1-[2-(*o*-Hydroxyphenyl)ethenyl]cyclobutene (10g): yield 0.11 g (0.64 mmol, 64%); IR (neat) 3300, 960 cm^{-1}; ^1H NMR δ 2.30–2.80 (m, 4 H, CH_2), 4.70–5.70 (br, 1 H, OH), 6.0 (t, J = 1.1 Hz, 1 H, -C*H*=C<), 6.60–7.60 (m, 6 H, olefinic and aromatic H); HRMS, m/z calcd for $C_{12}H_{12}O$ 172.0888, found 172.0858.

1-[2-(*o*-Hydroxyphenyl)ethenyl]cyclopentene (10h): yield 0.10 g (0.54 mmol, 54%); IR (neat) 3250, 1620, 960 cm^{-1}; ^1H NMR δ 1.50–2.20 (m, 2 H, CH_2), 2.20–2.80 (m, 4 H, CH_2), 4.60–5.60 (br, 1 H, OH), 5.82 (br s, 1 H, -C*H*=C<), 6.40–7.48 (m, 6 H, olefinic and aromatic H); HRMS, m/z calcd for $C_{13}H_{14}O$ 186.1044, found 186.1042.

1-[2-(*o*-Hydroxyphenyl)ethenyl]cyclohexene (10i): yield 0.14 g (0.72 mmol, 72%); IR (neat) 3350, 1630, 965 cm^{-1}; ^1H NMR δ 1.32–1.88 (m, 4 H, CH_2), 1.88–2.40 (m, 4 H, CH_2), 5.36 (s, 1 H, OH), 5.86 (br, 1 H, -C*H*=C<), 6.48–7.50 (m, 6 H, olefinic and aromatic H); HRMS, m/z calcd for $C_{14}H_{16}O$ 200.1200, found 200.1170.

Acknowledgment. We thank reviewers for advice and discussion for the formation mechanism of the Wittig products. We are also grateful for financial support of this work by a Grant-in-Aid for Developmental Scientific Research (62850150) from the Japan Ministry of Education, Science and Culture and by the Yoshida Society for Promotion of Science.

Registry No. **1a**, 114507-05-0; **1b**, 114507-07-2; **1c**, 114507-09-4; **1d**, 114507-11-8; **2b**, 114507-13-0; **2c**, 114507-15-2; **2d**, 114507-17-4; **3**, 791-28-6; **4**, 114507-20-9; **5**, 114507-22-1; **6c**, 114507-23-2; **6d** (X = ClO_4), 114507-25-4; **6d** (X = Br), 57380-65-1; **9a**, 100-52-7; **9b**, 104-55-2; **9c**, 107-86-8; **9d**, 3116-83-4; **10a**, 109432-85-1; **10b**, 114507-26-5; **10c**, 114507-27-6; **10d**, 68826-53-9; **10e**, 114507-28-7; **10f**, 114507-29-8; **10g**, 114507-32-3; **10h**, 114507-33-4; **10i**, 114507-34-5; **11d**, 59643-63-9; **11e**, 114507-30-1; **11f**, 114507-31-2; **16a**, 583-03-9; **16b**, 20157-19-1; (cyclopropylmethylene)triphenylphosphorane, 14902-12-6; (cyclobutylmethylene)triphenylphosphorane, 114507-18-5; (cyclopentylmethylene)triphenylphosphorane, 114507-19-6; (cyclohexylmethylene)triphenylphosphorane, 21960-28-1; benzeneselenenyl bromide, 34837-55-3; 1-methylcyclopentene, 693-89-0; 1-methylcyclobutene, 1489-60-7; 1-methylcyclohexene, 591-49-1; 1-cyclohexenylmethyl bromide, 37677-17-1; cyclopropylmethyl bromide, 7051-34-5; cyclobutylmethyl bromide, 17247-58-4; cyclopentylmethyl bromide, 3814-30-0; cyclohexylmethyl bromide, 2550-36-9.

1-Phenylisobenzofuran, 1-Phenylnaphtho[2,3-*c*]furan, 1-Phenylnaphtho[1,2-*c*]furan, and 3-Phenylnaphtho[1,2-*c*]furan via Cyclic Hemiaminal, Hemiacetal, and Acetal Precursors

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The title compounds have been generated via cyclic hemiaminal, hemiacetal, and acetal precursors and trapped in Diels–Alder reactions with several dienophiles. The precursors are easily prepared from *o*-bromobenzyl alcohol, 2-bromo-3-naphthalenemethanol, or 1-bromo-2-naphthalenemethanol. Metalation of the bromo alcohols followed by reaction with benzonitrile gave cyclic hemiaminals. In the presence of acid, the hemiaminals eliminate NH_3, generating 1-phenylisobenzofuran, 1-phenylnaphtho[2,3-*c*]furan, and 1-phenylnaphtho[1,2-*c*]furan. Metalation of 1-bromo-2-(phenylhydroxymethyl)naphthalene (prepared by reaction of PhMgBr with 1-bromo-2-naphthaldehyde) followed by reaction with dimethylformamide gives a cyclic hemiacetal precursor to 3-phenylnaphtho[1,2-*c*]furan. Cyclic acetal precursors to 1-phenyl- and 1-(2-naphthyl)naphtho[1,2-*c*]furan were prepared by the metalation of 1-bromo-2-(dimethoxymethyl)naphthalene, reaction with benzaldehyde and 2-naphthaldehyde, respectively, and cyclization in methanol/Dowex 50W-X8. The various transient furanoid species were trapped with dimethyl acetylenedicarboxylate, forming oxabicyclo adducts which aromatized in situ. With methyl acrylate, all of the furans reacted to give ortho adducts almost exclusively. The Diels–Alder reaction of 3-phenylnaphtho[1,2-*c*]furan with methyl acrylate is reversible. Ortho or meta adducts predominated, depending on the reaction conditions. Oxabicyclo adducts formed in these Diels–Alder reactions could usually be aromatized, giving phenyl-substituted naphthalenes, anthracenes, and phenanthrenes. Other polycyclic aromatic systems are also accessible: annelated fluorenones, phenylnaphthacene- and phenylpentacenequinones, and annelated pyrenes. The hemiaminals were hydrolyzed in water/THF/Dowex, giving a series of compounds that exhibited ring–chain tautomerism between hemiketal and ketone forms.

Isobenzofuran (IBF, **1**) and its derivatives are very reactive dienes[1] and readily undergo Diels–Alder reactions with a wide variety of dienophiles to give oxabicyclo adducts. These adducts have proven to be extremely versatile intermediates in the preparation of arylnaphthalene[2-5] and aryl tetralin lignans,[6-9] anthracyclinones,[10,11] and polycyclic aromatic hydrocarbons (PAHs).[12-15] Isonaphthofurans (INFs) naphtho[2,3-*c*]furan (**2**) and naphtho[1,2-*c*]furan (**3**), homologues of IBF, have also been useful intermediates in PAH synthesis.[16,17] 1-Benzyl derivatives of **1** and **2** have recently been employed in the preparation of a variety of PAH ring systems.[18] Despite the substantial interest in IBF, its 1-phenyl derivative **4** has received very little attention[19-21]

† Professor of Chemistry, University of Waterloo, deceased August 1st, 1985.

(1) Two excellent and complementary reviews of isobenzofuran chemistry have recently appeared: (a) Rodrigo, R. *Tetrahedron*, in press. (b) Rickborn, B. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, CT, 1988. Other reviews: Friedrichsen, W. *Adv. Heterocycl. Chem.* **1980**, *26*, 135. Wiersum, U. E. *Aldrichimica Acta* **1981**, *14*(3), 53.

(2) Plaumann, H. P.; Smith, J. G.; Rodrigo, R. *J. Chem. Soc., Chem. Commun.* **1980**, 354.

(3) Iwao, M.; Inoue, H.; Kuraishi, T. *Chem. Lett.* **1984**, 1263.

(4) De Silva, S. O.; St. Denis, C.; Rodrigo, R. *J. Chem. Soc., Chem. Commun.* **1980**, 995.

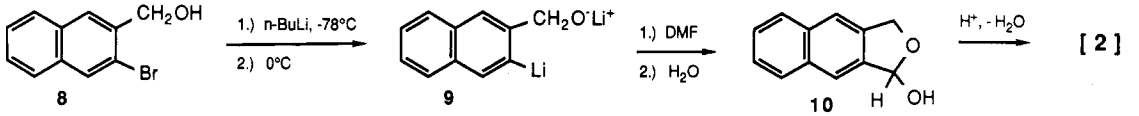
(5) Keay, B. A.; Rodrigo, R. *J. Am. Chem. Soc.* **1982**, *104*, 4725.

(6) Rodrigo, R. *J. Org. Chem.* **1980**, *45*, 4538.

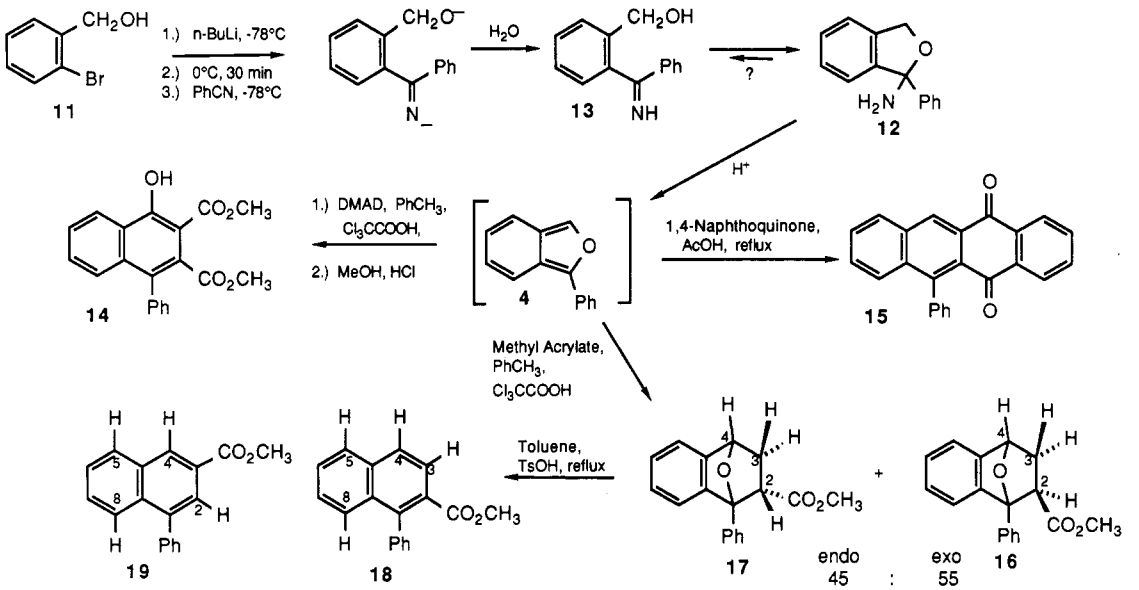
(7) Forsey, S. F.; Rajapaksa, D.; Taylor, N. J.; Rodrigo, R., unpublished results.

0022-3263/88/1953-2942$01.50/0

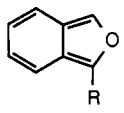
Scheme I



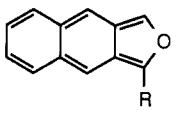
Scheme II



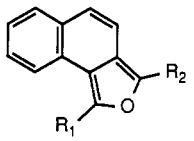
although many substituted derivatives of **4** have been generated and trapped in situ.[2-9] The preparation of the homologous INF derivatives **5**, **6**, and **7** has not been reported. We have developed several methods of generating aryl-substituted isobenzo- and naphtho[*c*]furans and studied the reaction of the transient furanoid species with several dienophiles. The oxabicyclo adducts give a variety of PAHs directly or upon subsequent reaction with acid.



