# The Preparation and Reactions of Naphtho[1,2-*c*]furan and Naphtho[2,3-*c*]furan

James G. Smith,[1] Peter W. Dibble,*[2] and Richard E. Sandborn

*Guelph Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada*

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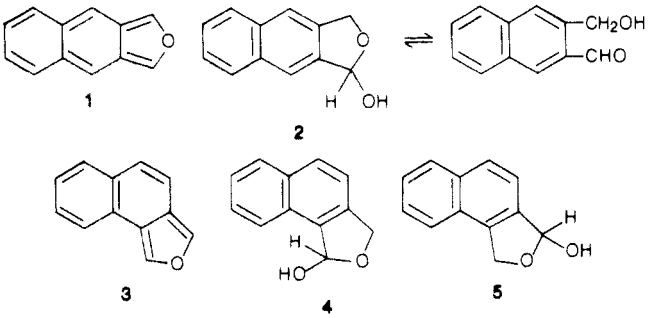
The syntheses of 1,3-dihydro-1- and 1,3-dihydro-3-hydroxynaphtho[1,2-*c*]furan are described. Upon treatment with acid, these compounds undergo 1,4-elimination of water to generate the reactive naphtho[1,2-*c*]furan, which is trapped in situ by a variety of dienophiles. Aromatization of the resulting adducts gives access to 2,3-disubstituted phenanthrenes or benz[*a*]anthracenes. In addition, it has been shown that the hemiacetal, 1,3-dihydro-1-hydroxynaphtho[2,3-*c*]furan, which exists in tautomeric equilibrium with 3-(hydroxymethyl)-2-naphthaldehyde, serves as a convenient source of naphtho[2,3-*c*]furan. This furan can also be trapped by a variety of dienophiles. The resulting Diels–Alder adducts can be aromatized, giving substituted anthracenes. The use of aromatic 1,4-quinones as dienophiles leads to linear polycyclic aromatic quinones of four to seven rings.

We wish to describe the generation of the unsymmetrical isomer of **1**, naphtho[1,2-*c*]furan[3-5] (**3**), from the hemiacetals 1,3-dihydro-1- and 1,3-dihydro-3-hydroxynaphtho[1,2-*c*]furan (**4** and **5**, respectively). Also we wish to describe the preparation of naphtho[2,3-*c*]furan (**1**) from 1,3-dihydro-1-hydroxynaphtho[2,3-*c*]furan (**2**) and some of its reactions with various reagents.

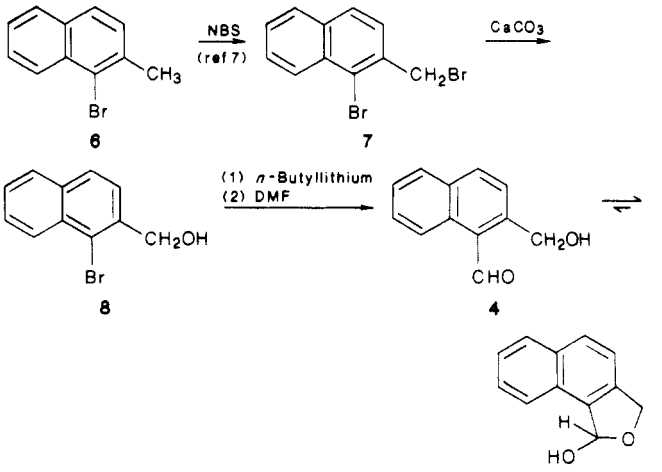



**Naphtho[1,2-*c*]furan.** Initial attempts to prepare 2-(hydroxymethyl)-1-naphthaldehyde, the open chain tautomer of **4**, involved metalation of the acetal 1-(dimethoxymethyl)naphthalene with *tert*-butyllithium. The anion was then treated with *N,N*-dimethylformamide (DMF). The metalation proceeded in low yield, and formylation produced two aldehydes as indicated by the $^1$H NMR spectrum of the product.

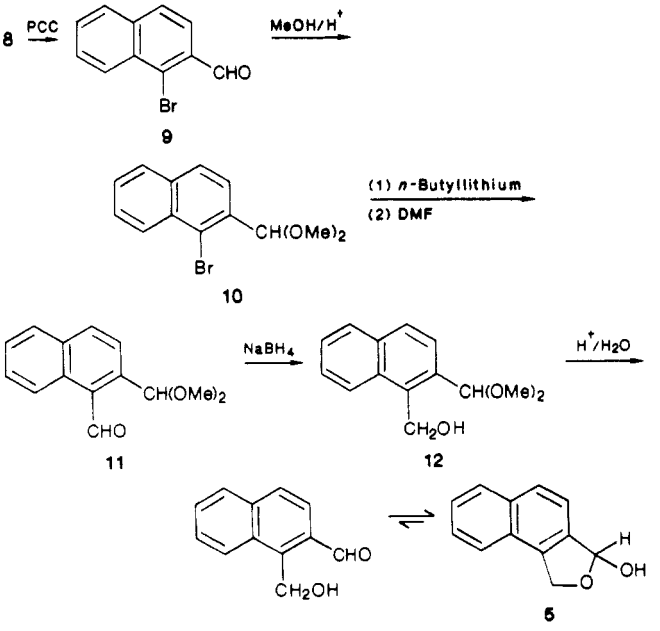
An alternative synthesis (Scheme I) involving the metal–halogen exchange of 1-bromo-2-(hydroxymethyl)naphthalene (**8**) was successful. The $^1$H NMR spectrum showed that in solution, **4** exists entirely in the ring-closed form. The isomeric 1,3-dihydro-3-hydroxynaphtho[1,2-*c*]furan (**5**) was prepared from **8** as shown in Scheme II. Again, $^1$H NMR showed only the hemiacetal form of **5** in solution.

In contrast to **4** and **5**, the ring-chain tautomerism of **2** lies 80% in favor of the ring-open form. It is believed that the difference is due to a destabilizing steric interaction in the ring-open forms of **4** and **5** between the peri hydrogen of the naphthalene ring and the oxygenated functional group (CHO in **4**, $CH_2OH$ in **5**). In **5**, for example, the hydrogens of the $CH_2OH$ group can achieve a staggered conformation relative to the peri proton by ring closure. The same effects have been observed in 1,3-dihydro-1-hydroxyisobenzofurans which are substituted in both ortho positions. 1,3-Dihydro-1-hydroxy-4,7-dimeth-

**Scheme I. Preparation of 1,3-Dihydro-1-hydroxynaphtho[1,2-*c*]furan**




**Scheme II. Preparation of 1,3-Dihydro-3-hydroxynaphtho[1,2-*c*]furan**




(1) Deceased Aug. 1, 1985.
(2) Author to whom correspondence should be addressed.
(3) Stringer, M. B.; Wege, D. *Tetrahedron Lett.* **1980**, *21*, 3831.
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(5) A preliminary report of this research has appeared. Smith J. G.; Dibble, P. W.; Sandborn, R. E. *J. Chem. Soc., Chem. Commun.* **1983**, 1197.
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**Chart I**

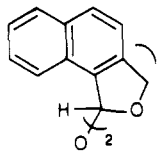

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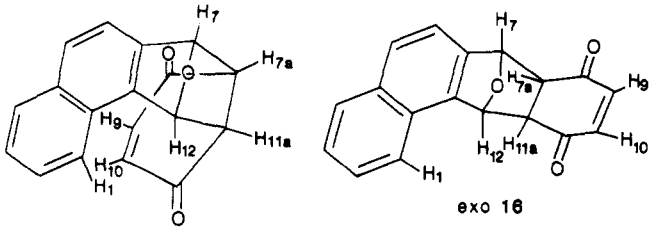
**Chart II**



