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Polycyclic Aromatic Hydrocarbons via 1-(Arylmethyl)isobenzo- and -naphtho[2,3-*c*]furans

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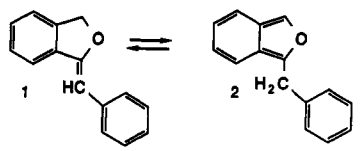
1,3-Dihydro-1-(arylmethylene)isobenzofurans exist in prototropic tautomerism with 1-(arylmethyl)isobenzofurans. The importance of acid catalysis in the mechanism of this process is examined. This tautomerism is also exhibited by the homologous naphtho[2,3-*c*]furan system. The furanoid species of these systems can be trapped in situ with dimethyl acetylenedicarboxylate and the resulting adducts transformed into polycyclic aromatic hydrocarbons. Variation of the aryl substituent gives access to dibenzanthracene, pentaphene, and benzopentaphene ring systems.

The prototropic tautomerism between 1-(phenylmethylene)-1,3-dihydroisobenzofuran (**1**) and 1-benzylisobenzofuran (**2**) was originally demonstrated by trapping the latter (a reactive diene)[1] with a variety of dieneophiles.[2] The Diels–Alder adducts so formed proved to be useful intermediates in the synthesis of polycyclic aromatic hydrocarbons,[3] particularly benz[*a*]anthracenes.[4]

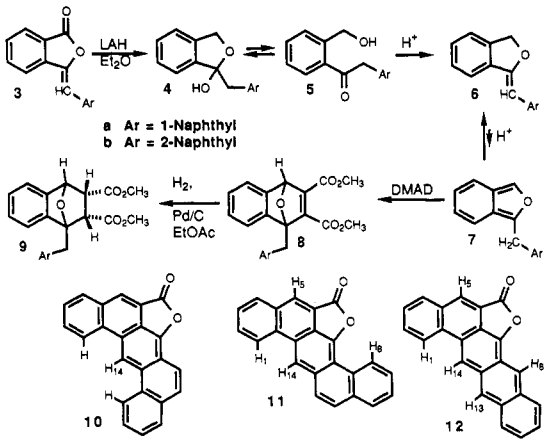


The present report proposes a mechanism for this tautomerism which demonstrates the importance of acid catalysis. In addition, we show that this tautomerism is also exhibited by the 1-(arylmethyl)naphtho[2,3-*c*]furan system (**16** ↔ **17**, Scheme III). Varying the aryl substituent of both of the isobenzo- and isonaphthofuran systems gives access to a variety of polycyclic aromatic systems containing up to six rings by using established methodology.[3,4]

Results and Discussion

Phthalide starting materials (**3**, Scheme I) were prepared by the condensation of phthalic anhydride with 1-naphthyl- or 2-naphthylacetic acid.[5] The phthalides were easily reduced to 1-hydroxy-1-(arylmethyl)-1,3-dihydroisobenzofurans **4** by using lithium aluminum hydride (LAH) in Et_2O. The hemiketal products exhibit a spectrally observable ring-chain tautomerism (**4** ↔ **5**) which has been reported previously.[6] Dehydration was effected by addition of a few drops of HCl to an ethereal solution

Scheme I



of the hemiketals forming **6**. The products were easily characterized by their ^1H NMR spectra, which consisted of a two-proton singlet at ca. 5.6 ppm, a one-proton vinyl singlet between 6.2 and 6.9 ppm, and complex aromatic signals. The IR spectra exhibited a C=C band at ca. 1650 cm^{-1} and a strong C–O–C stretch just above 1000 cm^{-1}.

† Professor of Chemistry, University of Waterloo, deceased Aug 1, 1985.

(1) For reviews of isobenzofuran chemistry, see: Wiersum, U. E. *Aldrichimica Acta* **1981**, *14*(3), 53. Haddadin, M. J. *Heterocycles* **1978**, *9*, 865. Freiderichsen, W. *Adv. Heterocycl. Chem.* **1980**, *14*, 331.

(2) Smith, J. G.; Wikman, R. T. *J. Org. Chem.* **1974**, *39*, 3648.

(3) Smith, J. G.; Welankiwar, S. S.; Shantz, B. S.; Lai, E. H.; Chu, N. G. *J. Org. Chem.* **1980**, *45*, 1817.

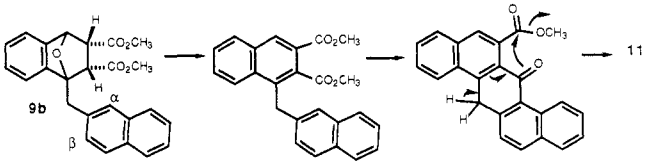
(4) Smith, J. G.; Welankiwar, S. S.; Lai, E. H.; Chu, N. G.; Sondheimer, S. J. *J. Org. Chem.* **1981**, *46*, 4658.

(5) This is a variation of the Perkin reaction: Johnson, J. R. *Org. React. (N.Y.)* **1963**, *1*, 210. The general procedure for the preparation of these compounds is that for 3-benzylidenephthalide: *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. 2, p 61.

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

0022-3263/88/1953-1841$01.50/0

Scheme II



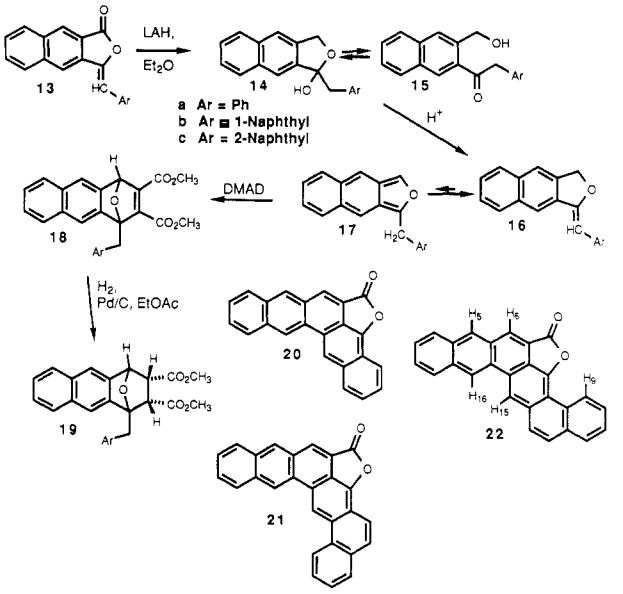
Isolation of the dehydration products prior to the Diels–Alder reaction is unnecessary; the hemiketal precursors are usually treated with acid in the presence of a dienophile. The furan species were trapped with dimethyl acetylenedicarboxylate (DMAD) in order to avoid regioisomeric and diastereomeric mixtures. Adducts **8a** and **8b** were obtained from hemiketals **4** (Scheme I) after reaction in the manner reported,[2-4] i.e., with a catalytic amount of HCl for 10 h in refluxing Et_2O.

Adducts **8a** and **8b** underwent catalytic hydrogenation (Pd/C) on the exo face as indicated by the ^1H NMR spectra of the products **9**, which exhibit doublets (J = 5 Hz) for their bridge protons. The fully aromatized products were prepared in one step from hydrogenated DMAD adducts **9** by heating in polyphosphoric acid (PPA). The reaction proceeds with aromatization and Friedel–Crafts acylation of the benzyl ring (Scheme II). Acid-catalyzed enolization followed by lactone ring closure gave the polycyclic lactones **10** and **11** (Scheme I). These compounds were high-melting, insoluble orange solids.