1 R = H
4 R = Ph



2 R = H
5 R = Ph



3 $R_1 = R_2 = H$
6 R_1 = Ph, R_2 = H
7 R_1 = H, R_2 = Ph

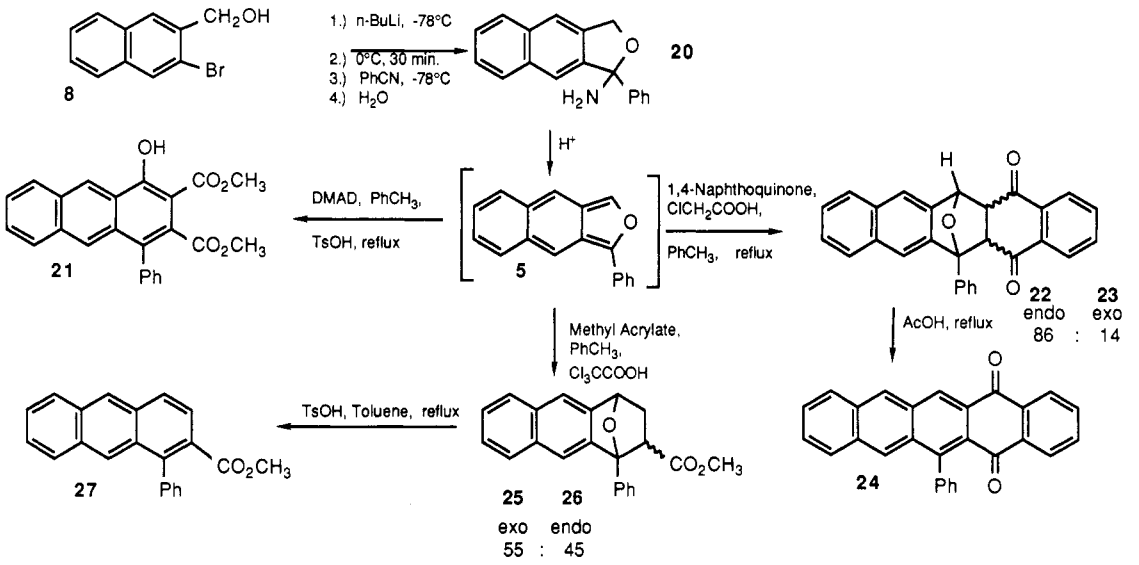
Results and Discussion

Our approach to the synthesis of hemiacetal precursors of **2** and **3**[16] involves lithiation of aryl bromides bearing an ortho hydroxymethyl group (such as **8**, Scheme I) and treatment of the dianion so formed (**9**) with dimethylformamide (DMF). In this way, a formyl group is introduced next to a hydroxymethyl group. Spontaneous cyclization to hemiacetal **10** gives a ring at the proper oxidation level for conversion to a furanoid species. Accordingly, treatment of **10** with acid effects a 1,4-elimination of H_2O to form **2** which is trapped in situ with several dienophiles. The key step in this synthesis is the reaction of aryl dianion **9** with an electrophile to yield a formyl substituent on hydrolysis. For preparation of 1-substituted derivatives of **1–3**, a substituted electrophile is needed that will yield a ketone (or equivalent) functional group. A wide variety of carbonyl compounds have been prepared by the reaction of alkyl- and aryllithiums by using nitrile electrophiles.[22] For this reason benzonitrile was explored as a potentially useful electrophile in reaction with dianions such as **9** to give suitable precursors of **4–6**.

2-Bromobenzyl alcohol (**11**) (Scheme II) was metalated by treatment with 2.1 equiv of *n*-BuLi at −78 °C. Warming to 0 °C gave the dianion which was cooled to −78 °C and treated with dry benzonitrile. The mixture was warmed to room temperature overnight and hydrolyzed with water (no acid). The product obtained was 1-amino-1,3-dihydro-1-phenyl-1-isobenzofuran (**12**), formed by cyclization of *o*-hydroxymethyl imine **13**. No hydrolysis to a ketone or hemiketal was observed. Compound **12** is comparable to the tetrahedral intermediate formed in the hydrolysis of imines and in the formation of imines from aldehydes and ketones.[23] For this reason, we refer to **12** as a hemiaminal. Hemiaminals are usually very reactive and not isolable, but like the closely related hemiacetals, are relatively stable in cyclic form.[24,25]

(8) Rajapaksa, D.; Rodrigo, R. *J. Am. Chem. Soc.* **1981**, *103*, 6208.
(9) Weeratunga, G.; Rajapaksa, D.; Rodrigo, R. *J. Org. Chem.* **1985**, *50*, 5902.
(10) Kende, A. S.; Curran, D. P.; Tsay, Y.-S.; Mills, J. E. *Tetrahedron Lett.* **1977**, 3537.
(11) Keay, B. A.; Rodrigo, R. *Tetrahedron* **1984**, *40*, 4597.
(12) Levy, L. A.; Kumar, V. P. S. *Tetrahedron Lett.* **1983**, *24*, 1221.
(13) Netka, J.; Crump, S. L.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 1189.
(14) Camenzind, R.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 1914.
(15) Smith, J. G.; Dibble, P. W. *J. Org. Chem.* **1983**, *48*, 5361.
(16) Smith, J. G.; Dibble, P. W. *J. Org. Chem.* **1986**, *51*, 3762.
(17) Pollart, D. J.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 3155.
(18) Dibble, P. W.; Smith, J. G. *J. Org. Chem.* **1988**, *53*, 1841.
(19) Faragher, R.; Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **1976**, 336.
(20) Tobia, D.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 3849.
(21) Hayakawa, K.; Yamaguchi, Y.; Kanematsu, K. *Tetrahedron Lett.* **1985**, *26*, 2689.
(22) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: New York, 1974; pp 116–121.
(23) March, J. *Advanced Organic Chemistry*, 3rd. ed.; John Wiley and Sons: New York, 1985; pp 796–802.
(24) Zhdanov, S. L.; Potekhin, A. A. *Khim. Geterosikl. Soedin.* **1977**, *8*, 417. Potekhin, A. A.; Zhdanov, S. L. *Khim. Geterosikl. Soedin.* **1979**, *10*, 1317.
(25) Tesse, J.; Glacet, C.; Couturier, D. *C. R. Acad. Sci. Ser. C.* **1975**, *280*, 1525.

Scheme III



Hemiaminal **12** proved to be a good source of 1-phenylisobenzofuran. A mixture of **12**, dimethyl acetylenedicarboxylate (DMAD), and a catalytic amount of TsOH was refluxed in toluene for 10 h. The intermediate oxabicyclo adduct aromatized in situ, giving naphthol **14**. With 1,4-naphthoquinone in refluxing AcOH, **12** gave 6-phenyl-5,12-naphthacenedione (**15**) without isolation of any bridged intermediate. This is comparable to the reaction of **1** and **2** with quinone dienophiles in refluxing AcOH and aqueous AcOH.[15,16]

Reaction of **12** with methyl acrylate in toluene with trichloroacetic acid gave a 55:45 exo:endo mixture of ortho adducts **16** and **17** with only traces of the meta products. The isomers could be distinguished by their ^{1}H NMR spectra. Chromatography of the crude reaction product gave a mixture that was 85% enriched in endo adduct **17**. The structural assignment was based on the shift of the H-2 signal (3.65 ppm), found downfield of its counterpart in **16** (3.07 ppm) due to shielding of the latter by the benzo ring. Coupling constants between H-3-endo and H-2 in each adduct were also diagnostic. The regiochemical outcome of the Diels–Alder reaction between **4** and methyl acrylate was confirmed by aromatization of a crude mixture of oxabicyclo adducts in MeOH/HCl. The ^{1}H NMR spectrum of the aromatized product indicated >96% ortho product, based on the upfield methoxy resonance at 3.61 ppm. A value of 3.90 has been reported[27] for the methoxy resonance of **18**. Of the many examples (vide infra) of aromatic methyl esters having ortho phenyl substituents prepared in the course of this work, none exhibit the methoxy resonance at higher field than 3.7 ppm.[28] A more detailed analysis was nevertheless undertaken in order to verify the identity of **18**. Its ^{1}H NMR spectrum at 500 MHz shows a downfield peak group consisting of three protons: an AB quartet (J = 8.7 Hz) and a broad doublet (J = 8.6 Hz). Due to ring current and substituent effects the H_3, H_4, and H_5 signals are expected to make up the downfield peak group. (H_8 is shielded by the peri phenyl substituent). The AB quartet is due to H_3 and H_4. Since an ortho coupling constant of 8.7 Hz is observed, **19** can be ruled out. Further verification that this downfield peak group contained two protons, ortho-coupled to one another, was obtained by simplifying the spectrum by the addition of Eu(fod)$_3$ (see Experimental Section).

Yields of adducts or aromatized products are good, ranging from 43% to 83% on the basis of *o*-bromobenzyl alcohol (**11**).

A linearly annelated homologue of **12** (Scheme II) was prepared in an identical manner, beginning with 2-bromo-3-(hydroxymethyl)naphthalene (**8**) (Scheme III). The crystalline product **20**, lost NH_3 when treated with acid, generating 1-phenylnaphtho[2,3-*c*]furan (**5**), which was trapped in situ with DMAD. The oxabicyclo adduct aromatized, giving bright yellow anthrol **21**. Oxabicyclo adducts of **5** and 1,4-naphthoquinone were isolated by using a milder acid catalyst (monochloroacetic acid) in refluxing toluene. Endo adduct **22** and exo adduct **23** were obtained in an 86:14 ratio (by ^{1}H NMR). Exo and endo isomers are easily distinguishable since the bridgehead proton of the former appears as a singlet while that of the latter is a doublet. The quinone adducts were aromatized to 6-phenyl-5,14-pentacenedione (**24**) in refluxing AcOH.

With methyl acrylate, **5** gave a reaction mixture completely analogous to the corresponding reaction of **4** (Scheme II). The ^{1}H NMR spectrum of the crude product was very similar to the mixture of **16** and **17** (Scheme II) and was interpreted in the same manner. Thus, a product mixture of **25** (exo) and **26** (endo) was obtained in a 55:45 ratio. Aromatization with TsOH in refluxing toluene gave ortho product **27** only.

Hemiaminal **28** (Scheme IV), prepared from 1-bromo-2-(hydroxymethyl)naphthalene (**29**), proved to be an excellent precursor to **6**. Reaction with DMAD (TsOH, toluene, reflux) gave phenanthrol **30** directly. In the ^{1}H NMR spectrum of **30**, two doublets (J = 9 Hz) appear at 7.86 (2 H) and 8.47 (1 H). The latter signal is due to H-10, peri to the OH function. The two-proton doublet is the result of coincident overlap of H-9 and H-5 signals. These assignments were established by comparing the ^{1}H NMR spectra of **31**, formed by acetylation of **30** (pyridine, acetic anhydride), and **30** itself. The acetyl group shields the H-10 proton,[29] which then becomes coincident with H-9 at 7.88 ppm forming an apparent two-proton singlet. The

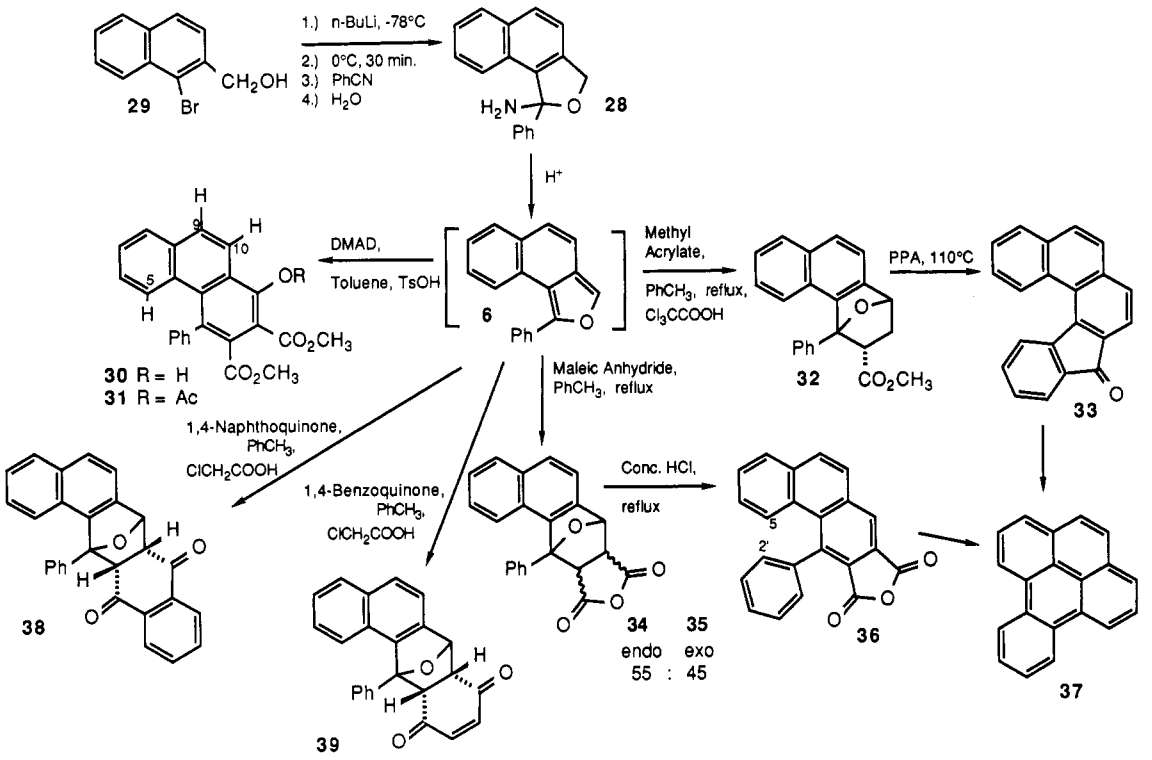
(26) A similar species was used to prepare a substituted 1-phenylisobenzofuran in the total synthesis of resistomycin.[5]

(27) Pfau, M.; Rowe, J. E., Jr.; Heindel, N. D. *Tetrahedron* 1978, *34*, 3469.