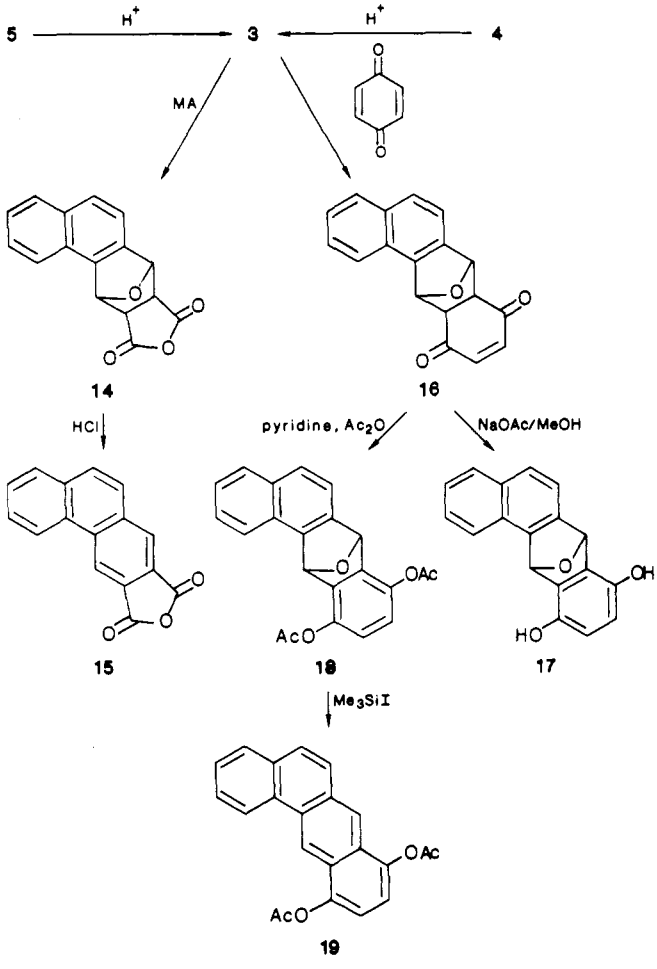
endo-16 exo 16

oxyisobenzofuran is 100% ring-closed[8] while the unsubstituted compound is only 60% ring-closed. 1-Benzyl-1,3-dihydro-1-hydroxy-4,7-dimethylisobenzofuran[9] is also 100% ring-closed while the same compound without the methyl groups is 75% ring-closed.[10]

Naphtho[2,3-c]furan precursor **2** undergoes reactions characteristic of each of the various functional groups. For the purpose of comparison, these reactions were also carried out on **4**. Thus the product obtained from a solution of **4** in methanol treated with Brady's reagent gave a $^1$H NMR spectrum consistent with that of a normal (2,4-dinitrophenyl)hydrazone. Treatment of **4** with concentrated HBr resulted in decomposition of the material, however **2** underwent bromination of the benzylic alcohol to form 3-bromomethyl-2-naphthaldehyde. Cyclic acetals were easily prepared from **2** by stirring in alcohol with an acid catalyst, however, under the same conditions, **4** gave a mixture of products. It was found that **4**, like **2**, can react with itself to form a cyclic acetal. In the case of **2**, the ring-closed form reacted with the benzylic alcohol group of the ring-open form. In contrast, **4** forms **13** (Chart I), a compound containing two cyclic acetals. Of the two possible diastereomers of **13** only one was observed. It is not known which diastereomer this is.

Naphtho[1,2-c]furan (**3**) was easily generated from either **4** or **5** under identical conditions, giving identical results. Reaction with maleic anhydride (MA) in refluxing diethyl ether with *p*-toluenesulfonic acid (TsOH) gave a 1:1 mixture of endo/exo adducts **14**. Aromatization of **14** was effected in refluxing concentrated HCl, giving the known 2,3-phenanthrenedicarboxylic anhydride (**15**, Scheme III). On the other hand, reaction of **3** with *p*-benzoquinone under the same conditions gave a 20:1 mixture of endo/exo adducts **16**. The structural differences (Chart II) between these two adducts have a number of interesting effects in the $^1$H NMR spectra. In the exo adducts the dihedral angle between $H_{11a}$ and $H_{12}$ ($H_7$ and $H_{7a}$ also) is approximately 90°. No coupling is observed in consequence, and these protons appear as singlets. In the endo adduct, coupling results in complex multiplets for all of these protons (ABXY spin system). In both adducts, one of the bridge protons, $H_{12}$, is deshielded relative to the other, presumably because of a Van der Waals interaction with the nearby peri-proton $H_1$. The protons at the quinone

**Scheme III. Diels–Alder Reaction of Naphtho[1,2-c]furan**

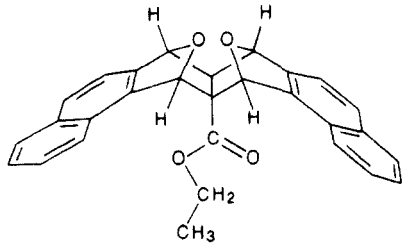



ring junction, $H_{7a}$ and $H_{11a}$, are substantially shielded in the exo adduct by the naphthalene ring current. The vinyl protons $H_9$ and $H_{10}$, which are remote from the naphthalene ring, appear at 6.87 ppm, very close to the shift of protons in *p*-benzoquinone itself (6.80 ppm). In the endo adduct, it is the vinyl protons which are found in the proximity of the angular naphthalene ring. One of these, $H_{10}$, is found 1.3 ppm upfield from its exo counterpart.

Aromatization of **16** is highly desirable since it gives a benz[*a*]anthracene. Benz[*a*]anthracene and its analogues are the subject of continuing environmental and toxicological interest. All attempts to aromatize **16** directly with acid failed. Refluxing **16** with NaOAc in methanol proved successful on similar adducts[11] but in this case gave only hydroquinone **17**. An indirect method was finally used involving formation of the isomeric hydroquinone and subsequent acetylation in one step with pyridine–acetic anhydride. This was followed by removal of the 7,12-epoxide bridge with trimethylsilyl iodide ($Me_3SiI$). $Me_3SiI$ has been used previously to effect dehydration of 1,4-epoxides.[11] In the aromatization of **18**, the reaction appears to be vinylogous to the deoxygenation of 1,2-epoxides which has been reported.[25]

Diels–Alder reactions with unsymmetrical dienophiles such as methyl acrylate and acrolein showed no regioselectivity, as has been reported.[4] Reaction with ethyl propiolate gave a mixture of products, one of which crystallized. On the basis of its $^1$H NMR spectrum, it was identified as the exo,exo bis adduct **20**. Only two singlets

(8) Keay, B. A.; Plaumann, H. P.; Rajapaksa, D.; Rodrigo R. *Can. J. Chem.* **1983**, *61*, 1987.
(9) Wikman, R. T. Ph.D. Thesis, University of Waterloo, 1975.
(10) Smith, J. G.; Dibble, P. W. *Tetrahedron* **1984**, *40*, 1667.
(11) Smith, J. G.; Elankiwar, S. S.; Shantz, B. S.; Lai, E. H.; Chu, N. G. *J. Org. Chem.* **1980**, *45*, 1817.