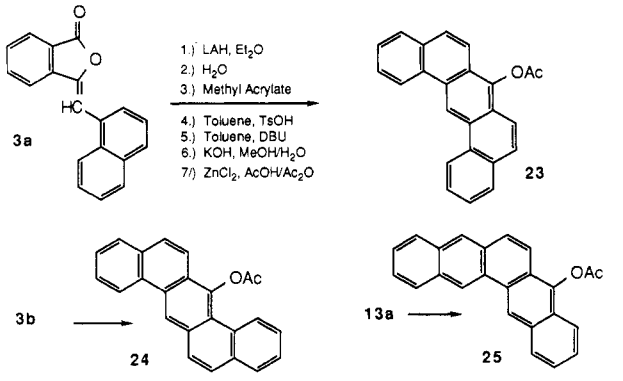
Heating **9b** in PPA results in acylation at the more reactive α position of the naphthyl substituent (Scheme II), giving **11** as the sole product by ^1H NMR. Interpretation of the ^1H NMR spectra of polycyclic aromatic compounds is made easier by several effects which deshield protons in particular environments, separating them from other resonances. One effect is that of cumulative ring currents as in the 9,10 protons of anthracene. Comparable protons in larger PAHs are seen as downfield singlets. Another effect is observed in sterically conjested bay-region protons.[7] These effects are additive and can cause substantial deshielding in some cases.[8] On the basis of these deshielding effects, two doublets (H_1, H_8) and two singlets (H_5, H_{14}) are expected to be found downfield in the spectrum of **11** and one doublet (H_1) and four singlets (H_5, H_8, H_{13}, H_{14}) downfield in the spectrum of **12**. The former pattern is observed establishing **11** as the product formed from **9b**. Of particular diagnostic value is the H_8 doublet. This bay-region proton is in close proximity to the lactone oxygen. As a result of this steric interaction, this proton is strongly deshielded, its signal found at 9.39 ppm.

The sequence of reactions in Scheme I was carried out for the homologous naphtho[2,3-*c*]furan system beginning with naphthalides **13** (Scheme III). The naphthalides were prepared directly from 2,3-naphthalenedicarboxylic acid,[9] the anhydride being formed in situ at the high reaction temperature. Yields were generally lower for the naphthalides (compared to the phthalides), probably due to the higher melting point of the diacid component and the resulting incomplete fusion. Low yields are not a substantial problem since the starting materials can be recovered by base extraction. Reduction and dehydration was effected in the same manner applied to the phthalides. Attempts to form Diels–Alder adducts under conditions successful for the preparation of **8** (Scheme I) were unsuccessful. Under these conditions, no reaction for the naphthofuran compounds (**14**) occurred other than dehydration to **16** (Scheme III). A variety of solvents was used in an effort to trap the (arylmethyl)naphtho[2,3-*c*]furans in Diels–Alder reactions with DMAD. Glacial acetic acid was found to give the desired products, but a large number of byproducts are formed. The best results were obtained by using refluxing toluene with trichloroacetic acid (TCAA) as the catalyst.[10] Long reaction times were required for the preparation of **18a** to **18c** (2 days). Under these conditions, the corresponding isobenzofuran adducts **8a** and **8b** (Scheme I) were formed much more quickly.

Scheme III



Scheme IV



Catalytic hydrogenation of adducts **18a–c** gave endo adducts **19a–c** and aromatization in PPA gave pentaphene **20** and benzopentaphenes **21** and **22**, respectively (Scheme III). As in the aromatization of **9b** (Scheme II) two products are possible in the comparable reaction of **19c** (Scheme III). The ^1H NMR spectrum of the product obtained from the aromatization of **19c** exhibits a doublet at 9.41 ppm. By analogy with **11**, this must be H_9. The spectrum also exhibits four downfield singlets (H_5, H_6, H_{15}, and H_{16}), establishing **22** as the product.

The same PAH skeletons can be prepared without a carbonyl substituent by using methyl acrylate as the dieneophile, but a mixture of regio- and diastereomeric products results. Aromatization of the mixture, followed by treatment with DBU, eliminates all but the regioisom-

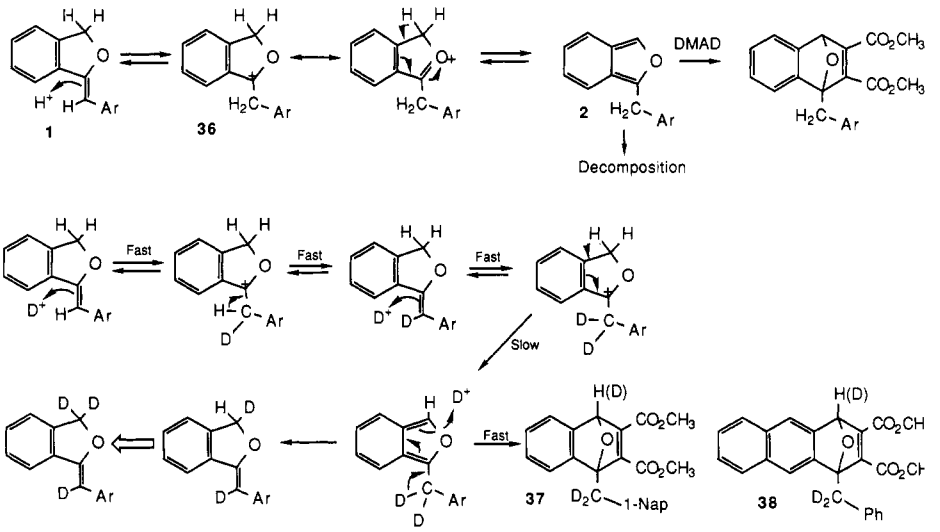
(7) Memory, J. D.; Wilson, N. K. *NMR of Aromatic Compounds*; John Wiley and Sons: New York, 1982; pp 40–49.

(8) In **10**, for example, H_{14} experiences substantial ring current deshielding, and in addition, is located in two bay regions. This proton's signal is found far downfield at 9.57 ppm.

(9) *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 810.

(10) The catalysis of Diels–Alder reactions by trichloroacetic acid has been reported: Wassermann, A. *J. Chem. Soc.* **1942**, 618.

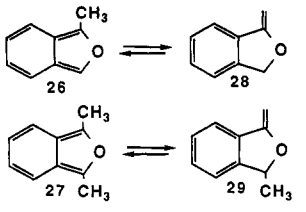
Scheme V



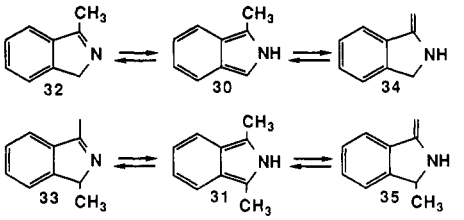
ers.[4] Only one of these isomers can undergo cyclization, after which separation of the desired product is a simple matter. 7-Acetoxydibenzanthracenes **23** and **24** and 8-acetoxypentaphene **25** were obtained from this seven-step synthesis without isolation of intermediates (Scheme IV). Products **23** and **24** crystallized out of the reaction mixture in 40% and 28% yields, respectively. Pentaphene **25** was obtained in only 22% yield and the Diels–Alder reaction required 8 days. 7-Acetoxydibenz[*a,j*]anthracene has been converted into the unsubstituted hydrocarbon in two steps.[11] The parent hydrocarbons may also be accessible by using the method of Harvey,[12] though this has not been attempted.

The absence of any signals due to isobenzofuran **2** in the ^{1}H NMR spectrum of **1** indicates that the equilibrium favors the former, as expected on the basis of its greater aromatic character relative to **2**. Bornstein et al. studied this phenomenon[13] by examining the spectral behavior of **2** (prepared by flash vacuum thermolysis). Over a 4-h period, the ^{1}H NMR spectrum showed the gradual emergence of tautomer **1** at the expense of **2**. Equilibrium was established immediately upon addition of a trace of TFA and could be arrested by addition of triethylamine, implying that acid catalysis is necessary for the tautomerism to occur.

1-Methylisobenzofuran (**26**) and 1,3-dimethylisobenzofuran (**27**), on the other hand, did not equilibrate to their respective tautomers **28** and **29**.[14] Only gradual decomposition was seen, being retarded by base and accelerated by acid. The absence of an equilibrium is surprising since the greater aromatic character of tautomers **28** and **29** should make them more stable than their isobenzofuran forms. Tautomer **28**,[15] like **26**, is a reactive species which decomposes readily in the presence of acid.[16] Assuming that acid is essential for the tautomerism, it seems probable that facile decomposition of either or both tautomers occurs faster than equilibration. This implies that compounds **1** and **2**, for which equilibrium is observed, must be relatively stable to acid. The presence of the phenyl substituent clearly stabilizes **1** by extending conjugation. Isobenzofurans are destabilized by electron-releasing substituents (as in **26** and **27**) and stabilized by electron-withdrawing groups. The Taft σ^* value for the benzyl group is +0.27,[17] which suggests that it belongs in the latter category. In consequence, **1** and **2** would be expected to be less reactive than the methyl-substituted isobenzofurans.