(28) Interestingly, the original report[27] gives ^{1}H NMR data for a remotely substituted (6-methyl) derivative of **18** in which the shift position quoted for this methoxy resonance is 3.57 ppm. This value is very close to what we observe for **18**.

(29) Keay, B. A.; Rodrigo, R. *Can. J. Chem.* 1985, *63*, 735.

Scheme IV



H-5 signal at 7.86 ppm in **30** is shielded to the extent of ca. 1 ppm (compared with phenanthrene) by the phenyl substituent at C-4.

With methyl acrylate (refluxing toluene, trichloroacetic acid) **28** gave endo, ortho adduct **32** in 79% isolated yield. Cyclization of the carbomethoxy group with the bridgehead phenyl substituent was attempted to see if methyl acrylate adducts could give access to annelated fluorenones. A modest yield (27%) of **33** was obtained after heating **32** in polyphosphoric acid (PPA) at 110 °C.

Reaction of **28** with maleic anhydride (MA) in refluxing toluene with a catalytic amount of TsOH gave a 55:45 mixture of adducts **34** (endo) and **35** (exo). This ratio is partly the result of equilibration since a sample of **34** refluxed in toluene was largely converted into **35**. A similar observation was reported for the endo MA adduct of **3**.[16] Refluxing adducts **34** and **35** in concentrated HCl resulted in aromatization to anhydride **36**. Phenanthrenes substituted with phenyl groups at C-4 are capable of forming condensed PAHs by dehydrogenation between C-5 and C-2′ (shown for **36**).[30] Both **33** and **36** have previously been converted to benzo[*e*]pyrene **37**.[31]

A 91% isolated yield of endo quinone adduct **38** was obtained on reaction of **28** with 1,4-naphthoquinone using monochloroacetic acid as the catalyst. 1,4-Benzoquinone adduct **39** was prepared in the same way. Longer reaction times in the preparation of **38** did not give the aromatized product but led to the formation of a purple product which has not been identified. The failure of this quinone adduct of **6** to aromatize while comparable adducts of **4** and **5** do so parallels the behavior of related adducts of **1**–**3**.[15,16]

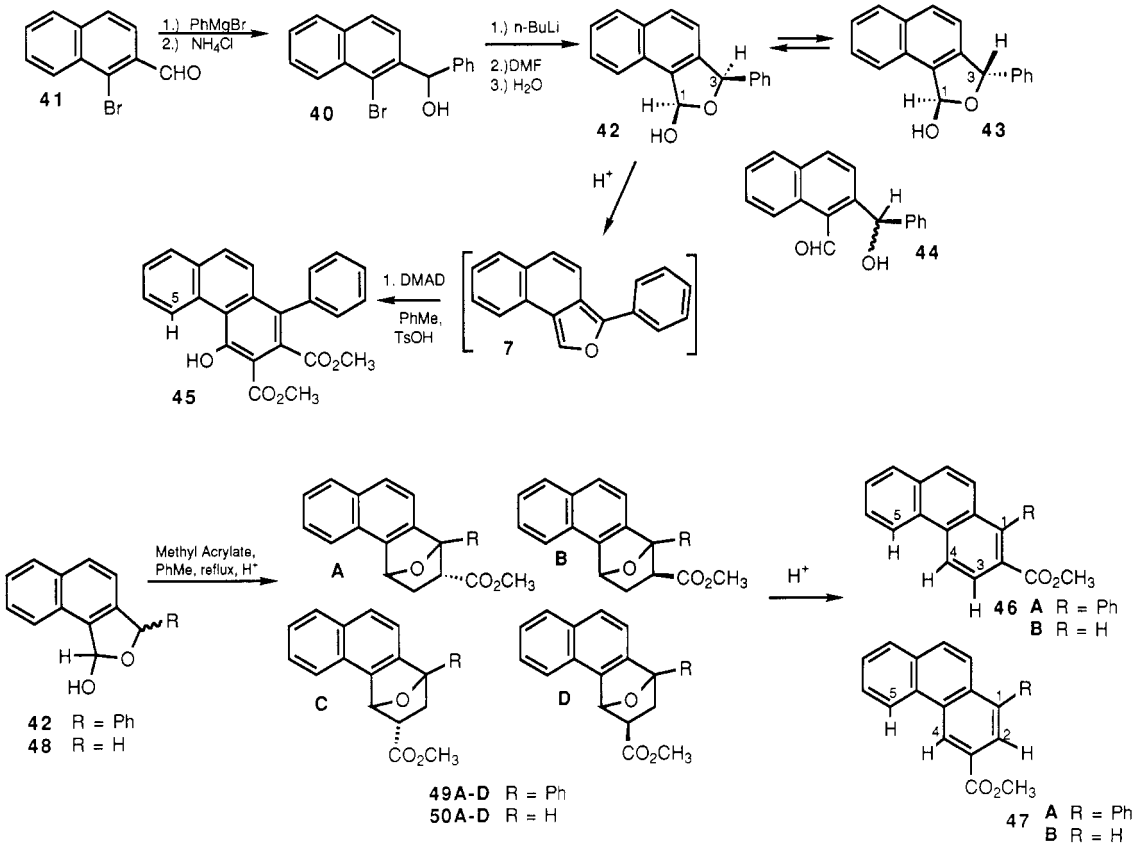
The use of alkyl nitriles (acetonitrile and valeronitrile) instead of benzonitrile appears to result in α-proton abstraction from the electrophile. No variations of reaction conditions have been attempted, nor has transmetalation of the lithiated species with anhydrous $MgBr_2$ been investigated.

A hemiacetal precursor (**42**) to 3-phenylnaphtho[1,2-*c*]furan (**7**) was prepared by using the strategy previously applied to the preparation of **10** (Scheme I). Bromo alcohol **40** (Scheme V) was prepared by the addition of excess PhMgBr to aldehyde **41**. Metalation with *n*-BuLi, addition of DMF, and hydrolysis gave crystalline cis hemiacetal **42**. Freshly prepared NMR samples of **42** show H-3 as a singlet, indicating the cis configuration.[32] Over several hours, new signals appear, indicating the presence of trans isomer **43**. H-3 of **43** appears as a doublet with a coupling constant of J = 2.6 Hz, typical of trans coupling in these systems.[16,33,34] The H-1 signals are in the aromatic region and could be distinguished from the H-3 signals on the basis of coupling observed in the hydroxyl proton resonances ($J_{H\text{-}1}$–J_{OH} = 7 Hz). Isomerization presumably occurs through ring-open tautomer **44**, which was not observed. The rate at which equilibrium is approached is probably limited by the opening of **42** to **44**. The equilibration, which takes several hours, can be compared to the equilibration of **10** to 3-(hydroxymethyl)-2-naphthaldehyde which occurs in less than 1 h.[16] Ring-opening of **42** is probably impeded by steric interactions between the angular ring and the aldehyde substituent of **44**. No such steric interactions develope when **10** opens. Similar considerations account for the variations in equilibrium constants observed for the hydrolysis products of **12**, **20**, and **28** (vide infra).

In the presence of TsOH, **42** generated **7** which was trapped with DMAD. Aromatization in situ gave phenanthrol **45**. As a result of steric crowding in the bay region, H-5 is found far downfield at 9.93 ppm. The hydroxyl proton is also substantially deshielded, found at 13.4

(30) For example, the dehydrogenation of 4-phenylphenanthrene to benzo[*e*]pyrene: Studt, P. *Liebigs Ann. Chem.* **1978**, 530.
(31) Campbell, A. D. *J. Chem. Soc.* **1954**, 3659.
(32) Barfield, M.; Spear, R. J.; Sternhell, S. *J. Am. Chem. Soc.* **1975**, *97*, 5160.
(33) Keay, B. A.; Plaumann, G. P.; Rajapaksa, D.; Rodrigo, R. *Can. J. Chem.* **1983**, *61*, 1987.
(34) Mirsadeghi, S.; Rickborn, B. *J. Org. Chem.* **1987**, *52*, 787.

Scheme V



ppm. This is >1 ppm further downfield than the O–H signal of **30** (Scheme IV) found at 12.3 ppm.

Reaction of **42** with methyl acrylate (toluene, reflux, trichloroacetic acid) gave two surprising results. Firstly, under the same conditions employed for the reactions of **4–6** with methyl acrylate, the oxabicyclo adducts aromatized to a major extent. (Aromatization was completed by adding TsOH and refluxing briefly.) Secondly, the regioselectivity in this reaction was very poor in contrast with analogous reactions of **4–6**. A 60:40 mixture of esters **46A** and **47A** was obtained. These regioisomers were distinguished by their ^{1}H NMR spectra. Distinctly different methoxyl resonances were observed, the upfield signal (3.64 ppm) being attributed to **46A** and the downfield signal (4.03 ppm) to **47A**. The downfield regions of the ^{1}H NMR spectra of these compounds are also diagnostic. The shift positions of bay-region protons H-4 and H-5 are differentiated by the ester substituent in **47A**, but not in **46A**.

Poor regioselectivity in the reaction of **7** with methyl acrylate results from reversibility of the Diels–Alder reaction and partial equilibration to thermodynamically more stable products. In the early stages of the reaction between **7** and methyl acrylate (**42**, refluxing toluene, $ClCH_2COOH$, 2 h), ortho addition predominates. Ortho adducts **49A**, **49B**, and meta adduct **49C** (**A**:**B**:**C** = 51:46:3) were characterized by ^{1}H NMR after partial chromatographic separation. A 65:35 mixture of endo adducts **A** and **C** was refluxed for 9 h in toluene/methyl acrylate to give a mixture of all four adducts: **49A**:**B**:**C**:**D** = 23:18:53:6. After a further 16 h of heating the amounts of **C** and **D** increased at the expense of **A** and **B**. These observations clearly indicate that the Diels–Alder reaction is reversible. If TsOH is used as the acid catalyst in the generation of **7** from **42**, aromatization of the adducts occurs before substantial equilibration. Thus, **46A** predominates over **47A** 11:1 (**42**, methyl acrylate, TsOH, refluxing toluene, 1 h) and was isolated in 62% yield. If a weaker acid (AcOH) is used in the generation of **7**, aromatization does not occur. After heating for 4 days, meta adducts predominate (**49A**:**B**:**C**:**D** = 8:8:63:21). Subsequent aromatization of this mixture with TsOH gave **47A** in 70% isolated yield.

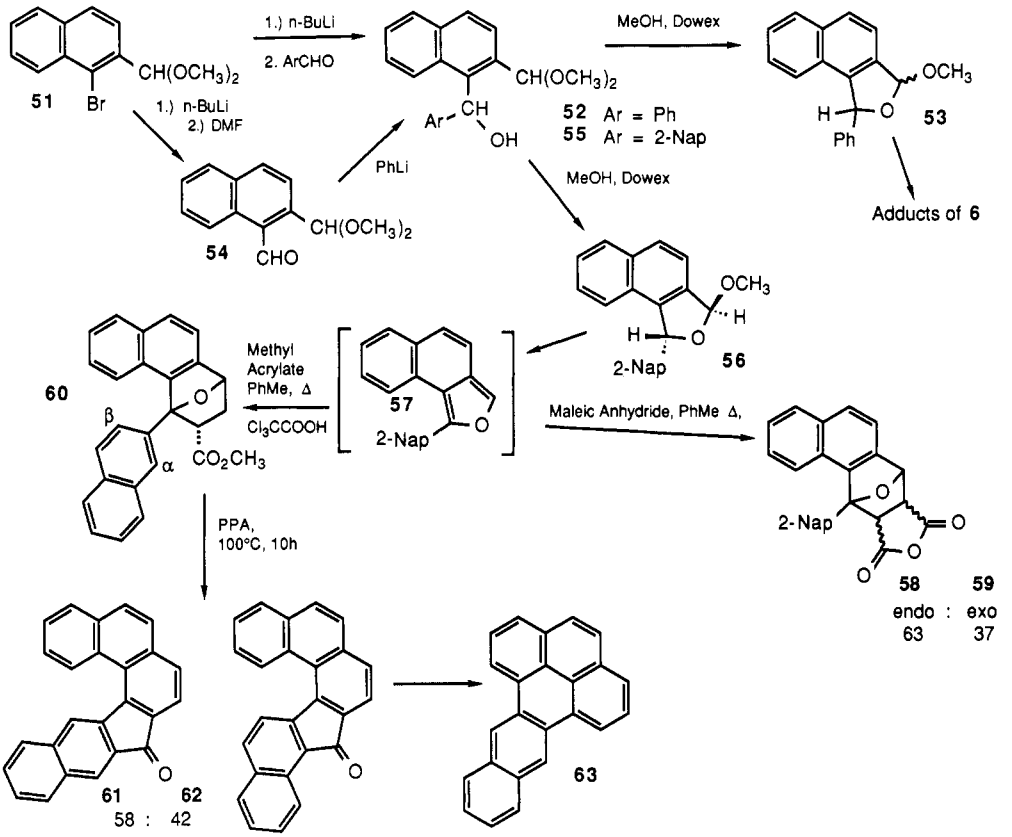
Of the Diels–Alder reactions between **4–7** and methyl acrylate, the reaction with **7** appears to be the only example that is reversible in refluxing toluene. Endo methyl acrylate adducts of **4** and **5** (**17**, Scheme II, and **26**, Scheme III) are unchanged after 12 h in refluxing toluene and adduct **32** (unlikely to be the most thermodynamically stable) is formed almost exclusively in the reaction between **6** and methyl acrylate. The reversibility observed for **7** may be a reflection of its greater stability relative to **4–6**. The angular naphtho[1,2-*c*]furan (**3**) is substantially more stable than **1** or **2**.[1] A phenyl substituent in the 3-position (i.e. **7**) will be a further stabilizing influence.[35] Since the phenyl substituent in **6** cannot become coplanar with the angular ring system due to steric interactions, **6** will not be stabilized to the same degree as **7** by the phenyl group. This may account for the ease with which **7** undergoes reversible Diels–Alder reaction where **6** does not.