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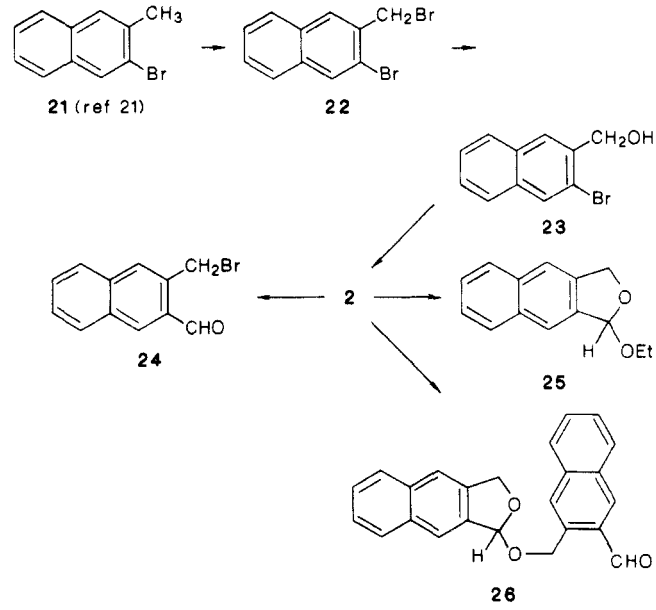
are observed for the bridgehead protons. This establishes that the product is exo,exo and that the angular naphthalene rings must be syn to one another. The position of the $CO_2Et$ group is assigned by comparison of the shift positions of the bridgehead singlets. A 0.54-ppm downfield shift is seen for one of the bridge protons relative to the other. A comparison with other systems suggests that this is caused by the deshielding effects of both the $\beta$ ester carbonyl and the Van der Waals interaction with the peri proton of the naphthalene ring. The most striking feature of the spectrum is the position of the ethyl group. The methyl triplet occurs at 0.35 ppm and the methylene quartet at 2.7 ppm. Clearly, the ethyl group lies between the two naphthalene rings, in the shielding regions of both.

**Naphtho[2,3-*c*]furan.** Extensive interest in the reactions of isobenzofuran[12,13] had led to the investigation of its linearly annulated analogue naphtho[2,3-*c*]furan (**1**).[5,14] Earlier work involved the generation of isobenzofurans from cyclic ortho esters,[15,16] hemiacetals,[5,11] or equivalent precursors.[17,18] Dehydration of the hemiacetal 1,3-dihydro-1-hydroxynaphtho[2,3-*c*]furan (**2**) was proposed as a route to **1** by analogy with this work. In addition, the ring chain tautomerism of **2** was itself of interest.[10] The strategy used to prepare **2** involved metalation of 2-bromo-3-(hydroxymethyl)naphthalene by metal–halogen exchange followed by the introduction of a formyl group using dimethyl formamide (DMF). Direct deprotonation was not considered practical since $CH_2OH$ is a weak directing group,[19] and similar deprotonations have been shown to occur in poor yield with low regioselectivity.[20] The synthesis is shown in Scheme IV.

As reported earlier,[5] **2** exists in $CDCl_3$ solution as a tautomeric equilibrium between a ring-closed hemiacetal form (20%) and a ring-open aldehyde form (80%). The rate of interconversion between the two forms must be slow on the NMR time scale since in both $^1H$ and $^{13}C$ NMR there is no evidence of line broadening of any signals. In the case of 2-(hydroxymethyl)benzaldehyde it is the cyclic tautomer 1,3-dihydro-1-hydroxyisobenzofuran which predominates (60%).[22] Thus, there is clearly a preference

**Scheme IV. Preparation of 1,3-Dihydro-1-hydroxynaphtho[2,3-*c*]furan**



for the open-chain tautomer when the carbonyl group is conjugated with a naphthalene ring rather than a benzene ring. Such a structural effect has been noted in similar equilibria.[10] The absence of a C=O stretching vibration in the IR spectrum of solid **2** indicates that only the hemiacetal form is present in the solid. Solution spectra ($CHCl_3$) show a prominent C=O band.

Reactions of **2** were similar to those reported earlier in this paper for **4**. When treated with Brady's reagent, **2** forms an orange precipitate whose NMR spectrum is that of a normal 2,4-dinitrophenylhydrazone. Stirring **2** in concentrated HBr at room temperature gave 3-(bromomethyl)-2-naphthaldehyde (**24**). Cyclic acetals such as **25** were easily formed by stirring in alcohol with an acid catalyst. An impurity, **26**, was formed by reaction of **2** with itself. A pure sample of **26** was prepared by refluxing **2** in toluene using a Dean–Stark trap. These acetals may arise from addition of ROH to **1** as Rickborn has suggested[14] or by standard acetal formation.

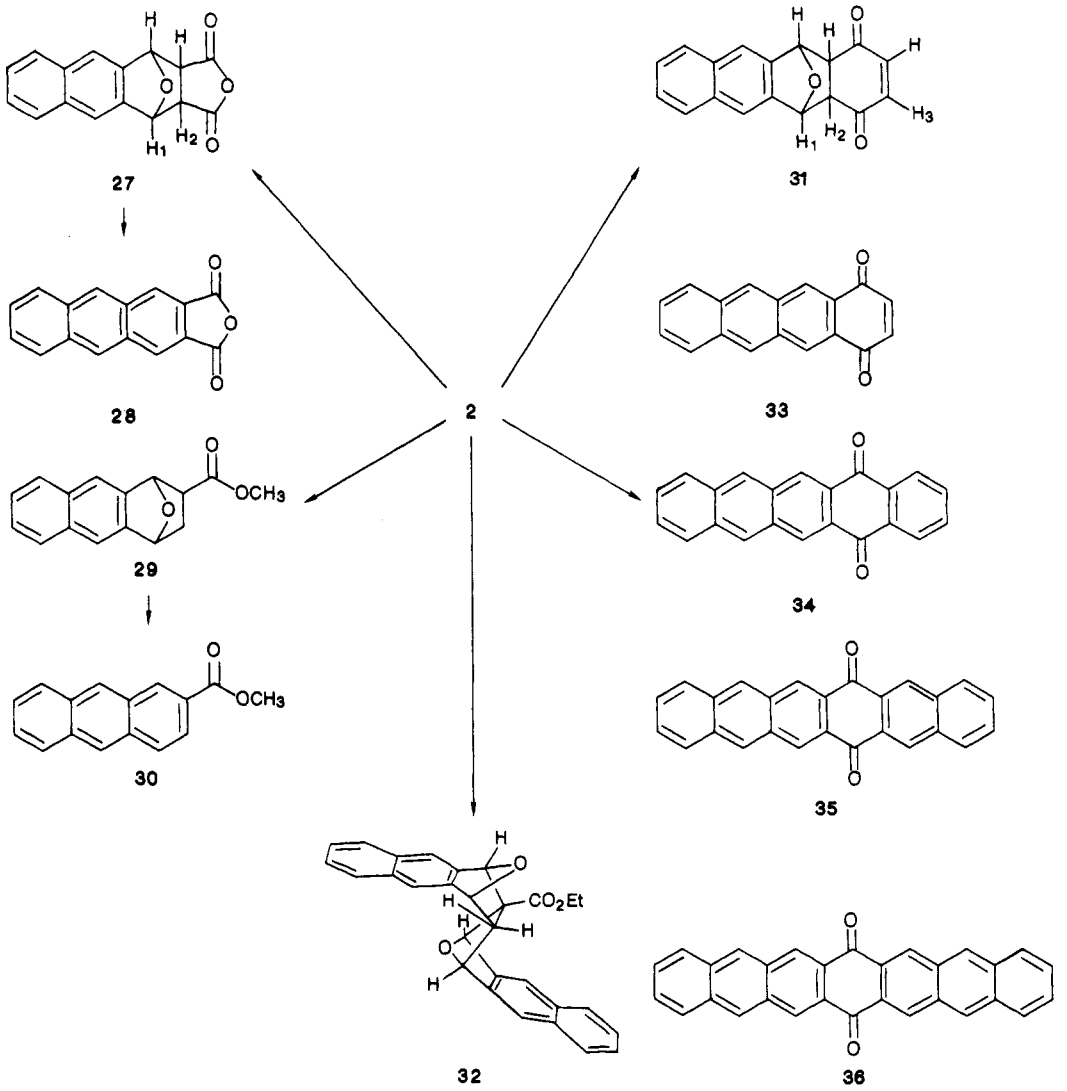
That this tautomeric mixture can be used as a source of **1** was established by reaction with a variety of dienophiles. Refluxing **2** in toluene with maleic anhydride gave a 1:1 mixture of the Diels–Alder adducts **27**.[14] An acid catalyst was not required in this reaction. While thermal eliminations of similar systems have been reported,[23] it is more likely that ring opening of maleic anhydride by a hydroxyl group of **2** forms a maleic acid derivative which serves as the catalyst. This implied that a generally useful acid catalyst might have a $pK_a$ near that of maleic acid. Chloroacetic acid and trichloroacetic acid were found to be suitable.