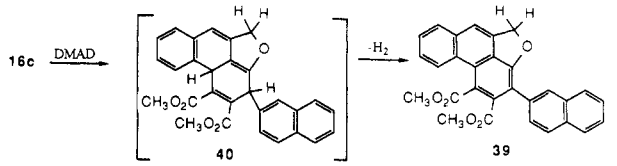
Isoindoles **30** and **31** have also been examined for tautomeric behavior.[18] These indoles are quite different from the isobenzofuran system since they are able to form benzenoid tautomers with endocyclic double bonds via a sigmatropic rearrangement. In both cases, the benzenoid tautomers predominated over the isoindole forms while exocyclic tautomers **34** and **35** were not observed. The influence of acid catalysis was not studied.



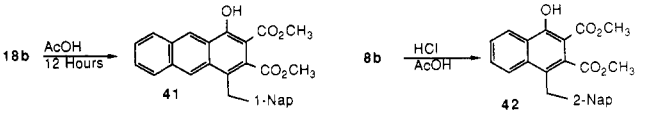
The mechanism of the tautomerism between **1** and **2** has not been investigated. The work of Bornstein[13] demonstrated the importance of acid catalysis. With this in mind, a very simple mechanism can be proposed (Scheme V). Protonation of the double bond of **1** gives cation **36**, which is stabilized by the adjacent oxygen atom. Elimination of H^+ can occur to give **2** or reform **1**. In the presence of a dienophile, **2** is consumed and the equilibrium shifts to the

(11) Snatzke, G.; Kunde, K. *Chem. Ber.* **1973**, *106*, 1341.
(12) This method has been applied to the conversion of 7-acetoxybenz[*a*]anthracene to benz[*a*]anthracene in high yield. Konieczny, M.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 4813.
(13) Chacko, E.; Sardella, D. J.; Bornstein, J. *Tetrahedron Lett.* **1976**, 2507.
(14) Tautomer **29** has been postulated as an intermediate in the high temperature decomposition (>750 °C) of **27**. Wiersum, U. E. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 365.
(15) Sidney, L. *Diss. Abs. Int. B.* **1982**, *43*, 1868.
(16) Bailey, W. J., Department of Chemistry and Biochemistry, University of Maryland, personal communication.
(17) *Langes' Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985; pp 3–135.
(18) Chacko, E.; Bornstein, J.; Sardella, D. J. *Tetrahedron* **1979**, *35*, 1055.

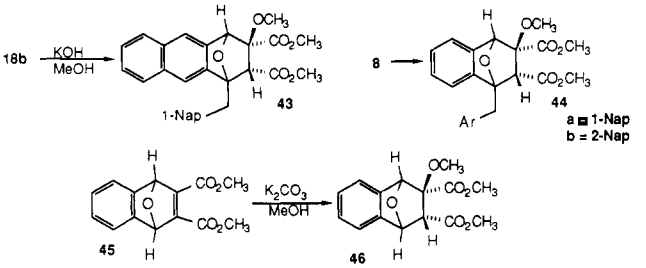
Scheme VI



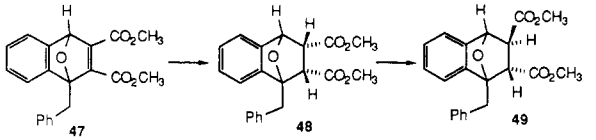
Scheme VII



Scheme VIII



Scheme IX



right. Decomposition of the isobenzofuran is a likely side reaction, particularly when no dienophile is present.

The proposed mechanism implies that all three nonaromatic protons should exchange in the presence of D^+ (bottom, Scheme V). Accordingly, a $CDCl_3$ solution of **1** was treated with acetic acid-d_4. Over several hours the vinyl proton singlet in the ^1H NMR spectrum gradually disappeared. TFA-*d* accomplished exchange in minutes. Decomposition began to complicate the spectrum before any exchange at the CH_2 was seen. In order to observe deuteration at the CH_2, the exchange was conducted under conditions known to accelerate the Diels–Alder reaction, i.e. refluxing AcOD. An example from the isobenzofuran series (**6b**, Scheme I) and naphtho[2,3-*c*]furan series (**16b**, Scheme III) was compared. Because of their stability and facile crystallization, these compounds could be isolated and purified even after strong heating in AcOD. After refluxing in AcOD for 35 min, **6b** was found to have deuteriated completely at both the CH and CH_2 positions. The signals corresponding to these protons were absent from the ^1H NMR spectrum while the aromatic region was identical to starting material. The ^2H NMR spectrum exhibited the characteristic pair of singlets at 5.59 and 6.17 ppm, integrating in the ratio 1:2. Naphtho[2,3-*c*]furan **16b** was refluxed in AcOD over a 90-min period. Samples were withdrawn at regular intervals and analyzed by ^2H NMR spectroscopy. Deuteriation of the CH_2 group (5.62 ppm) is almost complete after 90 min. An ^1H NMR spectrum of a sample withdrawn after 71 min lacked the vinyl signal at 6.9 ppm but exhibited a small doublet (J = 1.3 Hz) at 5.7 ppm, attributed to H–C–D coupling of partially deuteriated **16b**. It is clear that (arylmethyl)naphtho[2,3-*c*]furans (**17**, Scheme III) are formed much more slowly than their isobenzofuran counterparts. This is not surprising since their formation from **16** involves the sacrifice of much more resonance energy than the corresponding process **6** → **7** (Scheme I). This accounts for the sluggish reaction of the naphthofurans.

Diels–Alder reactions of **6a** and **16a** were carried out in AcOD, giving **37** and **38**, respectively (bottom, Scheme V). ^1H and ^2H NMR spectra of the products show complete deuteriation of the methylene group, but very little deuterium incorporation (2–5%) at the bridge, suggesting that the Diels–Alder reaction is much faster than protonation of the furanoid species. In the presence of a dienophile, then, very little equilibration occurs between **1** and **2** because most of **2** reacts as it is formed. This is consistent with the high reactivity associated with isobenzofurans.[1]

Diels–Alder reactions of the naphtho[2,3-*c*]furans **17** (Scheme III) in glacial acetic acid gave many products in addition to the desired DMAD adducts. This cannot be attributed solely to the reaction conditions since the corresponding isobenzofuran series (**7**, Scheme I), reacts cleanly in AcOH. One unexpected product was isolated from a Diels–Alder reaction between **16c** and DMAD; it eluted with the desired product and was separated by washing with methanol. It was identified as phenanthrene **39** (Scheme VI). The ^1H NMR spectrum shows two methoxy singlets, one of which is shielded by the adjacent aryl substituent. The two-proton doublet (J = 1.6 Hz) at 5.85 ppm is typical of this type of CH_2 group. This small coupling is often observed in similar compounds, such as **16** (Scheme III), instrument resolution permitting. The aromatic region integrates to 12 protons, one of which appears as a downfield doublet (bay-region proton H_4).[19,20] IR, MS, and HRMS spectra all corroborate this structure. Compound **39** is formed by Diels–Alder reaction of DMAD with the exocyclic double bond and adjacent naphthalenic double bond of **16c**. Analogous Diels–Alder reactions have been reported with styrenes[21-23] and vinylnaphthalenes.[24] Once formed, adduct **40** loses H_2 giving **39**.

Another byproduct of this reaction was isolated from reaction of **16b** with DMAD for 12 h in refluxing AcOH. The fluorescent yellow compound was identified as anthrol **41** (Scheme VII), formed by aromatization of adduct **18b**. This product was easily recognized by its ^1H NMR spectrum, which shows the exchangeable OH peak far downfield (11.6 ppm) due to hydrogen-bonding to the ortho carbonyl.[25] This hydrogen bond is also evident in the IR spectrum which shows two carbonyl bands, one at substantially lower wavenumber. The analogous naphthol **42** (Scheme VII) was prepared by refluxing the corresponding Diels–Alder adduct in MeOH with a catalytic amount of HCl.