Reactions of **3** with 1-acetoxyacrylonitrile and butenolide have been reported to occur with essentially no regioselectivity.[36] For comparison with **7**, the regioselectivity in the reaction of **3** and methyl acrylate was determined. Hemiacetal **48**[16] (Scheme V) was refluxed in methyl acrylate with trichloroacetic acid. The crude product was a complex mixture of all four possible products **50A–D** (by

(35) This is consistent with Rickborn's demonstration that **4** is 0.77 times as reactive as **1** with *N*-phenylmaleimide. Tobia, D.; Rickborn, B. *J. Org. Chem.* **1987**, *52*, 2611.

(36) Cornejo, J. J.; Ghodsi, S.; Johnson, R. D.; Woodling, R.; Rickborn, B. *J. Org. Chem.* **1983**, *48*, 3869.

Scheme VI



^{1}H NMR). Evidence of this was the presence of four methoxy signals at δ 3.20, 3.48, 3.80, and 3.82 in a ratio of 4.6:3.3:1:1. The two high-field signals can be assigned to the endo adducts in which the methoxy groups are shielded, lying under the naphthalene ring. It may therefore be concluded that endo addition predominates, making up ca. 80% of the mixture. Presumably, the methoxy signal of **50C** (scheme V) will be furthest upfield due to its greater proximity to the shielding influence of the angular naphthalene ring relative to **50A**. The crude reaction mixture was dissolved in MeOH and pipetted into refluxing concentrated HCl to effect aromatization. Examination of the 500-MHz ^{1}H NMR spectrum of the product established that **47B**, in which the carboxylate and angular ring are proximal, is the major product in a 60:40 ratio over **46B**. The downfield region of the ^{1}H NMR spectrum is comparable to a mixture of phenylsubstituted analogues **46A** and **47A** in that the chemical shifts of the bay-region protons are again quite different in **47B** as opposed to **46B**. Any directing influence of the angular ring system of **7** is overcome by the phenyl substituent. Ethoxy substituents in the 1- and 3-positions have also been demonstrated to give ortho products exclusively in reaction with butenolide and 1-acetoxyacrylonitrile.[36]

The method used for the preparation of **42** and subsequent generation of **7** should also prove useful in the preparation of 3-alkylnaphtho[1,2-*c*]furans and 1-alkylnaphtho[2,3-*c*]furans.[37] In combination with the strategy of Schemes I–III, disubstituted isobenzo- and isonaphthofurans are possible.

As a final approach to the synthesis of 1-arylnaphtho[1,2-*c*]furans, we investigated the extension to naphthalenic systems of Rodrigo's approach to the synthesis of a wide variety of substituted IBFs.[1,33] Bromo acetal **51** (Scheme VI) was metalated with *n*-BuLi and the resulting anion treated with benzaldehyde to give **52**. Stirring **52** in MeOH/Dowex or chromatography on silica gave a ca. 1:1 mixture of diastereomeric acetals **53** as an oil. As a source of **6**, **53** was identical with hemiaminal **28** in reactions with DMAD and MA. An alternative route to **52** was via aldehyde **54**, prepared by metalation of **51** and subsequent reaction of the anion with DMF. Treatment of **54** with PhLi gave **52**. While obviously not as efficient a route to **52**, **54** has more potential utility. The choice of aldehyde electrophiles is limited to those without α-hydrogens due to deprotonation by the anion formed from **51**.[33] In contrast, reaction of the aldehyde functional group of **54** with Grignard reagents, alkyllithiums, and other nucleophiles[38] circumvents this problem.[33]

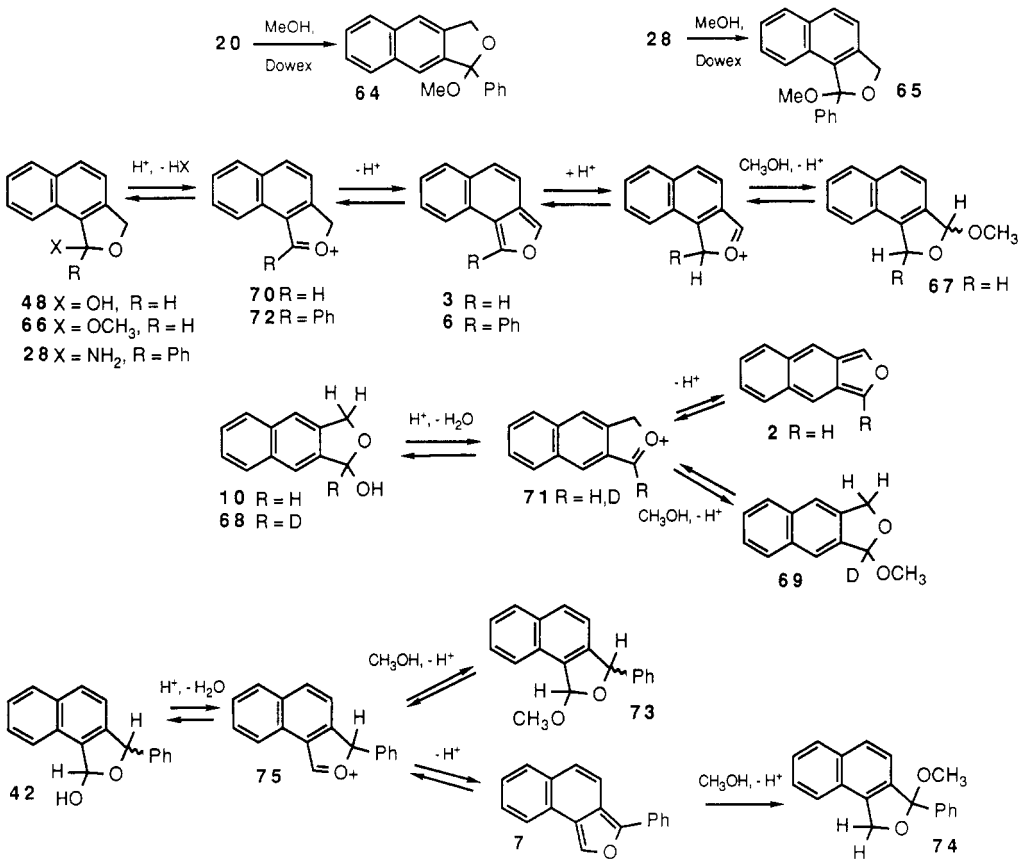
The anion formed from **51** also reacted with 2-naphthaldehyde to give alcohol **55**. Cyclization in MeOH/Dowex gave exclusively trans acetal **56** as a crystalline solid. This acetal was not observed to equilibrate to its cis form.

When treated with acid, **56** generated 1-(2-naphthyl)naphtho[1,2-*c*]furan (**57**), which was trapped in situ with MA and methyl acrylate. The behavior of **57** closely parallels that of phenyl analogue **6**. A 63:37 endo:exo ratio of MA adducts **58** and **59** was obtained. With methyl acrylate, the major product was endo, ortho adduct **60**. Adduct **60** was heated with PPA to effect intramolecular acylation of the naphthyl substituent by the carboxylate group. There are two possible sites of acylation and the selectivity of this process was of interest. Acylations of

(37) The latter via 2-bromo-3-naphthaldehyde prepared by dibromination of 2-bromo-3-methylnaphthalene and subsequent hydrolysis: Smith, J. G.; Dibble, P. W.; Sandborn, R. E. *J. Chem. Soc., Chem. Commun.* **1983**, 1197. Alternatively, this aldehyde can be prepared by PCC oxidation of 2-bromo-3-naphthalenemethanol using the standard method: Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647. We have found that the latter preparation gives a product of superior quality.

(38) 1-Cyano and ester IBF's have been prepared from similar intermediates: Rodrigo, R.; Knabe, S. M.; Taylor, N. J.; Rajapaksa, D.; Chernishenko, M. J. *J. Org. Chem.* **1986**, *51*, 3973.

Scheme VII



similar adducts bearing 2-naphthylmethyl substituents occur exclusively at the α-position.[18] In this case, however, a mixture of products was obtained, the major product, **61**, resulting from acylation at the β-position. Both **61** and **62** have previously been converted into naphtho[2,3-*e*]-pyrene (**63**).[31]

Methanolysis and Hydrolysis of the Hemiaminals. Hemiacetals **10** (Scheme I) and **48** (Scheme V) have previously been converted into cyclic acetals[16] by refluxing in MeOH with Dowex (Scheme VII). Cyclic acetal intermediates have been useful precursors to IBFs and INFs by the strong-base-induced 1,4-elimination of alcohol.[39-41] This technique has several advantages over the acid-catalyzed process in that the furan species may often be isolated and a wider range of dienophiles employed. Hemiacetal **48** gave a mixture of regioisomeric acetals **66** and **67**.[16] The interconversion between **66** and **67** (under different conditions) has been explained by postulating the intermediacy of **3**.[36] In the acetalization of **10**, **2** is not formed. This was established by refluxing deuteriated hemiacetal **68**[42] in MeOH/Dowex. The product obtained was **69**, having deuterium exclusively on the acetal carbon. The difference between these two cases is probably due to the substantially greater loss of resonance energy involved in the deprotonation of **71** → **2** relative to **70** → **3**. Under these conditions (MeOH, Dowex), hemiaminals **20** and **28** were converted to cyclic acetals **64** and **65**. In contrast to angular hemiacetal **48**, **28** did not give regioisomeric acetal products, implying that **6** is not formed under these conditions. In this case it is likely that carbocation **72** is stabilized (by the phenyl substituent) to the extent that deprotonation to **6** becomes unfavorable. Because carbocation **75** is not stabilized by a phenyl substituent, hemiacetal **42** would be expected to form **7** readily and give a mixture of acetals **73** and **74**. Under the reaction conditions employed, however, **42** decomposes into a bright orange polymer. This is indirect evidence that **7** is being formed, but is not conclusive.

Table I[a]

	R = Ph		R = H	
	% ring	% chain	% ring	% chain
12 → **76** ⇌ **77**	7	93	60	40
20 → **78** ⇌ **79**	2	98	25	75
28 → **80** ⇌ **81**	46	54	100	0

[a] Numbers apply to compounds with R = Ph.

Hemiaminals **12**, **20**, and **28** were hydrolyzed in 1:1 THF/water by using Dowex as acid catalyst. The products of hydrolysis all exhibited spectrally (NMR) visible ring–chain tautomerism,[43] the ring forms being hemiketals, the chain forms *o*-hydroxymethyl ketones. The results of these hydrolyses are shown in Table I (R = Ph) in comparison with unsubstituted systems (R = H) prepared previously.[16]

(39) Naito, K.; Rickborn, B. *J. Org. Chem.* **1980**, *45*, 4061.
(40) Crump, S. L.; Netka, J.; Rickborn, B. *J. Org. Chem.* **1984**, *49*, 304.
(41) Pollart, D. J.; Rickborn, B. *J. Org. Chem.* **1987**, *52*, 792.
(42) Prepared by the substitution of DMF-d_7 for DMF in the preparation of **10** previously described.[16]
(43) A book has recently been published on this field: Valters, R. E.; Flitsch, W. *Ring-Chain Tautomerism*; Katritzky, A. R., Ed.; Plenum Press: New York, 1985.

The proportions of ring and chain tautomers were determined by ^1H NMR in $CDCl_3$ solution at ambient temperature.