Aromatization of the endo/exo mixture **27** in refluxing concentrated HCl gave the anhydride of anthracene-2,3-dicarboxylic acid (**28**). An aliquot taken from the reaction mixture before complete aromatization contained only *exo*-**27** and the product **28**, indicating that aromatization takes place more readily with *endo*-**27** than exo-**27**, however, the same results would have been observed if the reaction underwent a thermal retro-Diels–Alder reaction.

Refluxing **2** with methyl acrylate and trichloroacetic acid in toluene gave a 2:1 endo/exo mixture of Diels–Alder adducts **29** (Scheme V). The endo isomer was separated

(12) Wiersum, U. E. *Aldrichimica Acta* **1983** *14(3)*, 53.
(13) Friedrichsen, W. *Adv. Heterocycl. Chem.* **1980**, *45*, 4061.
(14) Mir-Mohamad-Sadeghy, B.; Rickborn, B. *J. Org. Chem.* **1983**, *48*, 2237 and references cited therein.
(15) Makhlouf, M. A.; Rickborn, B. *J. Org. Chem.* **1981**, *46*, 2734.
(16) Keay, B. A.; Lee, D. K. W.; Rodrigo, R. *Tetrahedron Lett.* **1980**, *21*, 3663.
(17) Smith, J. G.; Dibble, P. W. *J. Org. Chem.* **1983**, *48*, 5361.
(18) Smith, J. G.; Kruger, G. *J. Org. Chem.* **1985**, *50*, 5759.
(19) Snieckus, V. *J. Heterocycl. Chem.* **1984**, 95.
(20) Comins, D. L.; Brown, J. D. *J. Org. Chem.* **1984**, *49*, 1078.
(21) This compound was prepared via bromination of the commercially available bis(hexachlorocyclopentadiene) adduct of 2-methylnaphthalene. Look, M.; Padgett, W. M., II; Hyman, J.; Fenyes, G. E.; Lee, H. P. C. Fr. Patent 1 366 805, **1964**; U.S. Patent 3 480 646, **1969**; *Chem. Abstr.*, **1965**, *62*, 503b. For a review of these interesting reagents, see: Look, M. *Aldrichimica Acta* **1974**, *7* (2), 23.
(22) Harron et al. (Harron, J.; McClelland, R. A.; Thankachan, C.; Tidwell, T. T. *J. Org. Chem.* **1981**, *46*, 903) report $k_{eq} = 3$ favoring the cyclic product. We have prepared the same material from 2-bromobenzyl alcohol and consistently obtained the 60/40 equilibrium mixture.
(23) McCormick, J. P.; Shinmyozu, T. *J. Org. Chem.* **1982**, *47*, 4011.

Scheme V




for characterization and the endo/exo mixture was aromatized with concentrated HCl to the known methyl 2-anthracenecarboxylate (**30**). The reaction of **2** with excess *p*-benzoquinone using chloroacetic acid as catalyst gave a 2:1 endo/exo mixture of Diels–Alder adducts **31**. The $^1$H NMR spectrum of this mixture can be interpreted in the same manner as maleic anhydride adducts **27** with respect to the bridge and ring junction protons. In addition to these signals, **31** also has peaks corresponding to the vinyl protons, $H_3$. In the exo adduct, this vinyl peak occurs at 6.88 ppm, very close to *p*-benzoquinone itself (6.80 ppm). In the endo adduct, this peak is substantially upfield at 5.94 ppm. This shielding effect is the same in origin, though larger in magnitude, as that described for the $H_2$ protons of *exo*-**27**.

Reaction of **2** with ethyl propiolate gave predominantly the exo–endo bis adduct **32**. The monoadduct was not found in significant amounts even when the dienophile was used as solvent.

A series of linear aromatic quinones, **33–36**, was prepared via **1** in a manner similar to that described for isobenzofuran.[17] Refluxing **2** with 1,4-naphthoquinone in glacial acetic acid led directly to the formation of the 5,14-pentacenedione (**34**). Similarly, reaction with 1,4-anthraquinone gave 6,15-hexacenedione (**35**). Treating **2** with an excess of *p*-benzoquinone in toluene with trichloroacetic acid gave 1,4-naphthacenedione **33** in poor yield. This compound has been reported to be unstable[24] presumably due to the terminal quinone function. Using *p*-benzoquinone as the limiting reagent with 2 equiv of **2** gave 7,16-heptacenedione (**36**). The higher yield of this material relative to **33** suggests that either **33** is trapped in a second Diels–Alder reaction before substantial side reactions occur or that a bis bridged adduct is formed prior to aromatization.

**Summary.** Access to 1-substituted naphtho[1,2-*c*]furans can be gained by the reaction of **11** with Grignard reagents, followed by dehydration of the product. The reaction of the dianions derived from **8** and **23** by metal–halogen exchange can be exploited in a similar manner by reaction with nitriles or carbonyl containing compounds. Naphtho[2,3-*c*]furan (**1**) can be easily generated from the hemiacetal **2** and trapped in Diels–Alder reactions. Aromatization of these adducts gives access to a variety of substituted anthracenes or linear polycyclic aromatic quinones.

## Experimental Section

**1-Bromo-2-(bromomethyl)naphthalene (7).** 2-Methylnaphthalene was converted into **6** as previously described.[6] To 150 mL of carbon tetrachloride were added 15.3 g (69 mmol) of

(24) Cohen, A.; Deschamps, J.; Abboud, J. L. *Tetrahedron Lett.* **1968**, 4409.

(25) Denis, J. N.; Magnane, R.; Van Eenoo, M.; Krief, A. *Nouv. J. Chim.* **1979**, *3*, 705.

1, 12.4 g (70 mmol) of *N*-bromosuccinimide, and 0.3 g of benzoyl peroxide. The solution was refluxed for 3 h, cooled, and washed with $NaHCO_3$ solution. The solution was dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. Recrystallization from hexane gave 15 g of **7** (72%): mp 103–105 °C (lit.[7] mp 105–106 °C); NMR ($CDCl_3$, 80 MHz) $\delta$ 4.87 (s, 2 H), 7.4–7.9 (m, 5 H), 8.2–8.5 (m, 1 H); IR (Nujol) 1501, 1332, 1210, 980, 812, 757 $cm^{-1}$.

**1-Bromo-2-(hydroxymethyl)naphthalene (8).** Water (100 mL) and $CaCO_3$ (18 g, 180 mmol) were added to a solution of 10.5 g (35 mmol) of **7** in 100 mL of *p*-dioxane, and the mixture was refluxed for 10 h. The solution was cooled and the dioxane removed under reduced pressure. Methylene chloride (200 mL) was added followed by treatment with dilute HCl until all solids had dissolved. The organic phase was separated, washed with $NaHCO_3$ solution, dried over $MgSO_4$, and filtered. Removal of the solvent left a white solid, which was recrystallized from hexane to give 7.9 g of **8** (95%): mp 101–102 °C (lit.[26] mp 103–104 °C); NMR ($CDCl_3$, 80 MHz) $\delta$ 2.09 (t, $J$ = 6 Hz, 1 H, exchanges with $D_2O$), 4.98 (d, $J$ = 6 Hz, 2 H), 7.4–7.9 (m, 5 H), 8.2–8.5 (m, 1 H); IR (Nujol) 3200 (br, OH), 1501, 1062, 809, 766, 738 $cm^{-1}$.