The Diels–Alder adducts were found to be reactive toward Michael addition. This was first noticed when a flask containing a crude sample of **14b** was discarded into a cleaning solution of methanolic KOH. When removed the next day, the sample was crystalline. Recrystallization and characterization showed it to be **43**, formed by Michael addition of MeOH to **18b** (Scheme VIII). Compounds **44a** and **44b** were prepared under more controlled conditions. The ^1H NMR spectra of these compounds were very sim-

(19) By analogy with "4-(methoxycarbonyl)phenanthrene", H_5 at 8.15 ppm: Bartle, K. D.; Smith, J. A. S. *Spectrochim. Acta* **1967**, *23A*, 1715.
(20) This bay-region proton is shielded by the C=O of the bay-region substituent. An analogous effect has been reported: Keay, B. A.; Rodrigo, R. *Can. J. Chem.* **1985**, *63*, 735.
(21) Manning, W. B.; Tomaszewski, J. E.; Muschik, G. M.; Sato, R. I. *J. Org. Chem.* **1977**, *42*, 3465.
(22) Manning, W. B.; Muschik, G. M.; Tomaszewski, J. E. *J. Org. Chem.* **1979**, *44*, 699.
(23) Middleton, W. J.; Heckert, R. E.; Little, E. L.; Krespan, C. G. *J. Am. Chem. Soc.* **1958**, *80*, 2783.
(24) Ciganek, E. *J. Org. Chem.* **1969**, *34*, 1923.
(25) Dudek, G. O. *Spectrochim. Acta* **1963**, *19*, 691.

ilar, implying that the same relative regio- and stereochemistry exists. The structural assignment is based on the assumption that attack on the exo face is most likely, from the less hindered side (away from the benzyl substituent). Cis addition is assumed by analogy with the reaction of isobenzofuran adduct **45** with methanol, giving **46** (Scheme VIII).[26] In the ^1H NMR spectrum of **46**, coupling to the bridge proton indicates that protonation occurs on the exo face.

Treatment of DMAD adducts **8** (Scheme I) with $NaBH_4$ in methanol resulted in Michael addition of hydride to the double bond (Scheme IX). The product isolated after several hours proved to be trans-diester **49** (Scheme IX) but several experiments showed that the reaction initially takes the same course proposed for the addition of methanol. Aliquots taken shortly after addition of $NaBH_4$ show a mixture of **49** and cis-diester **48**. Under the basic conditions of this reaction, **48** can epimerize at C_3 to give the trans product. If this experiment is repeated in methanol-*d*, the bridge proton signal of **48** still appears as a doublet, implying hydride adds to the side opposite to the benzyl substituent. In the final product, **49**, the C_2 signal is absent. The selective epimerization at C_3 has been reported for **48**.[2,3] This addition of H_2 serves as an alternative to catalytic hydrogenation.

The work discussed above has demonstrated that the prototropic tautomerism between benzylisobenzofuran (**2**) and 1-(phenylmethylene)-1,3-dihydroisobenzofuran (**1**) also exists for the homologous naphtho[2,3-*c*]furans. This feature has been exploited in the preparation of more complex PAH systems. Using 1- and 2-naphthylacetic acids further extends the range of ring systems which can be made. This route to PAHs is both efficient and versatile; a variety of substituted phthalic anhydride and arylacetic acid starting materials are easily accessible.

The importance of acid in the prototropic tautomerism has been rationalized mechanistically. The proposed mechanism was supported by regioselective incorporation of deuterium from AcOD as solvent, which may prove useful in the preparation of labelled PAH systems.

Experimental Section

Melting points were determined in open capillaries with a Mel-Temp apparatus and are uncorrected. IR spectra were recorded on either a Perkin-Elmer 983 or Beckman Acculab 10 spectrophotometer. NMR spectra were recorded on Bruker WP-80, AM-250, or WH-400 instruments, using tetramethylsilane (TMS) as an internal reference. Peaks are reported in ppm downfield from TMS using the δ scale. Analyses were performed by M-H-W Laboratories, Phoenix, AZ, and Uniroyal Research, Guelph, Ontario.

Dry diethyl ether was freshly distilled from sodium benzophenone ketyl.

Preparation of the (Arylmethylene)phthalides and (Arylmethylene)naphthalides. The preparations of compounds **3** and **13** and their reduction have been described.[6]

Dehydration of Hemiketals. General Procedure. These compounds were generally not isolated. They could be obtained by treating ethereal solutions of the hemiketals with a few drops of concentrated HCl and stirring for several hours. Washing with $NaHCO_3$ solution, drying over $MgSO_4$, filtration, and removal of solvent gave the dehydrated products. In some cases, dehydration occurred spontaneously without added acid. Attempts to obtain analytical data of some of these products were frequently unsuccessful, presumably due to facile oxidation. On standing for several days, the aromatic aldehydes could frequently be detected by their characteristic smell.

1,3-Dihydro-1-(1-naphthalenylmethylene)isobenzofuran (6a). ^1H NMR ($CDCl_3$, 80 MHz) δ 5.49 (s, 2 H), 6.65 (s, 1 H), 7.2–7.9 (m, 9 H), 8.1–8.4 (m, 2 H); IR (neat) 1642, 1467, 1044, 1012, 993, 754 cm^{-1}.

1,3-Dihydro-1-(2-naphthalenylmethylene)isobenzofuran (6b). The ether solution obtained from the reduction of 2.0 g (7.2 mmol) of **3b** was stripped of solvent, leaving a white solid which proved to be **6b**, 1.8 g (95%). A portion recrystallized from $CHCl_3$ had mp 174–177 °C: ^1H NMR ($CDCl_3$, 80 MHz) δ 5.57 (s, 2 H), 6.10 (s, 1 H), 6.9–8.3 (m, 11 H); IR (Nujol) 1657, 1618, 1595, 1039, 997, 833, 749 cm^{-1}; MS(EI), *m/e* (rel intensity) 258 (100), 257 (14), 229 (33), 228 (27), 129 (18), 128 (25), 114 (17), 113 (9).

Anal. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.38; H, 5.50.

1,3-Dihydro-1-(phenylmethylene)naphtho[2,3-*c*]furan (16a). A portion recrystallized from ethanol–diethyl ether had mp 169–173 °C: ^1H NMR ($CDCl_3$, 80 MHz) δ 5.64 (s, 2 H), 6.17 (s, 1 H), 7.0–8.1 (m, 11 H); IR (Nujol) 1651, 1172, 1114, 1023, 879, 748 cm^{-1}; MS(EI), *m/e* (rel intensity) 258 (100), 257 (23), 230 (9), 229 (31), 228 (26), 215 (9), 129 (12), 114 (1).

1,3-Dihydro-1-(1-naphthalenylmethylene)naphtho[2,3-*c*]furan (16b): ^1H NMR ($CDCl_3$, 80 MHz) δ 5.64 (s, 2 H), 6.90 (s, 1 H), 7.2–8.5 (m, 13 H).

1,3-Dihydro-1-(2-naphthalenylmethylene)naphtho[2,3-*c*]furan (16c). A solution of **14c** in diethyl ether was treated with dilute HCl. Water was added, and the mixture was heated until the ether had evaporated. A yellow solid was filtered, washed with water, and dried, giving **16c** in 50% yield, mp 255 °C dec; ^1H NMR (DMSO-d_6, 80 MHz) δ 5.77 (s, 2 H), 6.54 (s, 1 H), 7.3–8.1 (m, 11 H), 8.21 (s, 1 H), 8.42 (s, 1 H); IR (Nujol) 1651, 1347, 1020, 884, 831, 744 cm^{-1}; MS(EI), *m/e* (rel intensity) 308 (M^+, 100), 307 (17), 279 (27), 278 (23), 276 (9), 154 (15), 139 (22), 138 (9).

1,4-Epoxy-1,4-dihydro-1-(1-naphthalenylmethyl)-2,3-naphthalenedicarboxylic Acid, Dimethyl Ester (8a). In 100 mL of AcOH were refluxed **4a** (from the reduction of **3a**, 0.75 g, 2.8 mmol) and 1.4 g of DMAD (10 mmol) for 1 h. Water (100 mL) was added and the mixture extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water and twice with $NaHCO_3$ solution, dried over $MgSO_4$, and filtered. Solvent was removed by rotary evaporation and DMAD was removed under high vacuum with heating. The residue was crystallized and recrystallized from EtOH, giving 0.77 g of **8a** (70% from **3a**): mp 149–150 °C; IR (Nujol) 1726, 1710 (C=O), 1300, 1247, 980, 792, 785, 766 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 3.56 (s, 3 H), 3.70 (s, 3 H), 4.05 and 4.37 (AB q, J = 16 Hz, 2 H), 5.96 (s, 1 H), 7.0–8.4 (m, 11 H); MS(EI), *m/e* (rel intensity) 400 (M^+, 7), 309 (41), 308 (25), 281 (46), 258 (36), 257 (35), 252 (30), 141 (100).