Comparison of the equilibrium data in Table I shows that the phenyl (relative to H) substituted compounds are substantially shifted in favor of the chain form. Structural factors that stabilize the chain form and/or destabilize the ring form will causes a shift in this direction. For R = Ph, the chain forms are stabilized by conjugation of the carbonyl with the Ph substituent.[44] If a methylene is substituted between the carbonyl and the phenyl substituent (i.e. R = CH_2Ph), conjugation is interrupted and the equilibria shift toward the ring form.[45] An illustrative comparison is **44** versus **81**. Both species are angular chain tautomers bearing phenyl substituents, but only **81**, in which the carbonyl is conjugated with both aryl systems, is visible in equilibrium with **80**. In fact, the equilibrium between **80** and **81** is unusual in that *any* chain form is observed. Similar systems bearing a substituent ortho to the ring usually exist only in the ring form.[16,33,46] Steric factors can also play a role. Steric interaction between the ortho protons of the phenyl substituent and the rest of the ring tautomer will destabilize this form. Such interactions are diminished or eliminated upon formation of the chain form.[47,48]

In principle, ring–chain tautomerism can also exist between the hemiaminals and their corresponding imines (i.e. **12** ⇌ **13**, Scheme II). This is not observed in the ^1H NMR spectra of these compounds. Tautomerism has been observed in similar systems in very polar solvents.[24] The lower thermodynamic stability associated with imines in comparison to ketones would tend to disfavor the chain tautomers of the former, accounting for the lack of any observable tautomerism in the current case.

Experimental Section

Melting points were determined in open capillaries with a Mel-Temp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. NMR spectra were recorded on Bruker WP-80, AC-200, AM-250, or AM-500 instruments, using tetramethylsilane (TMS) as an internal reference. Peaks are reported in ppm downfield from TMS using the δ scale. Mass spectra were run on VG-2020 and VG-ZABE mass spectrometers. Analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Dry diethyl ether was freshly distilled from sodium (benzophenone ketyl). DMF was stirred over CaH_2 at 90 °C for 10 h and then distilled onto NaH for storage. Commercial benzonitrile and benzaldehyde were distilled and stored in a desiccator. 1,4-Naphthoquinone was steam-distilled.

1-Amino-1,3-dihydro-1-phenylisobenzofuran (12). In 150 mL of dry diethyl ether was dissolved 2 g (11.0 mmol) of **11** and the solution was cooled to −78 °C. *n*-Butyllithium (9 mL of a 2.6 M solution in hexanes, 23 mmol) was added and the mixture stirred for 5 min. The solution was warmed to 0 °C and after 30 min cooled to −78 °C. Benzonitrile (1.2 mL, 12 mmol) was injected, giving an orange solution. The reaction was left to warm to room temperature overnight. An equal volume of water was added, and the organic layer was separated. The aqueous phase was washed once with ether, and the organic phases were combined and then dried over $MgSO_4$. After filtration, the solvent was removed and the residue pumped under high vacuum, leaving 2.58 g of a crude oil which was used without further purification: ^1H NMR ($CDCl_3$, 200 MHz) δ 2.40 (br s, 2 H, exchanges with D_2O), 5.18 and 5.28 (AB, q, J = 12.6 Hz, 2 H), 7.21–7.41 (m, 7 H), 7.66–7.71 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 70.63, 99.22, 120.89, 123.21, 125.56, 127.57, 128.08, 128.19, 138.49, 143.36, 144.83; IR (neat) 3363, 3299 (w, N–H), 1022, 1011, 750, 723, 697 cm^{-1}; MS (EI), *m/e* (rel intensity) 211 (M^+, 8), 210 (14), 195 (55), 194 (100), 193 (23), 180 (14), 166 (18), 165 (100), 134 (54), 77 (32); HRMS found 211.0990, calcd for $C_{14}H_{13}NO$ 211.0997.

Dimethyl 1-Hydroxy-4-phenyl-2,3-naphthalenedicarboxylate (14). In 50 mL of toluene were refluxed 0.30 g (ca. 1.5 mmol) of **12**, 1 g (7 mmol) of DMAD, and a few crystals of TsOH for 10 h. The solvent was removed under reduced pressure and the residue taken up in 15 mL of MeOH. Concentrated HCl, 1 mL, was added and the mixture refluxed for 4 h. The mixture was cooled to room temperature and then refrigerated to afford 0.18 g of crystalline **14** (43% from **11**): mp 150–152 °C (lit.[19] mp 149–150 °C); ^1H NMR ($CDCl_3$, 200 MHz) δ 3.51 (s, 3 H), 3.95 (s, 3 H), 7.27–7.62 (m, 8 H), 8.48–8.53 (m, 1 H), 12.40 (s, 1 H, exchanges with D_2O).[49]

6-Phenyl-5,12-naphthacenedione (15). 1,4-Naphthoquinone (0.35 g, 2.2 mmol) and **12** (0.47 g, 2.2 mmol) were refluxed in glacial AcOH for 5 h. A red-brown precipitate was collected by filtration and recrystallized from AcOH to give 0.31 g of product (48% from **11**): mp 305–307 °C (lit.[50] mp 282–283 °C); ^1H NMR ($CDCl_3$, 200 MHz) δ 7.20–7.25 (m, 2 H), 7.46–7.79 (m, 9 H), 8.12–8.16 (m, 1 H), 8.36–8.39 (m, 1 H), 8.61–8.65 (m, 1 H).

Methyl 1,4-Epoxy-1,2,3,4-tetrahydro-1-phenyl-2-naphthalenecarboxylate (16/17). In 20 mL of toluene were refluxed 0.48 g (2.3 mmol) of **12**, 2.5 g (30 mmol) of methyl acrylate, and a catalytic amount of trichloroacetic acid for 10 h. The reaction was cooled, washed with $NaHCO_3$ solution, and dried over $MgSO_4$ and the solvent was removed, giving a crude oil, 55% exo (**16**) and 45% endo (**17**) by ^1H NMR. Chromatography on Kieselgel 60, eluting with toluene, gave 0.32 g of a mixture, ca. 86% **17** (57% from **11**): ^1H NMR ($CDCl_3$, 250 MHz) δ endo 1.98 (dd, J = 3.9 and 11.6 Hz, 1 H), 2.66 (dt, J_d = 5.1 Hz, J_t = 11.0 Hz, 1 H), 3.46 (s, 3 H), 3.66 (dd, J = 3.9 and 10.2 Hz, 1 H), 5.50 d, J = 5.0 Hz, 1 H), 7.02 (d, J = 7.2 Hz, 1 H), 7.16 (t, J = 7.3 Hz, 1 H), 7.24 (t, J = 7.0 Hz, 1 H), 7.26 (d, J = 5.8 Hz, 1 H), 7.31–7.48 (m, 3 H), 7.70–7.73 (m, 2 H) (The endo/exo mixture had additional signals: 3.06 (dd, J = 4.5 and 8.4 Hz, 1 H), 3.06 (s, 3 H), other signals overlap with the endo product.); IR (neat) endo 1734 (C=O), 1458, 1352, 1204, 1036, 982, 958, 762 cm^{-1}; MS (EI), *m/e* (rel intensity) 280 (M^+, 1), 249 (3), 195 (16), 194 (100), 165 (21), 139 (2), 105 (3), 77 (5).

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.31; H, 5.73.

Methyl 1-Phenyl-2-naphthalenecarboxylate (18). In 20 mL of toluene were refluxed 0.0967 g of crude **12**, 1 g of methyl acrylate (large excess), and a catalytic amount of trichloroacetic acid for 12 h. A few crystals of TsOH were added and heating was continued for 4 h more. The solvent was stripped off and the residue analyzed by ^1H NMR, showing it to be ca. 96% **18**. The crude mixture was chromatographed on silica gel, eluting with $CHCl_3$, to give 0.0876 g of **18**, an oil (83% from **11**): ^1H NMR ($CDCl_3$, 500 MHz) δ 3.61 (s, 3 H), 7.29–7.31 (m, 2 H), 7.39–7.51 (m, 4 H), 7.54 (t, J = 7.5 Hz, 1 H), 7.59 (d, J = 8.7 Hz, 1 H), 7.89 (d, J = 8.6 Hz, 1 H), 7.90 and 7.92 (partially obscured AB q, J = 8.7 Hz, 2 H). Addition of $Eu(fod)_3$ to a sample of this compound spread the three downfield protons into three ortho-coupled doublets. Irradiation of the downfield doublet caused the collapse of one of the other doublets. IR (neat): 1720 (C=O), 1277, 1240, 1130, 767, 703 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.53; H, 5.34.

1-Amino-1,3-dihydro-1-phenylnaphtho[2,3-*c*]furan (20). This compound was prepared from 5.0 g (21 mmol) of **8**,[16] *n*-BuLi (17 mL, 2.6 M, 45 mmol), and 2.5 mL (25 mmol) of benzonitrile, using the procedure described for the preparation of **12**. The product was crystallized from 20 mL of hexane, giving 4.69 g of

(44) An opposite effect has been observed in similar tautomerisms where electron-withdrawing groups, placed para to the carbonyl, destabilize the chain forms: Valters,[43] pp 246–248.

(45) Smith, J. G.; Dibble, P. W. *Tetrahedron* **1984**, *40*, 1667.

(46) 4,7-Dimethyl-1-benzyl-1,3-dihydro-1-hydroxyisobenzofuran is 100% ring form: Wikman, R. T. Doctoral Dissertation, University of Waterloo, 1975, p 112. 1-Benzyl-1,3-dihydro-1-hydroxyisobenzofuran is 75% ring form.

(47) Sorokina, V. S.; Savich, I. G.; Pavlova, L. A. *Zh. Org. Khim.* **1973**, *9*, 1967, 1970.

(48) Glinka, H.; Fabrycy, A. *Roczn. Chem.* **1970**, *44*, 1703, 1712.

(49) The downfield signal (OH) was not reported in the original data published for **14**.[19]

(50) Etienne, A.; Rutimeyer, B. *Bull. Soc. Chim. Fr.* **1956**, 1589.

20 (85%): mp 122–124 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.49 (br s, 2 H), 5.28 and 5.40 (AB q, J = 13 Hz, 2 H), 7.25–7.86 (m, 11 H); IR (Nujol) 3391, 3320 (w, N–H), 1019, 950, 793, 767, 751, 708 cm^{-1}; MS (EI), m/e (rel intensity) 262 (M^+ + 1, 20), 261 (M^+, 100), 260 (55), 245 (48), 244 (81), 243 (32), 215 (53), 184 (54).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.90; H, 5.72; N, 5.44.

Dimethyl 1-Hydroxy-4-phenyl-2,3-anthracenedicarboxylate (21). In 50 mL of toluene were refluxed 0.050 g (0.19 mmol) of **20**, excess DMAD, and a catalytic amount of trichloroacetic acid for 14 h. The solvent was removed and the residue taken up in $CHCl_3$. The solution was washed with $NaHCO_3$ solution, heated with $MgSO_4$ and decolorizing charcoal, and filtered, and the solvent was removed. Recrystallization from $CHCl_3$ gave 0.033 g (45%) of **21**, a yellow-green fluorescent solid: mp 245–247 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.53 (s, 3 H), 3.96 (s, 3 H), 7.36–7.54 (m, 7 H), 7.79–7.82 (m, 1 H), 7.92 (s, 1 H), 8.08–8.12 (m, 1 H), 9.12 (s, 1 H), 12.82 (s, 1 H, exchanges with D_2O); IR (Nujol) 2500–3400 (br O–H), 1727 and 1658 (C=O), 1349, 1330, 1256, 1233, 807, 755, 707 cm^{-1}.

Anal. Calcd for $C_{24}H_{18}O_5$: C, 74.60; H, 4.70. Found: C, 74.38; H, 4.70.

6,13-Epoxy-5a,6,13,13a-tetrahydro-6-phenylpentacene-5,14-dione (22/23). In 30 mL of toluene were refluxed 0.23 g (0.88 mmol) of **20**, 0.15 g (0.95 mmol) of 1,4-naphthoquinone, and a catalytic amount of monochloroacetic acid for 1 h. The residue was taken up in hot toluene, hexane was added, and the solution was cooled. Fitration gave 0.30 g (84%) of a mixture of endo and exo isomers. Endo isomer: 198–199 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.15 and 4.26 (AB of ABX, J_{AB} = 9.7 Hz, upfield portion is further split, J = 5.4 Hz, 2 H), 6.04 (d, J = 5.4 Hz, 1 H), 7.20–7.63 (m, 13 H), 7.95–8.01 (m, 2 H); IR (Nujol) 1673 (C=O), 1590, 1296, 1263, 757, 739 cm^{-1}.

Anal. Calcd for $C_{28}H_{18}O_3$: C, 83.57; H, 4.51. Found: C, 83.63; H, 4.40.

Dark red crystals of the exo isomer were separated by hand and washed with $CHCl_3$. Exo isomer: mp 194–199 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.50 and 3.61 (AB q, J = 7.8 Hz, 2 H), 5.94 (s, 1 H), 7.25–7.90 (m, 15 H); IR (Nujol) 1670 (C=O), 1588, 1264, 992, 954, 879, 754 cm^{-1}.