**1,3-Dihydro-1-hydroxynaphtho[1,2-*c*]furan (4).** *n*-Butyllithium (7.2 mL of a 2.6 M solution in hexanes, 19 mmol) was added dropwise under argon to a solution of 2 g (8.4 mmol) of **8** in 35 mL of dry ether cooled to −78 °C. The mixture was stirred for a half hour at −78 °C and then warmed to 0 °C for another half hour. Dry DMF (10 mL, 129 mmol) was added, and the mixture stirred 12 h. The reaction was quenched with water, the ether phase washed twice with brine, dried ($MgSO_4$), and filtered and the solvent removed. Recrystallization from toluene/hexane produced 1.35 g (85%) of **4**: mp 103–105 °C; NMR ($CDCl_3$, 400 MHz) $\delta$ 3.55 (br s, 1 H, exchanges with $D_2O$), 5.10 (d, $J$ = 13 Hz, 1 H), 5.37 (dd, $J_1$ = 13 Hz, $J_2$ = 3 Hz, 1 H), 6.89 (d, $J$ = 3 Hz, 1 H) 7.2–8.0 (m, 6 H); IR (Nujol) 3360 (br, OH), 1522, 1175, 1090, 1010, 890, 820 $cm^{-1}$; MS (EI), *m/e* (relative intensity) 186 ($M^+$, 40), 169 (51), 168 (89), 142 (32), 141 (100), 140 (43), 139 (77), 128 (29).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.48; H, 5.69.

**1-Bromo-2-naphthaldehyde (9).** 1-Bromo-2-(hydroxymethyl)naphthalene (**8**) was oxidized to **9** in 79% yield, using pyridinium chlorochromate (PCC) in the manner described:[27] mp 115–116 °C (lit.[28] mp 116–118 °C); NMR ($CDCl_3$, 80 MHz) $\delta$ 7.5–8.0 (m, 5 H), 8.3–8.6 (m, 1 H), 10.7 (s, 1 H).

**1-Bromo-2-(dimethoxymethyl)naphthalene (10).** To 200 mL of dry methanol was added 15.1 g (67 mmol) of **9**, 50 mL of trimethyl orthoformate, and 5 g of Dowex 50W-X8 resin. The mixture was refluxed for 12 h with a drying tube in place. The reaction was cooled and 5 g of $Na_2CO_3$ was added. The mixture was stirred for 10 min and filtered and the solvent removed under reduced pressure. The crude product was dissolved in hexane, filtered to remove a gel impurity, and then crystallized from hexane to give 16.3 g of **10** (90%): mp 55–56 °C; IR (Nujol) 2925, 1326, 1111, 1064, 827, 749 $cm^{-1}$; NMR ($CDCl_3$, 80 MHZ) $\delta$ 3.45 (s, 6 H), 5.9 (s, 1 H), 7.4–7.9 (m, 5 H), 8.2–8.4 (m, 1 H). Anal. Calcd for $C_{13}H_{13}BrO_2$: C, 55.54; H, 4.66. Found: C, 55.51; H, 4.65.

**2-(Dimethoxymethyl)-1-naphthaldehyde (11).** The procedure for the preparation of **4** was repeated with 3 g (11 mmol) of **10**, 5.0 mL of 2.6 M *n*-butyllithium (13 mmol), and 3.0 mL of DMF. The yellow oil produced was chromatographed on neutral alumina by using diethyl ether as eluant to give **11**, an oil: 2.3 g (94%); IR (neat) 2935, 2830, 1688, 1592, 1508, 1464, 1193, 1111, 1060, 832 $cm^{-1}$; NMR ($CDCl_3$, 80 MHz) $\delta$ 3.4 (s, 6 H), 5.9 (s, 1 H), 7.4–8.1 (m, 5 H), 8.7–8.9 (m, 1 H), 10.9 (s, 1 H); MS (EI), *m/e* (relative intensity) 230 ($M^+$, 3), 199 (28), 198 (46), 183 (100), 169 (17), 155 (17), 141 (46), 127 (43).

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 73.01, H, 6.14.

**1-(Hydroxymethyl)-2-(dimethoxymethyl)naphthalene (12).** To a slurry of 0.34 g (7.1 mmol) of sodium borohydride in 50 mL of methanol was added 2.0 g (8.7 mmol) of **11** dropwise with stirring. The mixture was stirred at room temperature for 2 h. Water (20 mL) was added, the solution was extracted three times with chloroform, the extracts were dried ($MgSO_4$) and filtered, and the solvent was removed to provide an oil, **12**, in quantitative yield: IR (neat) 3200–3650, (br OH), 2935, 1349, 1193, 1112, 1063, 1003, 973, 825 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 2.6 (t, 1 H, exchanges with $D_2O$), 3.4 (s, 6 H), 5.2 (d, 2 H), 5.75 (s, 1 H), 7.4–7.9 (m, 5 H), 8.2–8.4 (m, 1 H); MS (EI), *m/e* (relative intensity) 232 ($M^+$, 6), 201 (11) 200 (37), 199 (15), 170 (14), 169 (100), 168 (19), 141 (76), 140 (12). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.51; H, 7.11.

**1,3-Dihydro-3-hydroxynaphtho[1,2-*c*]furan (5).** To 100 mL of water and 15 mL of *p*-dioxane was added 4 mL of acetic acid and 2.0 g (9 mmol) of **12**. The mixture was stirred at room temperature for 2 h. The mixture was then extracted with diethyl ether and dried over $MgSO_4$ and the solvent removed. Recrystallization from toluene/hexane produced white, crystalline **5**: 1.35 g (84%); mp 102–103 °C; IR (Nujol) 3368, 1264, 1052, 1009, 884, 813, 756 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 3.5 (s, 1 H, exchanges with $D_2O$), 5.4 and 5.6 (AB of ABX, $J_{AB}$ = 13 Hz, $J_{AX}$ = 2.5 Hz, $J_{BX}$ = 0 Hz, 2 H), 6.7 (d, $J_{AX}$ = 2.5 Hz, 1 H), 7.4–8.0 (m, 6 H); MS (EI), *m/e* (relative intensity) 186 ($M^+$, 11), 169 (18), 168 (100), 141 (16), 140 (29), 139 (53), 84 (14), 28 (21). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.62; H, 5.42.

**Bis(1,3-dihydro-1-naphtho[1,2-*c*]furanyl) Ether (13).** This material was isolated while attempting to prepare endo **14**. Maleic anhydride (0.15 g, 1.5 mmol) and **4** (0.25 g, 1.3 mmol) were dissolved in the minimum amount of diethyl ether required for dissolution. A catalytic amount of TsOH was added. A precipitate formed after 10 min, which was collected by filtration. It proved to be **13** in a crude yield of approximately 40%: mp 116 °C dec; IR (Nujol) 1294, 1053, 994, 973, 958, 820, 804, 748 $cm^{-1}$; NMR ($CDCl_3$, 80 MHz) 5.29 and 5.60 (AB of ABX, $J_{AB}$ = 12.9 Hz, $J_{AX}$ = 2.3 Hz, $J_{BX}$ = 0 Hz, 4 H), 7.32 (d, $J_{AX}$ = 2.3 Hz, 2 H), 7.4–8.2 (m, 12 H). Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.17; H, 5.33.

**1,4-Epoxy-1,2,3,4-tetrahydro-2,3-phenanthrenedicarboxylic Anhydride (14).** In 150 mL of diethyl ether were refluxed 1.0 g (5.4 mmol) of **4**, 1.0 g (10.2 mmol) of maleic anhydride, and a catalytic amount of *p*-toluenesulfonic acid. The solvent was removed under reduced pressure, leaving a 1:1 mixture of endo and exo isomers by NMR. The exo adduct was crystallized from acetic acid and recrystallized from toluene, mp 213–214 °C (lit.[4] mp 214–215 °C). Addition of $CHCl_3$ to the mother liquor precipitated the endo adduct. All attempts to purify the endo adduct gave the exo adduct. Total yield was 0.77 g (77%): NMR exo ($CDCl_3$, 80 MHz) $\delta$ 2.90 (s, 2 H), 5.85 (s, 1 H), 6.20 (s, 1 H), 7.3–8.0 (m, 6 H); NMR endo ($CDCl_3$–$Me_2SO$-$d_6$, 80 MHz) $\delta$ 5.2 (d AB q, $J_1$ = 10 Hz, $J_2$ = 5 Hz, 2 H), 5.90 (d, 1 H), 6.30 (d, 1 H), 7.4–8.0 (m, 6 H).