Anal. Calcd for $C_{25}H_{20}O_5$: C, 74.99; H, 5.03. Found: C, 74.74; H, 5.16.

1,4-Epoxy-1,4-dihydro-1-(1-naphthalenyldideuteriomethyl)-2,3-naphthalenedicarboxylic Acid, Dimethyl Ester (37). This compound was prepared in the same way as **8a** using AcOD as the solvent, mp 147–148: ^2H NMR ($CDCl_3$, 101 MHz) δ 4.07 (s, 1 H), 4.39 (s, 1 H), 6.02 (s, 0.02 H); MS(EI), *m/e* (rel intensity) 402 (M^+, 5), 311 (29), 310 (31), 309 (25), 283 (32), 260 (27), 258 (27), 143 (100).

1,4-Epoxy-1,4-dihydro-1-(2-naphthalenylmethyl)-2,3-naphthalenedicarboxylic Acid, Dimethyl Ester (8b). In 100 mL of toluene were refluxed **4b** from the reduction of 0.6 g (2.2 mmol) of **3b**, 2 g of DMAD, and a catalytic amount of TCAA for 3 h. The reaction mixture was washed with $NaHCO_3$ solution, dried over $MgSO_4$, and filtered, and the solvent was removed. DMAD was pumped away under high vacuum using a steam bath to heat the residue. The residue was dissolved in 30 mL of MeOH from which was obtained 0.62 g of **8b** (70% from **3b**), mp 142–143 °C; IR (Nujol) 1704 (C=O), 1619 (C=C), 1285, 1237, 734, 648 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 3.62 (s, 3 H), 3.68 (s, 3 H), 3.76 and 4.02 (AB q, J = 15 Hz, 2 H), 5.96 (s, 1 H), 7.0–7.9 (m, 11 H); MS(EI), *m/e* (rel intensity) 400 (M^+, 16), 341 (20), 309 (27), 281 (24), 258 (52), 257 (37), 141 (100), 31 (24).

Anal. Calcd for $C_{25}H_{20}O_5$: C, 74.99; H, 5.03. Found: C, 74.97; H, 4.96.

1,4-Epoxy-1,4-dihydro-1-(phenylmethyl)-2,3-anthracenedicarboxylic Acid, Dimethyl Ester (18a). In 100 mL of toluene were refluxed **14a** from the reduction of 0.6 g (2.2 mmol) of **13a**, 2 g of DMAD, and a catalytic amount of TCAA for 72 h. The reaction was washed with $NaHCO_3$ solution, dried over $MgSO_4$,

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and filtered, and the solvent was removed. DMAD was removed under high vacuum using a steam bath to heat the residue. Crystallization from MeOH gave 0.50 g of **18a** (56% from **13a**), mp 170.5–172 °C: IR (Nujol) 1723 and 1706 (C=O), 1623 (C=C), 1294, 980, 880, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 3.68 (s, 3 H), 3.72 (s, 3 H), 3.69 and 3.96 (AB q, J = 15 Hz, 2 H), 6.06 (s, 1 H), 7.2–7.9 (m, 11 H); MS(EI), m/e (rel intensity) 400 (M^+, 19), 309 (30), 282 (20), 258 (43), 252 (28), 251 (26), 250 (100), 91 (52).

Anal. Calcd for $C_{25}H_{20}O_5$: C, 74.99; H, 5.03. Found: C, 74.79; H, 5.04.

1,4-Epoxy-1,4-dihydro-1-(phenyldideuteriomethyl)-2,3-anthracenedicarboxylic Acid, Dimethyl Ester (38). Into 12 mL of AcOD (10 mL of acetic anhydride, 2 mL of D_2O) at reflux were pipetted 0.5 mL of DMAD (4 mmol) and 0.23 g (0.83 mmol) of **14a**. After 1 h, the reaction was cooled, water was added, and the mixture was extracted with $CHCl_3$. The organic layer was washed with water, $NaHCO_3$ solution, dried over $MgSO_4$, filtered, and stripped of solvent. The oily residue was loaded onto a 6-in. Kieselgel 60 column in hexane. Excess DMAD was removed by elution with toluene, following which the desired product was eluted with CH_2Cl_2. The appropriate fractions (identified by TLC) were combined and stripped of solvent, and the residue was crystallized and recrystallized from EtOH, giving 0.08 g of the deuteriated product (24%), mp 170–171 °C: ^2H NMR ($CDCl_3$, 101 MHz) δ 3.74 (s, 1 H), 4.03 (s, 1 H), 5.98 (s, 0.07 H); MS(EI), m/e (rel intensity) 402 (M^+, 12), 309 (26), 283 (24), 261 (38), 253 (21), 251 (28), 250 (100), 93 (75).

1,4-Epoxy-1,4-dihydro-1-(1-naphthalenylmethyl)-2,3-anthracenedicarboxylic Acid, Dimethyl Ester (18b). In 60 mL of AcOH was dissolved **14b** from the reduction of 1.0 g (3.1 mmol) of **13b**. DMAD (2.5 g, 18 mmol) was added and the mixture refluxed for 2 h. The solvent was removed by rotary evaporation. The residue was taken up in $CHCl_3$, washed with $NaHCO_3$ solution, dried over $MgSO_4$, and filtered, and the solvent was removed. The residue was loaded on to an 8 in. × 1.5 in. column of Kieselgel 60 with 10% EtOAc in toluene and chromatographed using 10% EtOAc/toluene as eluant. The product was crystallized from EtOH and recrystallized from MeOH, giving 0.53 g of **18b** (38% from **13b**), mp 121–125 °C: IR (KBr) 1719 and 1701 (C=O), 1627 (C=C), 1440, 1306, 1119, 795, 759 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 3.54 (s, 3 H), 3.69 (s, 3 H), 4.13 and 4.48 (AB q, J = 16 Hz, 2 H), 6.05 (s, 1 H), 7.3–8.0 (m, 12 H), 8.1–8.3 (m, 1 H); MS(EI), m/e (rel intensity) 450 (M^+, 12), 386 (20), 359 (17), 331 (20), 330 (16), 302 (17), 250 (27), 141 (100).

Anal. Calcd for $C_{29}H_{22}O_5$: C, 77.32; H, 4.92. Found: C, 77.32; H, 5.07.

1,4-Epoxy-1,4-dihydro-1-(2-naphthalenylmethyl)-2,3-anthracenedicarboxylic Acid, Dimethyl Ester (18c). The product from the reduction of 1.17 g of **13c** (13 mmol) was refluxed in 100 mL of toluene with 2 g (14 mmol) of DMAD and ca. 0.1 g of TCAA for 55 h. The solution was cooled, washed with $NaHCO_3$ solution, dried over $MgSO_4$, and filtered, and the solvent was removed. DMAD was removed under high vacuum, heating the residue on a steam bath. The oily residue was heated with enough EtOH such that the product did not precipitate as an oil on cooling. A seed crystal induced crystallization. Filtration gave 0.62 g of **18c** (38% from **13c**), mp 146–147 °C: IR (Nujol) 1717 (C=O), 1630 (C=C), 1319, 1264, 1237, 1121, 748 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 3.61 (s, 3 H), 3.69 (s, 3 H), 3.83 and 4.13 (AB q, J = 15 Hz, 2 H), 6.08 (s, 1 H), 7.3–7.9 (m, 13 H).

Anal. Calcd for $C_{29}H_{22}O_5$: C, 77.32; H, 4.92. Found: C, 77.57; H, 4.92.