6-Phenylpentacene-5,14-dione (24). In 15 mL of glacial AcOH was refluxed 0.16 g of **22/23** for 3 h. The mixture was cooled and filtered to give 0.0783 g of **24**, an orange solid (50%): mp 315–318 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.32–7.36 (m, 2 H), 7.51–7.87 (m, 8 H), 8.07–8.22 (m, 3 H), 8.37–8.41 (m, 1 H), 8.74 (s, 1 H), 9.23 (s, 1 H); IR (Nujol) 1669 (C=O), 1295, 1277, 1257, 712 cm^{-1}.

Anal. Calcd for $C_{28}H_{16}O_2$: C, 87.48; H, 4.20. Found: C, 87.39; H, 4.35.

Methyl 1,4-Epoxy-1,2,3,4-tetrahydro-1-phenyl-2-*endo*-anthracenecarboxylate (25/26). A 55:45 exo/endo mixture was obtained from 0.40 g (1.5 mmol) of **20** and 2 mL of methyl acrylate by using the procedure described for the preparation of **16/17**. The exo adduct was obtained as plates from methanol; the endo adduct was then isolated from the mother liquor. The total yield was 0.40 g, 79%. Endo isomer: mp 159–162 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.15 (dd, J = 4.1 and 11.8 Hz, 1 H), 2.75 (ddd, J = 5.2, 10.8 and 11.7 Hz, 1 H), 3.42 (s, 3 H), 3.76 (dd, J = 4.0 and 10.6 Hz, 1 H), 5.62 (d, J = 5.1 Hz, 1 H), 7.37–7.53 (m, 6 H), 7.71–7.87 (m, 5 H); IR (Nujol) 1734 (C=O), 1346, 1208, 965, 886, 762 cm^{-1}.

Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.18; H, 5.52.

Exo isomer: mp 123–126 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.09 (dd, J = 8.5 and 11.8 Hz, 1 H), 2.73 (dt, J_d = 11.8 Hz, J_t = 5.0 Hz, 1 H), 3.20 (dd, J = 4.7 and 8.5 Hz, 1 H), 3.42 (s, 3 H), 5.80 (d, J = 5.2 Hz, 1 H), 7.36–7.51 (m, 6 H), 7.65–7.84 (m, 5 H); IR (Nujol) 1734 (C=O), 1199, 1172, 955, 881, 754, 702 cm^{-1}.

Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.10; H, 5.60.

Methyl 1-Phenyl-2-anthracenecarboxylate (27). In 25 mL of toluene was refluxed 0.24 g of **25/26** with ca. 0.050 g of TsOH for 3 h. The solvent was stripped away and the residue was taken up in MeOH from which large crystals of pale yellow **27** formed, 0.14 g (58%): mp 111–112 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.63 (s, 3 H), 7.36–7.54 (m, 7 H), 7.83 (d, J = 8.8 Hz, 1 H), 7.88–8.06 (AB q, J = 8.9 Hz, 2 H), 8.00 (d, J = 8.5 Hz, 1 H), 8.15 (s, 1 H), 8.46 (s, 1 H); IR (Nujol) 1707 (C=O), 1321, 1269, 1254, 1119, 886, 751, 743 cm^{-1}.

1-Amino-1,3-dihydro-1-phenylnaphtho[1,2-*c*]furan (28). This compound was prepared from 5.0 g (21 mmol) of **29**,[16] *n*-BuLi (17 mL, 2.6 M, 45 mmol) and 2.5 mL (25 mmol) of benzonitrile by using the procedure described for the preparation of **12**. The product was crystallized from 20 mL of hexane, giving **28**, 5.1 g (93%): mp 104–105 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.4 (br s, 2 H), 5.33 and 5.45 (AB q, J = 13 Hz, 2 H), 7.24–7.44 (m, 6 H), 7.57–7.61 (m, 2 H), 8.12–8.16 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 71.39, 100.31, 118.92, 124.06, 125.37, 126.06, 126.48, 127.67, 128.03, 128.18, 128.31, 129.97, 133.61, 136.74, 136.82, 144.32; IR (Nujol) 3386, 3299 (w, N–H), 1216, 1026, 912, 810, 760, 694 cm^{-1}; MS (EI), m/e (rel intensity) 261 (M^+, 37), 260 (12), 245 (24), 244 (30), 230 (12), 215 (23), 184 (100), 104 (13).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.58; H, 5.71; N, 5.40.

Dimethyl 1-Hydroxy-4-phenyl-2,3-phenanthrenedicarboxylate (30). In 50 mL of toluene were refluxed 0.20 g (0.77 mmol) of **28**, 0.6 g (4.2 mmol) of DMAD, and a few crystals of TsOH for 14 h. The solution was washed with water, dried over $MgSO_4$, and filtered. Removal of the solvent and recrystallization from aqueous acetone gave 0.23 g of **30** (82%): mp 165–166 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.48 (s, 3 H), 3.96 (s, 3 H), 7.04–7.50 (m, 8 H), 7.86 (d, J = 9 Hz, 2 H), 8.47 (d, J = 9 Hz, 1 H), 12.31 (s, 1 H, exchanges with D_2O). Irradiation of the doublet at 8.47 caused the collapse of a one-proton doublet at 7.86 ppm to a singlet. IR (Nujol): 2500–3400 (br, O–H), 1730 and 1665 (C=O), 1442, 1354, 1245, 1227, 805, 793, 756, 709 cm^{-1}.

Anal. Calcd for $C_{24}H_{18}O_5$: C, 74.60; H, 4.70. Found: C, 74.44; H, 4.76.

Dimethyl 1-Acetoxy-4-phenyl-2,3-phenanthrenedicarboxylate (31). A solution of **30** (0.02 g, 0.05 mmol) in acetic anhydride (5 mL) with a few drops of pyridine was heated on a steam bath for 2 h. Upon addition of water to the yellow solution, a white precipitate formed. Filtration gave a quantitative yield of **31**, which required no purification: mp 218–220 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.5 (s, 3 H), 3.5 (s, 3 H), 3.9 (s, 3 H), 7.1–7.6 (m, 8 H), 7.8–7.9 (m, 3 H); IR (Nujol) 1773 (C=O), 1726 (C=O), 1344, 1263, 1236, 1204, 1155, 826 cm^{-1}.

Methyl 1,4-Epoxy-1,2,3,4-tetrahydro-1-phenyl-*endo*-phenanthrenecarboxylate (32). This compound was obtained from 0.15 g (0.58 mmol) of **28** and 0.26 g (2.9 mmol) of methyl acrylate by using the procedure described for the preparation of **16/17**. Crystallization from aqueous MeOH gave **32**, 0.15 g (79%): mp 133–135 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.06 (dd, J = 3.4 and 11.5 Hz, 1 H), 2.66 (ddd, J = 4.9, 9.6, and 11.5 Hz, 1 H), 3.04 (s, 3 H), 3.98 (dd, J = 3.4 and 9.6 Hz, 1 H), 5.63 (d, J = 4.9 Hz, 1 H), 7.00 (d, J = 8.9 Hz, 1 H), 7.14 (ddd, J = 1.3, 6.8 and 8.4 Hz, 1 H), 7.30 (ddd, J = 1.3, 6.8, and 8.1 Hz, 1 H), 7.45–7.54 (m, 4 H), 7.79–7.86 (m, 4 H); IR (Nujol) 1727 (C=O), 1330, 1217, 960, 764, 701 cm^{-1}.

Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.91; H, 5.59.

Naphtho[1,2-*c*]fluorenone (33). In 10 mL of PPA at 110 °C was stirred 0.10 g of **32** for 5 h. The purple solution was poured into 150 mL of water and stirred overnight. A yellow solid was collected by filtration, which, after recrystallization from EtOH gave 0.023 g of **33** (27%): mp 147–149 °C (lit.[31] mp 148–149 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.2–8.0 (m, 10 H), 8.16 d, J = 8 Hz, 1 H), 8.94 (d, J = 8 Hz, 1 H).

1,4-Epoxy-1,2,3,4-tetrahydro-4-phenyl-2,3-phenanthrenedicarboxylic Acid Anhydride (34/35). In 25 mL of toluene were refluxed 0.20 g (0.77 mmol) **28**, 0.20 g (2.0 mmol) maleic anhydride, and a catalytic amount of TsOH for 14 h. The solution was cooled and filtered, and the solvent was stripped away. A ^{1}H NMR spectrum of crude material showed it to be a 55:45 endo/exo mixture. Recrystallization from toluene–acetone gave a mixture of crystalline adducts which were separable by hand. The exo adduct was a clear, tan, cubic crystalline solid, the endo a white, dendritic crystalline solid. The mother liquor was stripped of solvent and recrystallized from toluene, giving an unidentified product. Hexane was added to the mother liquor of this, from which 0.040 g of endo adduct was obtained. The total yield was 0.17 g (65%), mp exo 187–189 °C; mp endo 188–189 °C: ^{1}H NMR

(DMSO-d_6, 250 MHz) δ endo 4.46 and 4.62 (AB q, J_{AB} = 8.5 Hz, upfield portion further split, J = 5.7 Hz, 2 H), 6.02 (d, J = 5.7 Hz, 1 H), 6.99 (dd, J = 8.5 and 1.1 Hz, 1 H), 7.18 (ddd, J = 8.2, 6.8, and 1.3 Hz, 1 H), 7.38 (ddd, J = 8.2, 6.9, and 1.2 Hz, 1 H), 7.5–7.6 (m, 4 H), 7.8–8.0 (m, 4 H); ^{1}H NMR ($CDCl_3$, 250 MHz) δ exo 3.52 and 3.82 (AB q, J = 6.9 Hz, 2 H), 6.08 (s, 1 H), 7.1–7.6 (m, 8 H), 7.8–8.0 (m, 3 H); IR (Nujol) endo 1860 and 1785 (C=O), 1228, 1079, 926, 856 cm^{-1}; IR (Nujol) exo 1857 and 1779 (C=O), 1221, 1082, 992, 931, 815, 755, 745, 734, 702 cm^{-1}.

Anal. (endo product) Calcd for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12. Found: C, 77.43; H, 4.31.

4-Phenyl-2,3-phenanthrenedicarboxylic Acid Anhydride (36). A dispersion of **34**/**35** (0.30 g, 0.88 mmol) in concentrated HCl (10 mL) was refluxed for 1 h. The brown precipitate was filtered off and recrystallized from toluene to give a 91% yield of pale brown **36**, mp 293–295 °C (lit.[31] mp 283 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.1–8.0 (m, 9 H), 8.1 (s, 2 H), 8.7 (s, 1 H); IR (Nujol) 1839 (C=O), 1771 (C=O), 1257, 1219, 923, 739, 700 cm^{-1}.

***endo*-7,14-Epoxy-7,7a,13a,14-tetrahydro-14-phenyl-8,13-benzo[*a*]naphthacenedione (38).** In 40 mL of toluene were refluxed 0.40 g (1.5 mmol) of **28** and 0.25 g (1.6 mmol) of 1,4-naphthoquinone with a catalytic amount of monochloroacetic acid for 1 h. The reaction was cooled, washed with $NaHCO_3$ solution, dried over $MgSO_4$, filtered, and stripped of solvent. Recrystallization from toluene/hexane gave 0.56 g of **38** (91%): mp 162 °C dec to a red liquid; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.15 and 4.45 (AB of ABX, J_{AB} = 8.7 Hz, upfield portion further split, J = 5.3 Hz, 2 H), 6.03 (d, J = 5.3 Hz, 1 H), 6.90–7.60 (m, 13 H), 8.03–8.07 (m, 2 H); IR (Nujol) 1670 (C=O), 1586, 1337, 1284, 965, 819, 755, 746, 695 cm^{-1}.

Anal. Calcd for $C_{28}H_{18}O_3$: C, 83.57; H, 4.51. Found: C, 83.65; H, 4.40.

***endo*-7,12-Epoxy-7,7a,11a,12-tetrahydro-12-phenyl-8,11-benz[*a*]anthracenedione (39).** This compound was prepared from 0.30 g (1.1 mmol) of **28** and 0.14 g (1.3 mmol) of 1,4-benzoquinone by using the method described for the preparation of **38**. The product was recrystallized from toluene/hexane, giving 0.25 g (62%) of endo product **39**: mp 185 °C dec; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.93 (dd, J = 5.4 and 8.7 Hz, 1 H), 4.21 (d, J = 8.7 Hz, 1 H), 5.55 (d, J = 10.3 Hz, 1 H), 5.87 (d, J = 10.3 Hz, 1 H), 5.95 (d, J = 5.4 Hz, 1 H), 6.93–8.06 (m, 11 H); IR (Nujol) 1669 (C=O), 1336, 1290, 984, 824, 767, 746, 703 cm^{-1}.

Anal. Calcd for $C_{24}H_{16}O_3$: C, 81.80; H, 4.58. Found: C, 82.00; H, 4.68.