**2,3-Phenanthrenedicarboxylic Anhydride (15).** In excess concentrated HCl was stirred 0.20 g (0.8 mmol) of **14** at reflux for a half hour. The product was filtered and washed with water. Recrystallization from acetic anhydride gave 0.18 g (90%) of **15**: mp 277–279 °C (lit.[29] mp 277 °C); NMR $\delta$ 7.5–8.0 (m, 6 H), 8.3 (s, 1 H), 8.7–8.9 (m, 1 H), 9.1 (s, 1 H); IR (Nujol) 1830, 1780, 1261, 1249, 900, 733 $cm^{-1}$.

**7,12-Epoxy-7,7a,11a,12-tetrahydro-8,11-benz[*a*]anthraquinone (16).** In 100 mL of diethyl ether were refluxed 0.70 g (3.8 mmol) **4**, 0.8 g (7.4 mmol) *p*-benzoquinone, and a catalytic amount of TsOH for 2 h. The solution was washed with $NaHCO_3$ solution, dried over $MgSO_4$, and filtered and the solvent removed. The yellow, crystalline residue was heated with water and filtered. The crude product was a mixture of endo and exo adducts, 20:1 (by NMR). Recrystallization from toluene/hexane gave 0.84 g (84%) of the endo product: mp 144–147 °C; IR (Nujol) 1663, 1309, 1278, 1128, 870, 860, 819 $cm^{-1}$: NMR ($CDCl_3$, 80 MHz) $\delta$ 3.8 (m, 2 H), 5.57 and 5.90 (AB q, $J$ = 10 Hz, 2 H), 2.60 (m, 1 H), 6.3 (m, 1 H), 7.2–7.9 (m, 6 H). Anal. Calcd for $C_{18}H_{10}O_3$: C, 78.41; H, 4.51. Found: C, 78.25; H, 4.38. The exo adduct was obtained by washing the crude product with $CHCl_3$. Orange crystals of the exo adduct were left behind: IR (Nujol) 1666 (C=O), 1279,

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1150, 1115, 888, 819 $cm^{-1}$; NMR ($CDCl_3$) δ 2.87 (s, 2 H), 5.85 (s, 1 H), 6.19 (s, 1 H), 6.87 (s, 2 H), 7.4–8.1 (m, 6 H).

**7,12-Epoxy-7,12-dihydro-8,11-dihydroxybenz[a]anthracene (17).** In 15 mL of methanol were refluxed 0.4 g (1.4 mmol) of **16** and 0.08 g of NaOAc for 15 min. After cooling, the solution was poured into water, and a tan solid was collected by filtration. The solid was dried under vacuum at 56 °C for 6 h to give crude **17** in essentially quantitative yield. The material resisted recrystallization, and as a result only crude material was characterized. The solid gradually darkened on heating: IR (Nujol) 3184 and 3090 (br OH), 1485, 1259, 807 $cm^{-1}$; NMR ($Me_2SO$-$d_6$, 80 MHz) 6.22 (s, 2 H), 6.36 (s, 1 H), 6.74 (s, 1 H), 7.2–8.1 (m, 6 H), 8.57 (s, 2 H, exchanges with $D_2O$); HRMS calcd for $C_{18}H_{12}O_3$ 276.0787, found 276.0772.

**8,11-Diacetoxy-7,12-epoxy-7,12-dihydrobenz[a]anthracene (18).** In 25 mL of acetic anhydride and a small amount of pyridine was refluxed 0.45 (1.6 mmol) of **16** for 30 min. An equal volume of water was added, and the solution was left to stand until a precipitate formed. The precipitate was filtered, washed with water, and recrystallized from ethanol, giving **18** (0.36 g, 62%): mp 185–186 °C; IR (Nujol) 1758 (C=O), 1222, 1199, 1148, 823, 752 $cm^{-1}$; NMR ($CDCl_3$, 250 MHz) δ 2.39 (s, 3 H), 2.41 (s, 3 H), 6.19 (s, 1 H), 6.63 (s, 1 H), 6.72 and 6.74 (AB q, $J$ = 7 Hz, 2 H), 7.3–8.0 (m, 6 H).

Anal. Calcd for $C_{22}H_{16}O_5$: C, 73.33; H, 4.48. Found: C, 73.34; H, 4.46.

**8,11-Diacetoxybenz[a]anthracene (19).** In oven-dried glassware, 0.5 g (1.4 mmol) of **18** and 0.63 g (4.2 mmol) of NaI were mixed in 10 mL of acetonitrile (distilled from $P_2O_5$) under argon. Chlorotrimethylsilane (0.55 mL, 4.3 mmol) was added dropwise by syringe. The solution quickly went dark. After 1 h, 100 mL of $CH_2Cl_2$ and 50 mL of 5% $NaHSO_3$ solution were added. The aqueous portion was extracted once with $CH_2Cl_2$ and the organic phases were combined. They were washed once with $NaHSO_3$ and once with water. The organic phase was heated with decolorizing charcoal and $MgSO_4$ and filtered. The solvent was removed under reduced pressure, leaving a yellow oil, which solidified. Recrystallization from ethanol gave **19** (0.35 g, 73%): mp 172–173 °C; IR (Nujol) 1752 (C=O), 1196, 1056, 891, 835, 745 $cm^{-1}$; NMR ($CDCl_3$, 250 MHz) δ 2.55 (s, 3 H), 2.63 (s, 3 H), 7.32 (s, 2 H), 7.6–7.9 (m, 5 H), 8.36 (s, 1 H), 8.76 (d, $J$ = 8 Hz, 1 H), 9.18 (s, 1 H).

Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.93; H, 4.64.

**Exo,Exo Bis Adduct of Ethyl Propiolate and 3 (20).** In 100 mL of diethyl ether were refluxed 0.5 g (2.7 mmol) of **4**, 1.8 g (18 mmol) of ethyl propiolate, and a catalytic amount of TsOH for 11 h. The solution was washed with $NaHCO_3$ solution and dried over $MgSO_4$ and the solvent removed under reduced pressure. A small amount of crystalline material was obtained, mp 308–310 °C dec, and was judged to be **20** on the basis of the spectral evidence: IR (Nujol) 1727 (C=O), 1267, 1172, 817, 742 $cm^{-1}$; NMR ($CDCl_3$, 80 MHz) δ 0.35 (t, $J$ = 7 Hz, 3 H), 2.55 (s, 1 H), 2.71 (q, $J$ = 7 Hz, 2 H), 5.71 (s, 2 H), 6.25 (s, 2 H), 7.2–8.0 (m, 12 H). Anal. Calcd for $C_{29}H_{22}O_4$: C, 80.17; H, 5.10. Found: C, 79.89; H, 5.33.

**2-Bromo-3-methylnaphthalene (21).** The product from the bromination of the bis(hexachlorocyclopentadiene) adduct of 2-methylnaphthalene[21] was crystallized from $CCl_4$. Portions (50 g) were heated by flame under aspirator vacuum in a 500-mL round-bottomed flask equipped with a wide-bore Claisen head with the condenser mounted vertically. Hexachlorocyclopentadiene and 2-bromo-3-methylnaphthalene were distilled. The latter solidified into a waxy, pale yellow solid having a strong, musty smell. Recrystallization from hexane gave **3** in 80% yield based on commercially available starting material: mp 124–127 °C; IR (Nujol) 1596, 1247, 1092, 1070, 911, 770 $cm^{-1}$; NMR ($CDCl_3$, 80 MHz) δ 2.52 (s, 3 H), 7.3–7.8 (m, 5 H), 8.04 (s, 1 H).