***endo*-1,4-Epoxy-1,2,3,4-tetrahydro-1-(1-naphthalenylmethyl)-2,3-naphthalenedicarboxylic Acid, Dimethyl Ester (9a).** All of the DMAD adducts were hydrogenated in the following manner. To 75 mL of EtOAc in a Parr hydrogenation bottle were added 0.30 g of 5% Pd/C and 1.0 g (2.5 mmol) of **8a**. The bottle was purged 3 times with H_2 and then shaken on a Parr hydrogenator under 50 psi H_2 for 10 h. The solution was filtered through glass fibre filter paper, and the solvent was removed under reduced pressure. Crystallization from MeOH gave 0.93 g of **9a** (93%), mp 110–111 °C: IR (Nujol) 1751 (C=O), 1346, 1242, 1222, 1168, 781 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 3.16 and 3.50 (obscured AB of ABX, J_{AB} = 10 Hz, 2 H), 3.43 (s, 3 H), 3.52 (s, 3 H), 4.04 and 4.21 (AB q, J = 17 Hz, 2 H), 5.42 (d, J = 4.9 Hz, 1 H), 7.2–8.3 (m, 11 H); MS(EI), m/e (rel intensity) 402 (M^+, 8), 259 (21), 258 (100), 257 (14), 141 (9), 129 (9), 113 (9), 31 (14).

Anal. Calcd for $C_{25}H_{22}O_5$: C, 74.81; H, 5.51. Found: C, 74.81; H, 5.68.

***endo*-1,4-Epoxy-1,2,3,4-tetrahydro-1-(2-naphthalenylmethyl)-2,3-naphthalenedicarboxylic Acid, Dimethyl Ester (9b).** This compound was isolated in 80% yield beginning with 1.8 g of **8b**, mp 104–105 °C (MeOH): IR (Nujol) 1744 and 1736 (C=O), 1333, 1220, 1198, 996, 772 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 3.23 and 3.50 (obscured AB of ABX, J_{AB} = 11 Hz, 2 H), 3.44 (s, 3 H), 3.51 (s, 3 H), 3.74 and 3.87 (AB q, J = 16 Hz, 2 H), 5.46 (d, J = 4.7 Hz, 1 H), 7.2–7.9 (m, 11 H); MS(EI), m/e (rel intensity) 402 (M^+, 7), 259 (20), 258 (100), 129 (16), 128 (9), 46 (27), 45 (19), 31 (28).

Anal. Calcd for $C_{25}H_{22}O_5$: C, 74.81; H, 5.51. Found: C, 74.78; H, 5.58.

***endo*-1,4-Epoxy-1,2,3,4-tetrahydro-1-(phenylmethyl)-2,3-anthracenedicarboxylic Acid, Dimethyl Ester (19a).** This compound was prepared from 0.40 g of **18a** in 80% yield, mp 138–139 °C (MeOH): IR (KBr) 1763 (C=O), 1457, 1377, 1350, 1215, 1107, 1010, 897, 773, 721 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 3.27 and 3.55 (obscured AB of ABX, J_{AB} = 10 Hz, 2 H), 3.42 (s, 3 H), 3.45 (s, 3 H), 3.65 and 3.82 (AB q, J = 14 Hz, 2 H), 5.56 (d, J = 4.9 Hz, 1 H), 7.2–8.0 (m, 11 H).

Anal. Calcd for $C_{25}H_{22}O_5$: C, 74.81; H, 5.51. Found: C, 74.43; H, 5.54.

***endo*-1,4-Epoxy-1,2,3,4-tetrahydro-1-(1-naphthalenylmethyl)-2,3-anthracenedicarboxylic Acid, Dimethyl Ester (19b).** This compound was prepared from 0.15 g of **18b** in 73% yield, mp 167–168 °C (MeOH): IR (KBr) 1745 (C=O), 1437, 1358, 1332, 1210, 1166, 800, 747 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 3.24 and 3.59 (obscured AB of ABX, J_{AB} = 10.7 Hz, 2 H), 3.41 (s, 3 H), 3.48 (s, 3 H), 4.12 and 4.33 (AB q, J = 16 Hz, 2 H), 5.54 (d, J = 4.9 Hz, 1 H), 7.3–8.3 (m, 13 H); MS(EI), m/e (rel intensity) 402 (M^+ 2), 370 (6), 312 (9), 309 (25), 308 (100), 307 (9), 291 (7), 290 (9).

Anal. Calcd for $C_{29}H_{24}O_5$: C, 76.98; H, 5.35. Found: C, 76.83; H, 5.45.

***endo*-1,4-Epoxy-1,2,3,4-tetrahydro-1-(2-naphthalenylmethyl)-2,3-anthracenedicarboxylic Acid, Dimethyl Ester (19c).** This compound was prepared from 0.26 g of **18c** in 81% yield, mp 185–187 °C (acetone–EtOH): IR (Nujol) 1745 (C=O), 1332, 1234, 1212, 1163, 877 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.31 and 3.58 (AB of ABX, J_{AB} = 10.7 Hz, J_{AX} = 5.1 Hz, J_{BX} = 0 Hz, 2 H), 3.42 (s, 3 H), 3.47 (s, 3 H), 3.81 and 4.00 (AB q, J = 14.7 Hz, 2 H), 5.58 (d, J = 5.1 Hz, 1 H), 7.4–7.6 (m, 5 H), 7.7–7.8 (m, 8 H); MS(EI), m/e (rel intensity) 434 ($M^+ - H_2O$, 31), 375 (29), 371 (37), 370 (100), 343 (37), 315 (47), 314 (17), 308 (49).

Anal. Calcd for $C_{29}H_{24}O_5$: C, 76.98; H, 5.35. Found: C, 77.08; H, 5.30.

***8H*-Dibenzo[3,4:5,6]anthra[9,1-*b*,*c*]furan-8-one (10).** In 20 mL of PPA was placed 0.38 g (0.095 mmol) of **9a**. The mixture was heated in a wax bath at 90 °C for 2 h. The mixture was stirred intermittently with a glass rod. The warm reaction mixture was poured into 200 mL of water and stirred for several hours. An orange solid was collected by filtration and recrystallized from DMF, giving **10**, 0.24 g (79%), mp 288–290 °C: IR (Nujol) 1795, 1780 (C=O), 1606, 1014, 904, 743 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 7.66–8.01 (m, 6 H), 8.09 (d, J = 9 Hz, 1 H), 8.23 (d, J = 8 Hz, 1 H), 8.54 (s, 1 H), 8.96 (d, J = 8 Hz, 2 H), 9.57 (s, 1 H); MS(EI), m/e (rel intensity) 320 (M^+, 100), 264 (20), 263 (25), 160 (21), 132 (14), 131.5 (34), 131 (11), 130.5 (16).

Anal. Calcd for $C_{23}H_{12}O_2$: C, 86.24; H, 3.78. Found: C, 86.40; H, 4.00.

***6H*-Dibenzo[3,4:7,8]anthra[9,1-*b*,*c*]furan-6-one (11).** This compound was prepared from 1.0 g of **9b** in the same manner as **10** in 88% yield, mp 295–298 °C (acetone–DMF): IR (Nujol) 1772, 1762 (C=O), 944, 869, 802, 781, 758, 737 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 7.6–8.0 (m, 7 H), 8.22 (d, J = 8 Hz, 1 H), 8.58 (s, 1 H), 8.74 (s, 1 H), 8.85 (d, J = 8 Hz, 1 H), 9.39 (d, J = 8 Hz, 1 H); MS(EI), m/e (rel intensity) 320 (M^+, 100), 264 (24), 263 (34), 261 (9), 160 (14), 132 (17), 131.5 (28), 130.5 (12).

Anal. Calcd for $C_{23}H_{12}O_2$: C, 86.24; H, 3.78. Found: C, 86.34; H, 3.99.

***6H*-Pentapheno[5,6-*b*,*c*]furan-6-one (20).** This compound was prepared from **19a** in the same manner as **10** but was heated for 6.5 h at 120 °C. It was obtained in 61% yield from 0.12 g of

19a, mp 291–292 °C (DMF): IR (Nujol) 1790 (C=O), 1600, 987, 883, 734 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 7.6–7.8 (m, 4 H), 8.0–8.3 (m, 4 H), 8.51 (s, 1 H), 8.66 (s, 1 H), 8.80 (s, 1 H), 9.23 (s, 1 H); MS(EI), *m/e* (rel intensity) 321 (M^+ + 1, 25) 320 (M^+, 100), 264 (26), 263 (21), 160 (16), 132 (14), 131.5 (24), 130.5 (8).

Anal. Calcd for $C_{23}H_{12}O_2$: C, 86.24; H, 3.78. Found: C, 86.24; H, 4.00.

