5,8-dimethoxynaphthoquinone (**12***a*) (143 mg), anhydrous sodium acetate (100 mg), and absolute methanol (10 ml) was refluxed for 3 h, cooled and filtered, then concentrated and filtered again. The solid material was 2-chloro-3,5,8-trimethoxynaphthoquinone (**14**), m.p. 149–150° (benzene) (84%); ν_{max} (KBr) 1665, 1610 cm^{-1}; δ ($CDCl_3$) 3.95 s (5,8-OCH_3), 4.22 s (2-OCH_3), 7.30 s (6,7-CH).

Anal. Calcd. for $C_{13}H_{11}O_5Cl$: C, 55.23; H, 3.92. Found: C, 55.59; H, 3.74.

*2,3,5,8-Tetramethoxynaphthoquinone (**15**)*

2,3-Dichloro-5,8-dimethoxynaphthoquinone (**12***a*) (5.72 g) was added to a solution of sodium methoxide (1.4 g of sodium in 75 ml of methanol) and the mixture stirred at room temperature for 1 h and then cooled in ice. Upon filtration, 2,3,5,8-tetramethoxynaphthoquinone (**15**) was obtained, m.p. 139–139.5° (methanol) (86%); ν_{max} (KBr) 1656, 1624 cm^{-1}; δ ($CDCl_3$) 3.95 s (5,8-OCH_3), 4.05 s (2,3-OCH_3), 7.29 s (6,7-CH).

Anal. Calcd. for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.46; H, 5.14.

The Fries Rearrangement of 1,2,3,4,5,8-Hexaacetoxynaphthalene

*2,3-Dihydroxynaphthazarin (Spinazarin) (**16**)*

A solution of 2,3,5,8-tetramethoxynaphthoquinone (**15**) (4.2 g), $AlCl_3$ (50 g), and nitrobenzene (75 ml) was stirred for 24 h at 80° and then hydrolyzed with ice water (900 ml) and concentrated HCl (100 ml). The suspension was warmed until an orange precipitate was obtained, cooled and extracted with petroleum ether. Filtration of the aqueous phase gave spinazarin (**16**), (orange needles), m.p. 279–279.5° (acetic acid) (nearly quantitative) (lit. (15) m.p. 265°); ν_{max} (KBr) 3250, 1615 cm^{-1}; δ ($(CD_3)_2SO$) 7.65 s (6,7-CH).

*1,2,3,4,5,8-Hexaacetoxynaphthalene (**17**)*

A suspension of spinazarin (**16**) (0.55 g), zinc dust (2.5 g), anhydrous sodium acetate (1.5 g), and acetic anhydride (20 ml) was warmed slightly, then stirred at room temperature for 2 h and hydrolyzed. 1,2,3,4,5,8-Hexaacetoxynaphthalene (**17**) was extracted with chloroform and crystallized from acetic acid, m.p. 243–244° (83%) (lit. (15) m.p. 211.5–212°; (16) 245°); ν_{max} (KBr) 1792, 1778, 1766 cm^{-1}; δ (CF_3CO_2H) 2.40 s (2,3-OCOCH_3), 2.50 s (1,4,5,8-OCOCH_3), 7.30 s (6,7-CH).

The Fries Rearrangement of 1,2,3,4,5,8-Hexaacetoxynaphthalene (Table 2)

Method A. A mixture of the hexaacetoxynaphthalene **17** (240 mg) and $AlCl_3$ (500 mg) was heated at 160° for 1 h, hydrolyzed with ice and concentrated HCl and allowed to stand for 12 h. The products were separated by chromatography on silica gel using chloroform as eluant.

TABLE 2. The Fries rearrangement of **17**

Method	Conditions	Yield (%) **18**	**19**
A	$AlCl_3$; 1 h at 160°	16	20
B	$AlCl_3$; 20 min at 170°	50	25
C	$AlCl_3$ in CS_2; 30 min at 175°	20	20
D	BF_3 in acetic acid	0	44

Method B. As in method A, however the mixture was heated at 170° for 20 min.