**2-Bromo-3-(bromomethyl)naphthalene (22).** To a stirred refluxing solution of 10 g (45 mmol) of **21** in 150 mL of $CCl_4$ was added half of a mixture of 8.1 g (46 mmol) of NBS and 0.2 g of benzoyl peroxide. Heating was continued for 2 h, after which the remaining NBS–peroxide mixture was added in portions over 30 min. After an additional hour of heating, the solution was cooled and washed with $NaHCO_3$ solution. The organic phase was dried over $MgSO_4$ and filtered and the solvent removed under reduced pressure, leaving an oil, which solidified. Recrystallization from hexane gave **22** (12.2 g, 90%), mp 108–110 °C (lit.[30] mp 111–112 °C).

**3-Bromo-2-naphthalenemethanol (23).** In 200 mL of 1:1 dioxane/water were refluxed 12.2 g (41 mmol) of **22** and 20 g (200 mmol) of $CaCO_3$ for 10 h. The bulk of the solvent was removed under reduced pressure, and the residue was extracted with 200 mL of warm $CHCl_3$. The solution was filtered and separated and the organic phase dried over $MgSO_4$. The solvent was removed and the residue recrystallized from toluene–hexane to give **23** (8.0 g, 83%): mp 113–115 °C (lit.[31] mp 95–100 °C); IR (Nujol) 3300 (br, OH), 1206, 1132, 1054, 978, 877, 747 $cm^{-1}$; NMR ($CDCl_3$, 80 MHz) δ 2.10 (t, $J$ = 7 Hz, 1 H, exchanges with $D_2O$), 4.90 (d, $J$ = 7 Hz, 2 H, s with $D_2O$ wash), 7.3–7.9 (m, 4 H), 7.91 (s, 1 H), 8.07 (s, 1 H).

**3-(Hydroxymethyl)-2-naphthaldehyde (1,3-Dihydro-1-hydroxynaphtho[2,3-c]furan) (2).**[32] A solution of 10 g (42 mmol) of **23** in 250 mL of dry diethyl ether was cooled to −78 °C. After a few minutes **23** precipitated. To this was added, by syringe, 40 mL of 2.6 M *n*-butyllithium in hexanes (104 mmol). After 10 min, the solution was warmed to 0 °C, at which temperature it was maintained for 30 min. (A precipitate, probably the dianion, formed during this period). Dry DMF (5 mL, 69 mmol) was injected and the mixture stirred for 10 h. Addition of water (50 mL) resulted in the formation of a precipitate. After being stirred for 5 min, the solution was filtered. The precipitate was stirred in a mixture of $NH_4Cl$ solution and ether until all solids had dissolved. The ether layer was separated and dried over $MgSO_4$ and the solvent removed under reduced pressure. The residue was recrystallized from toluene/hexane to give **2** (6.0 g, 77%): mp 106–107 °C; IR (Nujol) 3050–3550 (br, OH), 1285, 1099, 994, 886, 740 $cm^{-1}$; IR ($CHCl_3$) 3200–3650 (br, OH), 1688 (C=O), 1464, 1231, 1020, 895 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 80 MHz, integrations given are with respect to the tautomer to which the peaks were assigned) δ [hemiacetal form] 3.18 (d, $J$ = 8 Hz, 1 H, exchanges with $D_2O$), 5.18 and 5.40 (AB q, $J$ = 12 Hz, 2 H), 6.61 (d, $J$ = 8 Hz, s with $D_2O$), 7.4–8.1 (m, 6 H), [aldehyde form] 3.77 (t, $J$ = 7 Hz, 1 H, exchanges with $D_2O$), 4.96 (d, $J$ = 7 Hz, 2 H, s with $D_2O$), 7.4–8.1 (m, 5 H), 8.37 (s, 1 H), 10.17 (s, 1 H); $^{13}C$ NMR ($CDCl_3$, 63 MHz, ppm) 64.36, 71.26, 101.11, 119.60, 122.15, 125.94, 126.59, 127.31, 127.95, 128.01, 128.58, 129.15, 130.03, 132.00, 132.88, 135.83, 137.01, 140.20, 194.95.

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.30; H, 5.42. Found: C, 77.15; H, 5.37.

**3-(Bromomethyl)-2-naphthaldehyde (24).** In 20 mL of concetrated HBr was stirred 60 mg of **2** for 10 h at room temperature. A white solid was collected by filtration and recrystallized from toluene/hexane, giving **24**: mp 96–97 °C; IR (Nujol) 1689 (C=O), 1238, 1221, 1184, 1159, 891, 752 $cm^{-1}$; NMR ($CDCl_3$, 80 MHz) δ 5.14 (s, 2 H), 7.5–8.1 (m, 5 H), 8.36 (s, 1 H), 10.32 (s, 1 H); MS (EI), $m/e$ (relative intensity) 248 ($M^+$, 10), 250 ($M^+$ + 2, 10), 170 (14), 169 (100), 141 (78), 140 (15), 139 (30), 115 (42).

**1-Ethoxy-1,3-dihydronaphtho[2,3-c]furan (25).** In 50 mL of absolute ethanol was refluxed 0.5 g (2.7 mmol) of **2** with 0.3 g Dowex 50W-X8 resin for 10 h. The solution was cooled and filtered and the solvent removed under reduced pressure. Recrystallization from ethanol gave **25** (0.53 g, 92%): mp 123–125 °C (lit.[14] 126–127 °C).

**1-[(3-Formyl-2-naphthalenyl)methoxy]-1,3-dihydronaphtho[2,3-c]furan (26).** In a 100-mL flask equipped with a Dean–Stark trap was refluxed 0.25 g (1.3 mmol) of **2** in toluene for 8 h. The solvent was removed under reduced pressure and the residue recrystallized from toluene to give **26** (0.17 g, 71%): mp 122–124 °C; IR (Nujol) 1690 (C=O), 1333, 1107, 1065, 1031, 1018, 895, 873, 750 $cm^{-1}$; NMR ($CDCl_3$, 250 MHz) δ 5.22 and 5.43 (AB q, $J$ = 13 Hz, 2 H), 5.35 (s, 2 H), 6.59 (s, 1 H), 7.44–8.04 (m, 11 H), 8.36 (s, 1 H), 10.34 (s, 1 H); $^{13}C$ NMR ($CDCl_3$, 63 MHz, ppm) 67.4, 71.9, 106.0, 119.6, 122.4, 125.9, 126.6, 127.0, 128.0, 128.6, 129.3, 129.4, 132.0, 132.1, 133.3, 134.2, 135.1, 135.7, 136.4.

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Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.56; H, 5.32.

***exo*- and *endo*-1,4-Epoxy-1,2,3,4-tetrahydro-2,3-anthracenedicarboxylic Anhydride (*exo*- and *endo*-27).** Maleic anhydride (0.7 g, 7.1 mmol) and 1 g (5.4 mmol) of **2** were refluxed for 12 h in toluene. The solvent was removed under reduced pressure and the residue recrystallized from toluene to give **27** (1.3 g, 92%), 55% endo and 45% exo by NMR. The isomers were separated by fractional crystallization from toluene, the exo adduct crystallizing out first: mp exo 291–292 °C (lit.[14] mp 285–286 °C); mp endo 201–203 °C (lit.[14] mp 195–198 °C).

**2,3-Anthracenedicarboxylic Anhydride (28).** In 100 mL of concentrated HCl was refluxed 0.24 g (0.90 mmol) **27** for 4 h. After dilution with water and filtration, a bright yellow solid was obtained. The solid was recrystallized from acetic anhydride to give 0.17 of **10** (77%), which sublimed without melting. The dimethyl ester was prepared by refluxing **28** in methanol with $H_2SO_4$, mp 149–151 °C (methanol) (lit.[33] mp 151 °C).