6*H*-Benzo[1,2]pentapheno[5,6-*b*,*c*]furan-6-one (21). This compound was prepared from 0.36 g (0.80 mmol) of **19b** in the manner described for **10** except that the reaction was heated for 3 h at 120 °C. Recrystallization from DMF gave 0.10 g of the desired product. Water was added to the filtrate until just turbid. Over several hours, starting material crystallized out and was recovered (0.17 g). The yield based on recovered material was 64%, mp 374–375 °C: IR (KBr) 1790 and 1764 (C=O), 1611, 1251, 1012, 892, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 7.6–8.3 (m, 9 H), 8.62 (s, 1 H), 8.75 (s, 1 H), 9.07 (d, *J* = 8 Hz, 1 H), 9.41 (s, 1 H), 9.70 (s, 1 H); MS(EI), *m/e* (rel intensity) 371 (M^+ + 1, 29) 370 (M^+, 100), 314 (30), 313 (29), 185 (16), 157 (16), 156.5 (31), 155.5 (14).

Anal. Calcd for $C_{27}H_{14}O_2$: C, 87.55; H, 3.81. Found: C, 87.36; H, 4.04.

6*H*-Benzo[3,4]pentapheno[5,6-*b*,*c*]furan-6-one (22). This compound was prepared from 0.15 g (0.33 mmol) of **19c** in the manner described for **10** except that the reaction was heated for 3 h at 120 °C. Recrystallization from DMF gave 0.036 g (29%). Water was added to the filtrate until just turbid. Over several hours, starting material crystallized out and was recovered. The starting material was heated with PPA for 10 h at 170 °C, giving an additional 0.038 g of product. The total yield obtained was 60%, mp 340–341 °C: IR (Nujol) 1791 (C=O), 950, 890, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 7.6–8.0 (m, 6 H), 8.04 (d, *J* = 8 Hz, 1 H), 8.19 (d, *J* = 8 Hz, 1 H), 8.25 (d, *J* = 8 Hz, 1 H), 8.65 (s, 1 H), 8.75 (s, 1 H), 8.86 (s, 1 H), 9.31 (s, 1 H), 9.41 (d, *J* = 8 Hz, 1 H); MS(EI), *m/e* (rel intensity) 371 (M^+ + 1, 27) 370 (M^+, 100), 283 (30), 271 (27), 184 (31), 181 (25), 155 (27), 140 (22).

Anal. Calcd for $C_{27}H_{14}O_2$: C, 87.55; H, 3.81. Found: C, 87.38; H, 3.96.

1-Hydroxy-4-(1-naphthalenylmethyl)-2,3-anthracenedicarboxylic Acid, Dimethyl Ester (41). In glacial acetic acid were refluxed **14b** and an excess of DMAD for 12 h. A yellow solid was collected by filtration and recrystallized from MeOH, giving **41**, mp 248–252 °C: IR (KBr) 2400–3300 (br OH), 1716 and 1650 (C=O), 1449, 1379, 1347, 1325, 1287, 1206, 784 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 3.73 (s, 3 H), 3.99 (s, 3 H), 4.81 (s, 2 H), 6.7–8.5 (m, 12 H), 9.13 (s, 1 H), 11.60 (s, 1 H, exchanges with D_2O).

Anal. Calcd for $C_{29}H_{22}O_5$: C, 77.32; H, 4.92. Found: C, 77.57; H, 5.09.

1-Hydroxy-4-(2-naphthalenylmethyl)-2,3-naphthalenedicarboxylic Acid, Dimethyl Ester (42). In 30 mL of glacial acetic acid was refluxed 0.20 g (0.5 mmol) of **8b**. After 14 h it was unchanged. When refluxed in 20% HCl in glacial acetic acid for 14 h, **42** was obtained in ca. 25% yield, mp 160–163 °C (EtOH–acetone): IR (Nujol) 2750–3200 (br OH), 1730 and 1659 (C=O), 1343, 1259, 1207, 744 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 3.82 (s, 3 H), 3.98 (s, 3 H), 4.44 (s, 2 H), 7.2–8.0 (m, 10 H), 8.4–8.6 (m, 1 H), 12.37 (s, 1 H, exchanges with D_2O).

Anal. Calcd for $C_{25}H_{20}O_5$: C, 74.99; H, 5.03. Found: C, 75.06; H, 5.02.

5*H*-3-(2-Naphthyl)-1,2-phenanthro[10,1-*bc*]furandicarboxylic Acid, Dimethyl Ester (39). In 100 mL of glacial acetic acid, 0.8 g (2.6 mmol) of **16c** and 2.2 g (16 mmol) DMAD were refluxed for 2 h. The reaction was filtered and 0.6 g of starting material, **16c**, was recovered. The filtrate was stripped of AcOH, taken up in $CHCl_3$, and washed with $NaHCO_3$ solution. The organic phase was dried over $MgSO_4$ and filtered, and the solvent was removed. The residue was chromatographed in the same manner described previously for **18b**. Fractions containing Diels–Alder adduct **18c** were combined and stripped of solvent. The residue was dissolved in MeOH and cooled overnight. Two crystalline products were visible, one white, one orange. The white product (**18c**) was dissolved in hot MeOH and the orange product was then collected by filtration. From the filtrate 0.06 g (21%) of **18c** was obtained. The orange compound was recrystallized from DMF–acetone–water, giving a white product (**39**) in very small quantity, mp 219–221 °C dec; IR (Nujol) 1730 and 1717 (C=O), 1247, 1230, 1213, 1113, 1071, 1024, 763 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.54 (s, 3 H), 4.08 (s, 3 H), 5.85 (d, *J* = 1.6 Hz, 2 H), 7.5–7.7 (m, 6 H), 7.9–8.3 (m, 5 H), 8.28 (d, *J* = 8 Hz, 1 H); MS(EI), *m/e* (rel intensity) 449 (M^+ + 1, 30), 448 (100), 385 (22), 330 (9), 224 (10), 200 (21), 192.5 (10), 150 (13); HRMS calcd for $C_{29}H_{20}O_5$ 448.1311, found 448.1295.

1,4-Epoxy-1,2,3,4-tetrahydro-3-*exo*-methoxy-1-(1-naphthalenylmethyl)-2-*endo*,3-*endo*-anthracenedicarboxylic Acid, Dimethyl Ester (43). This product was isolated from a reaction mixture containing **18b** which was placed in MeOH/KOH at 25 °C for about 24 h. Recrystallization from EtOH gave **43**, mp 185–187 °C: IR (Nujol) 1738 (C=O), 1293, 1176, 1105, 1081, 778 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.97 (s, 1 H), 3.21 (s, 3 H), 3.38 (s, 3 H), 3.57 (s, 3 H), 4.08 and 4.36 (AB q, *J* = 15.3 Hz, 2 H), 5.34 (s, 1 H), 7.4–7.6 (m, 7 H), 7.7–7.9 (m, 4 H), 8.03 (s, 1 H), 8.24 (dd, *J* = 1.3 and 8 Hz, 1 H); MS(EI), *m/e* (rel intensity) 482 (M^+, 0.2), 309 (27), 308 (100), 307 (8), 291 (7), 290 (7), 279 (6), 141 (6).

Anal. Calcd for $C_{30}H_{26}O_6$: C, 74.67; H, 5.43. Found: C, 74.58; H, 5.51.

1,4-Epoxy-1,2,3,4-tetrahydro-3-*exo*-methoxy-1-(2-naphthalenylmethyl)-2-*endo*,3-*endo*-naphthalenedicarboxylic Acid, Dimethyl Ester (44b). In 30 mL of MeOH were refluxed 0.33 g (0.83 mmol) of **8b** and 0.15 g KOH for 12 h. The solvent was stripped away and water added to the crystalline residue. A white solid was then collected by filtration and recrystallized from MeOH, giving **44b**, 0.27 g (62%), mp 166–168 °C: IR (Nujol) 1742 (C=O), 1300, 1273, 1169, 1100, 1077, 981, 777, 759 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.02 (s, 1 H), 3.31 (s, 3 H), 3.45 (s, 3 H), 3.59 (s, 3 H), 3.77 and 3.85 (AB q, *J* = 14.9 Hz, 2 H), 5.27 (s, 1 H), 7.1–7.6 (m, 7 H), 7.7–7.9 (m, 4 H).