Method C. As in ref. 6.

Method D. A solution of the hexaacetate **17** in acetic acid (3.0 ml) was saturated with BF_3 rapidly and without cooling.

6-Acetyl-2,3-dihydroxynaphthazarin (acetylspinazarin) (**18**), m.p. 227–228° (dioxan – petroleum ether) (lit. (16) m.p. 236°); ν_{max} (KBr) 3100, 1685, 1640, 1605 cm^{-1}; δ ($(CD_3)_2SO$) 2.61 s (6-$COCH_3$), 7.47 s (7-CH); *m/e* 264 (M^+).

Anal. Calcd. for $C_{12}H_8O_7$: C, 54.55; H, 3.05. Found: C, 54.94; H, 3.02.

1,3-Dimethyl-5,6,7,8-tetrahydroxynaphtho[2,3-*c*]furan-4,9-quinone (**19**), m.p. 305–310° (dec.) (methanol); ν_{max} (KBr) 3450, 1631, 1608 cm^{-1}; δ ($(CD_3)_2SO$) 2.61 s (1,3-CH_3); *m/e* 290 (M^+).

Anal. Calcd. for $C_{14}H_{10}O_7$: C, 57.94; H, 3.47. Found: C, 58.30; H, 3.36.

Tetraacetate of **19**, m.p. 212–213° (benzene – petroleum ether); ν_{max} (KBr) 1790, 1678, 1601 cm^{-1}; δ ($CDCl_3$) 2.31 s (6,7-$OCOCH_3$), 2.41 s (5,8-$OCOCH_3$), 2.63 s (1,3-CH_3).

6,7-Dimethyl ether of **19**, m.p. 218–219° (chloroform – petroleum ether); ν_{max} 1650, 1608 cm^{-1}; δ ($CDCl_3$) 2.68 s (1,3-CH_3), 4.08 s (6,7-OCH_3), 13.60 s (5,8-OH).

*1,3-Dimethyl-5,8-dihydroxynaphtho[2,3-c]furan-4,9-quinone (**21**)*

A solution of 2,5-dimethylfuran-3,4-dicarboxylic acid dichloride (**20**) (1.1 g) (19) and *p*-dimethoxybenzene (0.7 g) in methylene chloride (10 ml) was added dropwise to a suspension of $AlCl_3$ (4.5 g) in the same solvent (15 ml). After refluxing the mixture for 2 h, hydrolyzing it in the usual way and extracting with chloroform, 1,3-dimethyl-5,8-dihydroxynaphtho[2,3,-*c*]furan-4,9-quinone (**21**) was obtained, m.p. 260–260.5° (chloroform) (40%) (lit. (17) m.p. 258–258.5°); the i.r. and n.m.r. data were identical to those already published (17).

Diacetate, m.p. 229–229.5° (lit. (18) m.p. 226–226.5°).

*1,3-Dimethyl-5,6,7,8-tetrahydroxynaphtho[2,3-c]furan-4,9-quinone (**19**)*

A mixture of 2,5-dimethylfuran-3,4-dicarboxylic acid dichloride (**20**) (1.1 g) and 1,2-dihydroxy-3,4 dimethoxybenzene (0.9 g) was added in small portions to a molten mixture of $AlCl_3$ (4.5 g) and NaCl (1.0 g) at 140°. The cooled melt was hydrolyzed with ice and concentrated HCl, allowed to stand for 24 h and extracted repeatedly with chloroform. The crude extract, when chromatographed on silica gel using a mixture of chloroform and methanol (9:1) as eluant gave 1,3-dimethyl-5,6,7,8-tetrahydroxynaphtho[2,3-*c*]furan-4,9-quinone (**19**), m.p. and mixture m.p. 305–310° (dec.) (methanol) (22%). The i.r. and n.m.r. spectra were superimposable on those of the compound obtained from the Fries rearrangement.

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