**Methyl 1,4-Epoxy-1,2,3,4-tetrahydro-2-anthracenecarboxylate (29).** In 50 mL of toluene were refluxed 0.4 g (2.2 mmol) of **2**, 1.8 (21 mmol) methyl acrylate, and a catalytic amount of $CCl_3COOH$ for 9 h. The solvent was removed under reduced pressure and the residue analyzed by NMR showing it to be a 2:1 mixture of endo/exo isomers. A sample of the endo isomer was selectively crystallized from toluene. Further material was recovered from the mother liquor as a mixture. The total yield was 0.47 g, (85%). The endo adduct had mp 164–165 °C: IR (Nujol) 1734, 1287, 1210, 979, 880, 855, 747 $cm^{-1}$; NMR ($CDCl_3$, 250 MHz) $\delta$ 1.96 (dd, $J_1$ = 4.1 Hz, $J_2$ = 12.0 Hz, 1 H), 2.42 (ddd, $J_1$ = 5.2 Hz, $J_2$ = 10.6 Hz, $J_3$ = 12.0 Hz, 1 H), 3.45–3.53 (obscured m, 1 H), 3.51 (s, 3 H), 5.54 (d, $J$ = 5.2 Hz, 1 H), 5.67 (d, $J$ = 5.4 Hz, 1 H), 7.26–7.47 (m, 2 H), 7.59 (s, 1 H), 7.64 (s, 1 H), 7.77–7.82 (m, 2 H).

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.80; H, 5.61.

**Methyl 2-Anthracenecarboxylate (30).** In 50 mL of concentrated HCl was refluxed 0.3 g (1.2 mmol) of **29** for 1 h. After cooling, the mixture was diluted with water and filtered and the yellow precipitate washed with water. Recrystallization from methanol gave **30** (0.22 g, 79%): mp 188–191 °C (lit.[34] mp 192–193 °C); NMR ($CDCl_3$, 80 MHz) $\delta$ 4.01 (s, 3 H), 7.45–7.71 (m, 2 H), 7.87–8.18 (m, 4 H), 8.45 (s, 1 H), 8.82 (s, 1 H).

**5,12-Epoxy-4a,5,12,12a-tetrahydro-1,4-naphthacenedione (31).** In 100 mL of toluene were refluxed 0.2 g (1.1 mmol) of **2**, 0.23 g (2.1 mmol) of *p*-benzoquinone, and a catalytic amount of chloroacetic acid for 10 h. The solution was removed, cooled and filtered. The filtrate was stripped of solvent and taken up in $CHCl_3$. The solution was washed with $NaHCO_3$ solution, dried over $MgSO_4$, and filtered and the solvent removed under reduced pressure. The crystalline residue was recrystallized from $CCl_4$. The crystals obtained were then heated with water, filtered, and dried, giving a 2:1 endo/exo mixture of **31**, which was characterized by NMR only: NMR ($CDCl_3$, 80 MHz) $\delta$ [exo] 3.03 (s, 2 H), 5.82 (s, 2 H), 6.88 (s, 2 H), 7.4–7.9 (m, 6 H), [endo] 3.64–3.71 (m, 2 H), 5.85–5.90 (m, 2 H), 5.94 (s, 2 H), 7.4–7.9 (m, 6 H).

**Reaction of 2 with Ethyl Propiolate. Bis Adduct 32.** In 50 mL of toluene were refluxed 0.1 g (0.5 mmol) of **2**, 0.5 g (5.1 mmol) of ethyl propiolate, and a catalytic amount of chloroacetic acid for 8 h. The solution was cooled, washed with a $NaHCO_3$ solution, and dried over $MgSO_4$. The solvent was removed under reduced pressure, leaving a residue, which crystallized. Recrystallization from toluene gave **32**: mp 264–267 °C; IR (Nujol) 1731 (C=O), 1196, 962, 850, 749 $cm^{-1}$; NMR ($CDCl_3$, 80 MHz) $\delta$ 1.00 (t, $J$ = 7 Hz, 3 H), 3.47 (d, $J$ = 5.5 Hz, 1 H), 3.97 (q, $J$ = 7 Hz 2 H), 4.92 (s, 1 H), 5.03 (s, 1 H), 5.62 (d, $J$ = 5.5 Hz, 1 H), 5.72 (s, 1 H), 7.3–7.9 (m, 12 H); MS (EI), $m/e$ (relative intensity) 434 ($M^+$, 7), 332 (7), 331 (4), 315 (4), 250 (4), 181 (9), 169 (31), 168 (100).

Anal. Calcd for $C_{29}H_{22}O_4$: C, 80.17; H, 5.10. Found: C, 79.92; H, 5.25.

**1,4-Naphthacenedione (33).** In 100 mL of toluene were refluxed 0.5 g (2.7 mmol) **2**, 0.58 g (5.4 mmol) of *p*-benzoquinone, and a catalytic amount of $CCl_3COOH$ for 17 h. The mixture was washed with water, heated with decolorizing charcoal and $MgSO_4$, and filtered. Most of the solvent was removed under reduced pressure, precipitating the product. The solid was recrystallized from toluene to give 0.12 g of analytically pure **33** (17%): mp 250 °C dec; (lit.[24] mp 281–282 °C); NMR ($CDCl_3$, 80 MHz) $\delta$ 7.10 (s, 2 H), 7.55–8.15 (AA'BB', 4 H), 8.66 (s, 2 H), 8.82 (s, 2 H); IR (Nujol) 1663 (C=O), 1604 (C=C), 1307, 1251, 1244, 1136, 929, 872, 749 $cm^{-1}$; UV ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$) 480 nm (4.1), 410 (3.8), 386 (3.8), 345 (4.5), 329 (4.4).

**5,14-Pentacenedione (34).** In 50 mL of glacial acetic acid were refluxed 0.3 g (1.6 mmol) of **2** and 0.3 g (1.9 mmol) of 1,4-naphthoquinone for 2 h. An orange precipitate was filtered off and recrystallized from DMF, giving 0.25 (50%) of **34**: mp 352–354 °C (lit.[35] mp 374 °C dec; NMR ($CDCl_3$, 250 MHz) $\delta$ 7.60–7.63 (m, 2 H), 7.83–7.87 (m, 2 H), 8.09–8.12 (m, 2 H), 8.43–8.46 (m, 2 H), 8.73 (s, 2 H), 9.10 (s, 2 H).

**6,15-Hexacenedione (35).** In 5 mL of glacial acetic acid were refluxed 0.1 g (0.54 mmol) of **2** and 0.1 g (0.48 mmol) of 1,4-anthraquinone for 1 h. The solution was cooled and a brown precipitate was collected by filtration and washed with ethanol to give 0.13 g of crude product (76%). A portion recrystallized from DMF had mp 394 °C dec (lit.[36] mp 398 °C dec): NMR ($CDCl_3$, 250 MHz) $\delta$ 7.26–7.74 (m, 4 H), 8.09–8.17 (m, 4 H), 8.74 (s, 2 H), 8.99 (s, 2 H), 9.18 (s, 2 H); IR (Nujol) 1679 (C=O), 1615, 1297, 1266, 854, 754 $cm^{-1}$; UV ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$) 456 nm (3.8), 407 (3.8), 371 (3.9) 342 (4.4), 328 (4.3).

**7,16-Heptacenedione (36).** In 5 mL of glacial acetic acid were refluxed 0.1 g (0.93 mmol) of *p*-benzoquinone and 0.38 g (2.0 mmol) of **2** for 6 h. After the mixture was allowed to cool, a brown precipitate was collected by filtration and washed with ethanol. IR, NMR, and UV[37] spectra showed this material to be **36**, which, as reported, did not melt.[38] The yield of crude material was 0.17 g (45%): IR (Nujol) 1671 (C=O), 1598, 1565, 1331, 1301, 1235, 953, 726 $cm^{-1}$; UV ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$) 463 nm (4.0), 452 (4.0), 347 (4.6), 337 (4.4).

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