Anal. Calcd for $C_{26}H_{24}O_6$: C, 72.21; H, 5.59. Found: C, 72.24; H, 5.78.

1,4-Epoxy-1,2,3,4-tetrahydro-3-*exo*-methoxy-1-(1-naphthalenylmethyl)-2-*endo*,3-*endo*-naphthalenedicarboxylic Acid, Dimethyl Ester (44a). In 70 mL of MeOH were refluxed 0.75 g (1.9 mmol) of **8a** and 0.2 g of K_2CO_3 for 12 h. After the solvent was stripped away, water was added to the crystalline residue. A white solid was then collected by filtration and recrystallized from MeOH–water, giving **44a**, 0.72 g (92%), mp 124–125 °C: IR (Nujol) 1733 (C=O), 1211, 1178, 1108, 981, 786 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 2.91 (s, 1 H), 3.20 (s, 3 H), 3.45 (s, 3 H), 3.52 (s, 3 H), 3.90 and 4.33 (AB q, *J* = 15 Hz, 2 H), 5.22 (s, 1 H), 7.1–8.0 (m, 10 H), 8.1–8.3 (m, 1 H).

Anal. Calcd for $C_{26}H_{24}O_6$: C, 72.21; H, 5.59. Found: C, 72.48; H, 5.59.

Dibenz[*a*,*h*]anthracen-7-ol Acetate (24). Naphthalide **3b** (0.70 g, 2.6 mmol) was reduced with LAH (0.45 g) in the manner described previously. After hydrolysis, the ether solution was dried over $MgSO_4$ and filtered and the solvent removed. The residue was taken up in toluene and 2 mL (25 mmol) of methyl acrylate and a catalytic amount of TCAA was added. The mixture was refluxed for 9 h. A catalytic amount of TsOH was added and refluxing continued for 5 h. The reaction was cooled, washed with $NaHCO_3$ solution, and dried over $MgSO_4$. A few drops of DBU were added and the reaction was refluxed for 4 h. The solvent was removed under reduced pressure and the residue was refluxed in 20 mL of 1:1 MeOH/water with excess KOH for 21 h. After acidification with HCl, the mixture was extracted with two portions of CH_2Cl_2. The organic layer was heated with decolorization charcoal and $MgSO_4$ and filtered and the solvent was removed. The residue was refluxed in 60 mL of 1:1 AcOH/Ac_2O for 1 h with 0.3 g of $ZnCl_2$. White needle-like crystals formed on cooling to room temperature which proved to be **24**, 0.24 g, 28% yield overall, mp 244–246 °C (lit.[27] mp 235 °C): ^1H NMR ($CDCl_3$, 250 MHz) δ 2.66 (s, 3 H), 7.1–7.9 (m, 10 H), 8.76 (d, *J* = 7 Hz, 1 H), 8.98 (s, 1 H), 9.12 (dd, *J* = 2 and 8 Hz, 1 H).

Dibenz[*a*,*j*]anthracen-7-ol Acetate (23). This compound was prepared from 0.80 g of **3a** in the same manner as **24**, giving a crude yield of 40%. A portion was passed through a short column of silica gel, eluting with toluene, and then recrystallized from hexane–acetone, mp 262–263 °C (lit.[11] mp 255–256 °C): ^1H

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NMR ($CDCl_3$, 250 MHz) δ 2.66 (s, 3 H), 7.2–8.0 (m, 10 H), 8.98 (d, J = 8 Hz, 2 H), 9.96 (s, 1 H).

Pentaphen-5-ol Acetate (25). This compound was prepared from 0.75 g of **13a** in the same manner as **24** except that the reaction with DMAD was carried out for 8 days. Small amounts of TCAA were added daily after 4 days. To the final reaction mixture was added 150 mL of water. The resulting precipitate was filtered, air-dried, and chromatographed on silica gel, eluting with toluene. Removal of the solvent from the appropriate fractions and recrystallization from toluene–hexane gave **25** in 22% yield, mp 185–187 °C: IR (Nujol) 1757 (C=O), 1206, 1163, 1062, 873, 741 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.65 (s, 3 H), 7.56–7.63 (m, 4 H), 7.63 and 7.70 (AB q, J = 9.5 Hz, 2 H, upfield portion obscured), 7.94–7.97 (m, 1 H), 8.01–8.05 (m, 1 H), 8.15–8.19 (m, 2 H), 8.27 (s, 1 H), 9.19 (s, 1 H), 9.24 (s, 1 H).

Anal. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.46; H, 5.00.

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Registry No. **3a**, 34883-80-2; **3b**, 13102-93-7; **4a**, 92878-63-2; **4b**, 92878-64-3; **6a**, 113600-56-9; **6b**, 113600-57-0; **8a**, 113600-58-1; **8b**, 113600-59-2; **9a**, 113600-60-5; **9b**, 113600-61-6; **10**, 113600-62-7; **11**, 113600-63-8; **13a**, 4711-54-0; **13b**, 5060-75-3; **13c**, 53223-77-1; **14a**, 92878-65-4; **14b**, 92878-66-5; **14c**, 92878-67-6; **16a**, 113600-64-9; **16b**, 113600-65-0; **16c**, 113600-66-1; **18a**, 113600-67-2; **18b**, 113600-68-3; **18c**, 113600-69-4; **19a**, 113600-70-7; **19b**, 113600-71-8; **19c**, 113600-72-9; **20**, 113600-73-0; **21**, 113600-74-1; **22**, 113600-75-2; **23**, 41774-34-9; **24**, 63077-06-5; **25**, 113600-76-3; **37**, 113600-77-4; **38**, 113600-78-5; **39**, 113600-79-6; **41**, 113627-38-6; **42**, 113600-80-9; **43**, 113600-81-0; **44a**, 113600-82-1; **44b**, 113600-83-2; DMAD, 762-42-5; methyl acrylate, 96-33-3.

Type I Intramolecular Cycloadditions of Vinylketenes

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The scope of type I intramolecular [2 + 2] cycloadditions of alkenes with α,β-unsaturated ketenes (see eq 1) has been explored. These reactions generally produce bicyclo[3.2.0]heptan-6-ones containing an unsaturated substituent at position 5. Ketenes **4**, **7**, **13**, and **30** undergo the expected cycloaddition to give **5**, **8**, **14**, and **31** in 50–80% yield. Ketenes **10** and **16** undergo a 1,5-sigmatropic hydrogen shift to give dienals **11** and **17**. Ketenes **23** and **24** undergo a reversible electrocyclic ring closure instead of a cycloaddition to give cyclobutenones **25** and **26**. At higher temperatures electrocyclic ring closure is reversible and cyclobutenones **25** and **26** can be converted into **27** and **28** in 75% yield. Type I intramolecular cycloadditions cannot be used to produce bicyclooctanones such as **38**. These vinyl cyclobutanones are versatile synthetic intermediates. Treatment of **32** with potassium hydride gives **34** and **35**, suggesting that this approach will be useful for steroid synthesis. Treatment of **8** with boron trifluoride gives **39**.

Introduction

The stereospecific cycloaddition of ketenes to alkenes provides an attractive route to cyclobutanones and is one of the few general methods for carbofunctionalization of alkenes. We[1] and others[2] have recently recognized that the intramolecular version of this reaction provides a general method for the synthesis of polycyclic cyclobutanones. Although simple ketenes do undergo intramolecular [2 + 2] cycloaddition with some alkenes, satisfactory yields are not generally obtained unless activated ketenes are used.

Intramolecular [2 + 2] cycloadditions of alkenes with α,β-unsaturated ketenes proceed in mugh higher yield than with simple ketenes. The role of the double bond may be to either accelerate the cycloaddition and/or to retard oligomerization and other side reactions. These cycloadditions are particularly attractive since the resulting vinylcyclobutanones are versatile synthetic intermediates.[3-6] α,β-Unsaturated ketenes are versatile addends since the alkene containing side chain can be attached to the unsaturated ketene at either the ketene carbon (type I, eq 1),[1c,2e] the α-carbon (type II, eq 2),[1b,c,g,h,2c,g] or the β-carbon (type III, eq 3).[1a,c,2b] We report here a systematic study of the scope and limitations of type I reactions and an initial exploration of the reactivity of the adducts.[7]

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