1-Bromo-α-phenyl-2-naphthalenemethanol (40). In 100 mL of dry ether was dissolved 1.0 g (4.3 mmol) of **41**[16] and the solution was cooled to 0 °C. Phenylmagnesium bromide (ca. 9 mmol) was added and the reaction stirred for 4 h at room temperature. Saturated NH_4Cl was added, and after stirring, the organic phase was separated. The aqueous phase was extracted with ether and the organic phases were combined and dried over $MgSO_4$. After filtration and removal of solvent the residue was crystallized from methanol, giving 1.1 g of **40** (83%): mp 116–118 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.46 (d, J = 3.7 Hz, 1 H, exchanges with D_2O), 6.59 (d, J = 3.6 Hz, 1 H, s with D_2O), 7.25–7.85 (m, 10 H), 8.31–8.36 (m, 1 H); IR (Nujol) 3270 (br O–H), 1045, 810, 770, 749, 697 cm^{-1}.

Anal. Calcd for $C_{17}H_{13}BrO$: C, 65.20; H, 4.18. Found: C, 65.38; H, 4.28.

***cis*-1,3-Dihydro-1-hydroxy-3-phenylnaphtho[1,2-*c*]furan (42).** In 100 mL of dry ether was dissolved 2 g (6.4 mmol) of **40**. The solution was cooled to −78 °C under N_2. To this was added 6 mL of 2.5 M *n*-BuLi in hexanes (15 mmol). After being stirred for 5 min, the solution was warmed to 0 °C for 40 min. Dry DMF (6 mL, large excess) was added and the solution warmed to room temperature overnight. Water was added, giving a white precipitate which gradually dissolved. The ether layer was separated, dried over $MgSO_4$, and filtered. The solvent was removed and the residue recrystallized from toluene/hexane, giving 1.48 g of **42** (84%): mp 132–133 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ cis 3.35 (br d, J = 5 Hz, 1 H, exchanges with D_2O), 6.26 (s, 1 H), 7.03 (br d, J = 4 Hz, 1 H, s with D_2O), 7.14–7.67 (m, 8 H), 7.79–7.93 (m, 2 H), 8.16 (d, J = 8 Hz, 1 H). After 24 h, this sample was a 1:1 mixture of cis/trans diastereomers: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.40 (br d, J = 6.8 Hz, 1 H, exchanges with D_2O), 3.54 (br d, J = 6.7 Hz, 1 H, exchanges with D_2O), 6.25 (s, 1 H), 6.51 (d, J = 2.6 Hz, 1 H), 7.02 (br d, J = 6.2 Hz, 1 H, s with D_2O), 7.12–7.65 (m, 17 H), 7.80–7.92 (m, 4 H), 8.11 (overlapping doublets giving a triplet, J = 9 Hz, 2 H); IR (Nujol) cis 3321 (br O–H), 1006, 998, 808, 732 cm^{-1}; MS (EI), m/e (rel intensity) 262 (M^+, 25), 245 (28), 244 (INF, 100), 217 (33), 215 (86), 157 (77), 155 (25), 105 (25).

Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.54; H, 5.55.

Dimethyl 4-Hydroxy-1-phenyl-2,3-phenanthrenedicarboxylate (45). This was prepared from 0.20 g (0.76 mmol) of **42** and 0.4 g (2.8 mmol) of DMAD by using the method described for the preparation of **21**. The residue after workup was crystallized from MeOH, filtered, and washed with MeOH/hexane. More crystals were obtained from the mother liquor, giving a total yield of 0.15 g of product (51%): mp 143–145 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.51 (s, 3 H), 3.98 (s, 3 H), 7.30–7.48 (m, 6 H), 7.62–7.79 (m, 3 H), 7.88 (dd, J = 1.3 and 7.6 Hz, 1 H), 9.93 (d, J = 8.7 Hz, 1 H), 13.4 (s, 1 H, exchanges with D_2O); IR (Nujol) 1738, 1665 and 1654 (C=O), 1238, 1207, 834, 761, 705 cm^{-1}.

Anal. Calcd for $C_{24}H_{18}O_5$: C, 74.60; H, 4.70. Found: C, 74.41; H, 4.62.

Reaction of 7 (from 42) with Methyl Acrylate 49A–D. In 40 mL of toluene were refluxed 0.10 g of **42**, 1 mL of methyl acrylate, and a catalytic amount of $ClCH_2COOH$ for 2 h. Column chromatography of the residue on Kieselgel 60, eluting with CH_2Cl_2, gave two portions. Eluting first was a 65:35 mixture of endo adducts **49A** and **49C** characterized by ^{1}H NMR. **49A**: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.94 (dd, J = 4.0 and 11.5 Hz, 1 H), 2.80 (ddd, J = 5.0, 10.1, and 11.5 Hz, 1 H), 3.40 (s, 3 H), 3.77 (dd, J = 4.1 and 10.0 Hz, 1 H), 6.02 (d, J = 5.0 Hz, 1 H), 7.22 (d, J = 8.2 Hz, 1 H), 7.35–7.95 (10 H). **49C**: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.41 and 2.51 (AB of ABX, J_{AB} = 11.5 Hz, upfield portion split by J = 4.1 Hz, downfield portion split by J = 9.4 Hz, 2 H), 3.23 (s, 3 H), 3.71 (dd, buried beneath signal of **49A**, 1 H), 6.23 (d, J = 5.2 Hz, 1 H), 7.10 (d, J = 8.2 Hz, 1 H), 7.35–7.95 (m, 10 H). The second portion contained **49B**: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.95 (dd, J = 8.3 and 11.5 Hz, 1 H), 2.75 (dt, J_d = 11.4 Hz, J_t = 4.8 Hz, 1 H), 3.05 (dd, J = 4.4 and 8.3 Hz, 1 H), 3.35 (s, 3 H), 6.19 (d, J = 4.9 Hz, 1 H), 7.30–7.69 (m, 9 H), 7.89 (ddd, J = 1, 8.0, and 8.8 Hz, 2 H). Comparison of these spectra with that of the crude product showed the crude to be a 54:46:3 mixture **49A**:**49B**:**49C**. The mixture of endo adducts was refluxed for 12 h in toluene/methyl acrylate. Solvent and dienophile were removed under reduced pressure. Singlets at 6.30 (bridgehead proton) and 3.82 (methoxy) in the ^{1}H NMR of the mixture were attributed to **49D**. On the basis of this spectrum, the mixture was **49A**:**B**:**C**:**D** in proportions of **23**:18:53:6.

Methyl 1-Phenyl-2-phenanthrenecarboxylate (46A). A catalytic amount of TsOH was added to 0.080 g (0.31 mmol) of **42** and 1 mL of methyl acrylate in 40 mL of refluxing toluene. Heating was continued for 1 h. The reaction mixture was washed with $NaHCO_3$ solution, dried over $MgSO_4$, filtered, and stripped of solvent. The residue (11:1 **46A**:**47A** by ^{1}H NMR) was taken up in 0.5 mL of toluene and diluted with 20 mL of hexane. Crystals formed upon refridgeration. Filtration gave 0.051 g of **46A** (63%), which was free of **47A** (by ^{1}H NMR). A sample of **46A** recrystallized from methanol/hexane had the following: mp 118–119 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.64 (s, 3 H), 7.31–7.90 (m, 10 H), 8.12 (d, J = 8.8 Hz, 1 H), 8.75–8.81 (m, 2 H); IR (Nujol) 1723 (C=O), 1248, 1145, 1133, 756, 702 cm^{-1}.

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.50; H, 5.11.

Methyl 1-Phenyl-3-phenanthrenecarboxylate (47A). Methyl acrylate (1 mL, large excess) and 0.10 g (0.38 mmol) of **42** were refluxed in 40 mL of toluene with three drops of glacial AcOH for 4 days. A ^{1}H NMR spectrum of the crude product showed it to be **49A**:**B**:**C**:**D** in proportions of 8:8:63:21. A catalytic amount of TsOH was added and refluxing continued for 1 h. The reaction mixture was washed with $NaHCO_3$ solution, dried over $MgSO_4$, filtered, and stripped of solvent. The residue (85:15 **47A**:**46A** by ^{1}H NMR) was passed through a short column of Kieselgel 60, eluting with CH_2Cl_2. The solvent was removed and the residue crystallized in the same manner as **46A** to give 0.071 g of **47A** (70%), slightly contaminated by **46A** (3% by NMR). Compound **47A** recrystallized from methanol had the following: mp 147–148 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.03 (s, 3 H), 7.49–7.93 (m, 10 H), 8.17 (d, J = 1.4 Hz, 1 H), 8.87 (d, J = 7.9

Hz, 1 H), 9.48 (d, J = 1.4 Hz, 1 H); IR (Nujol) 1703 (C=O), 1276, 1240, 1110, 827, 756, 700 cm^{-1}.

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.28; H, 5.27.

Methyl 2-Phenanthrenecarboxylate (46B) and Methyl 3-Phenanthrenecarboxylate (47B). In 4 mL of methyl acrylate was refluxed 0.35 g of **48**[16] with trichloroacetic acid for 1 h. The mixture was taken up in $CHCl_3$, washed with $NaHCO_3$ solution, dried over $MgSO_4$, and filtered. Solvent was removed by rotary evaporation and high vacuum. ^1H NMR indicated a mixture of all possible cycloaddition products: ^1H NMR ($CDCl_3$, 250 MHz) δ multiplets at 1.71–1.89, 2.34–2.61, and 3.49–3.57 CH_2; singlets at 3.20, 3.48, 3.82, and 3.80, relative integrations of 4.6:3.3:1.1: OCH_3; bridge protons, two pair stand out, 5.60 (d, J = 4.9 Hz), 6.10 (d, J = 5.1 Hz) and 5.72 (d, 5.1 Hz), 5.95 (d, 4.9 Hz) with a relative integration of ca 3:2 (first pair:second pair); other bridge signals, 5.65 (d, J = 4.5 Hz), 5.80 (s), 5.99 (d, J = 4.5 Hz), 6.15 (s); aromatics, 7.3–7.9 (6 H). The mixture was taken up in 5 mL of MeOH and pipetted into refluxing concentrated HCl. After 30 min at reflux, the reaction was cooled, extracted with diethyl ether, washed with $NaHCO_3$ solution, dried over $MgSO_4$, and stripped of solvent. ^1H NMR showed aromatized products **46B** and **47B**. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.6–7.95 (m, ca. 6 H), 8.20 (dd, J = 1.6 and 8.3 Hz, H_2 of **47B**), 8.24 (dd, J = 1.7 and 8.7 Hz, H_3 of **46B**), 8.60 (d, J = 1.7 Hz, H_1 of **46B**), 8.69 and 8.70 (overlapping doublets, J = 8.4 and 7.2 Hz, H_4 and H_5 of **46B**), 8.78 (d, J = 8.2 Hz, H_5 of **47B**), 9.42 (br s, H_4 of **47B**). Irradiation of the 9.42 singlet (broadened by two small couplings) caused loss of the small coupling in the 8.20 dd.

2-(Dimethoxymethyl)-α-phenyl-1-naphthalenemethanol (52). Via 51. A solution of **51**[16] (3.2 g, 11.4 mmol) in 200 mL of dry ether under argon in an oven-dried flask was cooled to −78 °C. n-BuLi (5.3 mL of a 2.6 M solution in hexanes, 13.8 mmol) was added dropwise. The reaction was stirred for an hour and then warmed to 0 °C and stirred for an additional 30 min. Distilled benzaldehyde (1.9 mL, 18.7 mmol) was injected, and the solution was allowed to warm to room temperature. After being stirred for 12 h, the reaction was quenched with water, extracted with ether (5 × 25 mL), dried over $MgSO_4$, filtered, and stripped of solvent: ^1H NMR ($CDCl_3$, 250 MHz) δ 3.2 (s, 3 H), 3.4 (s, 3 H), 4.7 (d, J = 6 Hz, exchanges with D_2O, 1 H), 5.6 (s, 1 H), 6.9 (d, J = 6 Hz, s with D_2O, 1 H), 7.1–8.2 (m, 11 H).

Via 54. In 50 mL of dry diethyl ether was dissolved 0.10 g (0.44 mmol) of **54**,[16] and the solution was cooled to −78 °C. PhLi (0.3 mL of a 2.4 M solution in C_6H_{12}/Et_2O, 0.72 mmol) was added. The mixture was warmed to 0 °C for 3.25 h and water was then added. The ether phase was separated, dried over $MgSO_4$, filtered, and stripped of solvent, giving a quantitative yield of **52**, identical with that obtained via **51**.

1,3-Dihydro-3-methoxy-1-phenylnaphtho[1,2-*c*]furan (53). Chromatography of **52** on silica gel, using CH_2Cl_2 as eluent, resulted in cyclization to acetal **53**, an oil (71% from **51**). The ^1H NMR spectrum showed the product to be a 1:1 mixture of cis and trans acetals: ^1H NMR ($CDCl_3$, 250 MHz) δ 3.50 (s, 3 H), 3.53 (s, 3 H), 6.32 (s, 1 H), 6.46 (s, 1 H), 6.53 (d, J = 2.7 Hz, 1 H), 6.66 (d, J = 2.7 Hz, 1 H), 7.2–8.0 (m, 22 H). The same transformation could be achieved by using the reaction conditions given for the preparation of **56** (following). Acetal **53** and hemiaminal **28** gave identical results in reaction with DMAD and MA.

***trans*-1,3-Dihydro-3-methoxy-1-(2-naphthyl)naphtho[1,2-*c*]furan (56).** In 100 mL of dry ether was dissolved 0.65 g (2.3 mmol) of **51**. After cooling to −78 °C, 1.0 mL of 2.6 M n-BuLi (2.6 mmol) was added. After 10 min, the solution was warmed to 0 °C for 35 min. 2-Naphthaldehyde (0.4 g, 2.8 mmol) was added and the solution warmed to room temperature overnight. An equal volume of water was added. The organic phase was dried over $MgSO_4$ and then filtered. Removal of the solvent gave an oil, **55**: ^1H NMR ($CDCl_3$, 250 MHz) δ 3.2 (s, 3 H), 3.4 (s, 3 H), 3.5 (br s, 1 H, exchanges with D_2O), 5.7 (s, 1 H), 7.1 (br s, 1 H), 7.2–8.3 (m, 13 H); IR (neat) 3426 (br O–H), 1109, 1069, 822, 746 cm^{-1}. The oil was stirred for 14 h in absolute MeOH with Dowex 50W-X8 resin. $CHCl_3$ was added to dissolve the precipitate that had formed. The Dowex was removed by filtration and the solvent stripped off. The residue was recrystallized from MeOH giving **56**, 0.54 g (82% from **51**) mp 165–168 °C; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.54 (s, 3 H), 6.59 (d, J =2.7 Hz, 1 H), 6.84 (d, J = 2.7 Hz, 1 H), 7.1–8.0 (m, 13 H); IR (KBr) 1371, 1091, 1031, 1018, 981, 969, 812 cm^{-1}.

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.55; H, 5.59.

1,4-Epoxy-1,2,3,4-tetrahydro-4-(2-naphthyl)-2,3-phenanthrenedicarboxylic Acid Anhydride (58/59). A 63:37 endo/exo mixture (crude) was obtained from 0.30 g (0.76 mmol) of **56** and 0.10 g of MA by using the procedure described for the preparation of **34/35**. The endo adduct crystallized from $CHCl_3$ to give 0.15 g (42%): mp 200 °C dec; ^1H NMR ($CDCl_3$, 200 MHz) δ endo 4.41 and 4.64 (AB of ABX, J_{AB} = 8.7 Hz, upfield portion further coupled with J = 5.8 Hz, 2 H), 6.06 (d, J = 5.8 Hz, 1 H), 7.06–7.11 (m, 2 H), 7.35 (dt, J_d = 1.7 Hz, J_t = 8.3 Hz, 1 H), 7.55–7.64 (m, 3 H), 7.82–8.01 (m, 6 H), 8.52 (br s, 1 H); the crude reaction mixture had additional signals of the exo adduct: 3.55 (d, J = 7.0 Hz, 1 H), 3.90 (d, J = 7.0 Hz, 1 H), 6.13 (s, 1 H); IR (Nujol) 1856 and 1771 (C=O), 1236, 1061, 914, 820, 750 cm^{-1}.

Benzo[*a*]naphtho[2,1-*d*]fluoren-9-one (62) and Benzo[*b*]naphtho[2,1-*d*]fluoren-9-one (61). In 100 mL of toluene were refluxed 0.34 g of **56** (1.0 mmol), 2 mL of methyl acrylate (large excess), and a catalytic amount of trichloroacetic acid for 10 h. The reaction mixture was cooled, washed with $NaHCO_3$ solution, and dried over $MgSO_4$ and the solvent was removed. The crude product obtained was methyl 1,2,3,4-tetrahydro-4-(2-naphthyl)-3-*endo*-phenanthrenecarboxylate (**60**): ^1H NMR ($CDCl_3$, 250 MHz) δ 2.12 (dd, J = 3.4 and 11.6 Hz, 1 H), 2.71 (ddd, J = 4.9, 9.6, and 11.5 Hz, 1 H), 3.05 (s, 3 H), 4.13 (dd, J = 3.4 and 9.6 Hz, 1 H), 5.67 (d, J = 4.9 Hz, 1 H), 6.9–7.1 (m, 2 H), 7.2–7.3 (m, 1 H), 7.5–8.0 (m, 9 H), 8.55 (s, 1 H). To this product was added 20 mL of PPA, and the mixture was heated with stirring for 10 h. The mixture was poured into water, stirred for 3 h, and filtered. The residue was chromatographed on Kieselgel 60, using toluene as eluant. The first (yellow) band proved to be **62**: mp 244–245 °C (lit.[31] mp 238–239 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ 7.38–7.87 (m, 11 H), 8.20 (d, J = 8.5 Hz, 1 H), 8.83 (d, J = 8.1 Hz, 1 H), 9.03 (d, J = 8.2 Hz, 1 H). The second band, red, was **61**: mp 193–195 °C (lit.[31] mp 203–204 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ 7.42–7.92 (m, 11 H), 8.17 (s, 1 H), 8.51 (s, 1 H), 9.17 (d, J = 8.2 Hz, 1 H). Despite the low melting point obtained, this sample gave correct C, H analyses.

Anal. Calcd for $C_{25}H_{14}O$: C, 90.89; H, 4.27. Found: C, 90.88; H, 4.45.

1,3-Dihydro-1-methoxy-1-phenylnaphtho[1,2-*c*]furan (64). In 50 mL of absolute MeOH were refluxed 0.4 g of **20** and 0.20 g of Dowex 50W-X8 resin for 10 h. The reaction was cooled and solid Na_2CO_3 added. The mixture was filtered and stripped of solvent, giving **64**, an oil, as the sole product by ^1H NMR: ^1H NMR ($CDCl_3$, 250 MHz) δ 3.15 (s, 3 H), 5.38 and 5.42 (AB q, J = 13.1 Hz, 2 H), 7.26–7.48 (m, 8 H), 7.79 (d, J = 8.0 Hz, 1 H), 7.91 (t, J = 8.4 Hz, 2 H); IR (Neat) 1169, 1099, 1075, 1022, 902, 811, 761, 697 cm^{-1}.

1,3-Dihydro-1-methoxy-1-phenylnaphtho[2,3-*c*]furan (65). This compound was prepared from **28** by using the method described for the preparation of **64**: ^1H NMR ($CDCl_3$, 250 MHz) δ 3.26 (s, 3 H), 5.42 and 5.50 (AB q, J = 12.9 Hz, 2 H), 7.32–7.90 (m, 11 H); IR (neat) 1107, 1080, 1023, 874, 749, 701 cm^{-1}.

1,3-Dihydro-1-hydroxy-1-phenylisobenzofuran (76) [2-Benzoylbenzenemethanol (77)]. In 25 mL of 1:1 THF/water were refluxed 0.30 g (1.4 mmol) of **12** and 0.25 g Dowex 50W-X8 resin for 11 h. The solution was cooled and solid Na_2CO_3 added. The mixture was filtered and the solvent removed, leaving a crude oil whose ^1H NMR spectrum showed it to be a tautomeric mixture of 93% **77** and 7% **76**: ^1H NMR ($CDCl_3$, 200 MHz) δ 3.65 (br s, 1 H, exchanges with D_2O), 4.60 (s, 2 H chain), 5.25 and 5.38 (AB q, J = 12.8 Hz, 2 H ring), 7.21–7.66 (m, 7 H), 7.76–7.94 (m, 2 H); IR (neat) 3419 (br O–H), 1656 (C=O), 1447, 1316, 1291, 1271, 766, 700, 642 cm^{-1}; MS (EI), m/e (rel intensity) 212 (M^+, 49), 197 (29), 195 (28), 194 (65), 165 (52), 135 (27), 105 (52), 77 (100); HRMS found 212.0838, calcd for $C_{14}H_{12}O_2$ 212.0837.

1,3-Dihydro-1-hydroxy-1-phenylnaphtho[2,3-*c*]furan (78) [3-Benzoyl-2-naphthalenemethanol (79)]. This tautomeric mixture was prepared from **20** by using the method described for the preparation of **76/77**. The ^1H NMR spectrum showed this product to be 98% in the chain form, **79**: ^1H NMR ($CDCl_3$, 200 MHz) δ 3.90 (t, J = 4.6 Hz, 1 H, exchanges with D_2O), 4.80 (d, J = 4.6 Hz, 2 H), 7.45–7.70 (m, 5 H), 7.81 (m, 4 H), 8.00 (s, 2 H);

a small AB q appeared at 5.36 and 5.50, J = 13.0 Hz; IR (neat) 3385 (br O–H), 1635 (C=O), 1579, 1304, 1274, 1012, 873, 748, 723, 694 cm^{-1}; MS (EI), m/e (rel intensity) 262 (M^+, 97), 245 (44), 244 (100), 215 (66), 128 (35), 127 (42), 105 (37), 77 (76); HRMS found 262.0994, calcd for $C_{18}H_{14}O_2$ 262.0998.

1,3-Dihydro-1-hydroxy-1-phenylnaphtho[1,2-*c*]furan (80) [1-Benzoyl-2-naphthalenemethanol (81)]. This tautomeric mixture was prepared from **28** by using the method described for the preparation of **76**/**77**. The ^{1}H NMR spectrum showed the product to be a tautomeric mixture of 54% **81** and 46% **80**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.95 (br s, 1 H, exchanges with D_2O), 4.64 (s, 2 H chain), 5.36 and 5.45 (AB q, J = 13.1 Hz, 2 H ring), 7.21–7.66 (m, 11 H); IR (neat) 3419 (br O–H), 1662 (C=O), 1025, 813, 763, 699 cm^{-1}; MS (EI), m/e (rel intensity) 262 (M^+, 59), 245 (40), 244 (100), 215 (67), 185 (33), 127 (28), 105 (30), 77 (46); HRMS found 262.0994, calcd for $C_{18}H_{14}O_2$ 262.0993.

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Synthesis of a Structurally Modified Glycal. (–)-(2*R*,4*S*)-2-Methyl-2-vinyl-4-(benzyloxy)-3,4-dihydro-2*H*-pyran

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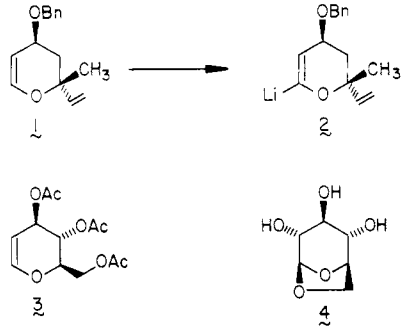
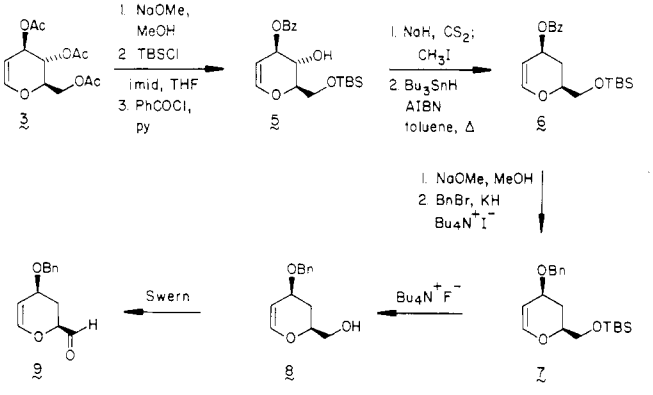
A synthetic procedure for the transformation of levoglucosan (**4**) to (–)-(2*R*,4*S*)-2-methyl-2-vinyl-4-(benzyloxy)-3,4-dihydro-2*H*-pyran (**1**) in 11 steps is described. The scheme relies on selective deoxygenation of the pair of α-hydroxyl groups, blocking of the β-hydroxyl, and formation of ester **16**. The presence of the carboxylate group allows for stereocontrolled methylation of the enolate anion, conversion of ester to vinyl, and ultimate eliminative removal of the methoxyl substituent in methyl glycoside **25**. This key transformation takes advantage of regioselective acetal cleavage by trimethylsilyl iodide and in situ dehydroiodination of the product so formed with hexamethyldisilazane. Certain unsuccessful attempts to form the α-lithio anion of **1** are also discussed.

In connection with a convergent synthesis of forskolin projected to utilize oxyanionic Cope rearrangement chemistry subsequent to a kinetic resolution,[1] a quantity of optically pure **1** was required as a prelude to its metalation as in **2**. The stereocontrolled C-5 alkylation of glycosides



Scheme I



or glycals appears to be a fundamental problem in the carbohydrate area that has not yet been meaningfully investigated. To us, the stereochemical correspondence at C-2 between **1** and tri-*O*-acetyl-D-glucal (**3**)[3a] as well as

(1) Oplinger, J. A.; Paquette, L. A. *Tetrahedron Lett.* **1987**, *28*, 5441.

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