$$R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| \quad (3)$$

$$R_w = [\Sigma(|F_o| - |F_c|)w^{0.5}]/\Sigma(|F_o|)w^{0.5} \quad (4)$$

In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 2.4580[\sigma(F)^2 + 0.000436F^2]^{-1}$ was employed for calculating R_w and in least-squares refinement.

The structure was solved by using Patterson techniques. The total number of parameters varied were 321 for 4529 observations. The phenyl rings were refined as rigid groups, and their carbon temperature factors were refined isotropically. An overall isotropic temperature factor was assigned to the phenyl hydrogen atoms. Parameters varied included a scale factor, coordinates of all remaining atoms except hydrogen atoms (which were refined in the riding mode), and anisotropic thermal parameters for all atoms other than hydrogen atoms, and an overall isotropic temperature factor was applied to the hydrogen atoms. The full-matrix least-squares refinement converged at $R = 0.0713$ and $R_w = 0.0623$.

There are two pairs of crystallographically nonequivalent molecules per unit cell. However, the bond lengths and bond angles do not differ significantly between these two molecules. Therefore, only the bond distances and bond angles for one of the molecules is presented in Table I. The final atomic coordinates and thermal parameters for both molecules are available as supplementary material in Table II, and the list of calculated and observed structure factors is available from the authors as Table III.

Registry No. 1, 33522-35-9; 4, 38305-28-1; 8, 82-43-9; 9, 33522-27-9; 10, 33522-37-1; 11, 14381-66-9; 12, 1714-09-6; 13, 50259-93-3; 14, 63605-29-8; 15, 73274-95-0; 16, 73274-96-1; 17, 73274-97-2; 18, 73274-98-3; 19, 73274-99-4; 20, 73275-00-0; 21, 73275-01-1; 22, 73275-02-2; 23, 1564-64-3; 24, 779-02-2; 25, 19096-07-2; 26, 73275-03-3; 27, 73275-04-4; 28, 73275-05-5; 29, 73275-06-6; 30, 90-44-8; 31, 2444-68-0; 32, 68941-26-4; 33, 13752-40-4; 34, 28871-54-7; 36 (isomer 1), 73275-07-7; 36 (isomer 2), 73275-08-8; 37, 73275-09-9; 38 (isomer 1), 73275-10-2; 38 (isomer 2), 73275-11-3; 39, 73275-12-4; 40, 73275-13-5; 41, 73275-14-6; 44, 73275-15-7; 45, 73275-16-8; anthraquinone, 84-65-1; 1,8-diiodo-9,10-anthraquinone, 30877-00-0; lithium acetylide, 1111-64-4; anthracene, 120-12-7; CH_2=CHBr, 593-60-2; Me_3SiCN, 7677-24-9; EtBr, 74-96-4.

Supplementary Material Available: Table II, containing atomic coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

Synthetic Routes to Derivatives of Polycyclic Aromatic Hydrocarbons Using Isobenzofurans as Transient Reactive Intermediates

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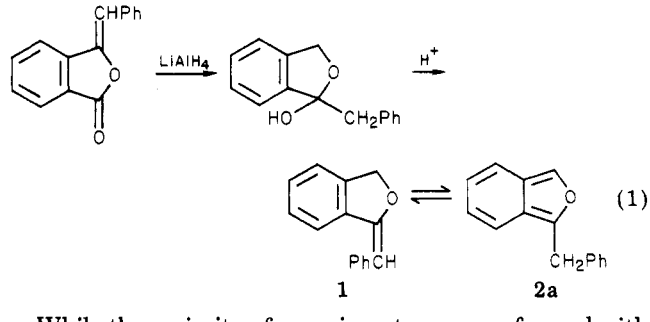
The known equilibrium between the tautomers benzalphthalan (1) and 1-benzylisobenzofuran (2) has been exploited as a synthetic route to novel substituted polycyclic aromatic compounds. The isobenzofuran was captured in a series of Diels–Alder reactions to provide epoxy-bridged Diels–Alder adducts. Aromatization of these adducts by dehydration was generally effected by using catalytic amounts of toluenesulfonic acid. Alternatively, trimethylsilyl chloride/sodium iodide was found superior in those cases where acid catalysis was unsatisfactory. The Diels–Alder adducts formed by using quinones were best aromatized under mild basic conditions (sodium acetate/methanol). When aromatization resulted in increased nonbonded interactions among the substituents attached to the developing polycyclic aromatic system, mixtures containing the desired aromatic compound and a product in which dehydration did *not* yield the new aromatic ring resulted. This problem was obviated by using basic conditions to isomerize the product mixture to the fully aromatic derivative.

1,3-Diarylisobenzofurans have been frequently used as intermediates for the synthesis of substituted polycyclic compounds.[1] More recently, less stable isobenzofurans have been generated as transient intermediates and utilized for the same purposes.[2] Earlier, we demonstrated[3] that the readily available benzalphthalan (1) (eq 1) existed in equilibrium with its tautomer 1-benzylisobenzofuran (**2a**) and the latter could be captured in Diels–Alder reactions. In this paper, the possibility of using this as a route to substituted polycyclic aromatic compounds is explored.



(1)

1 2a

While the majority of experiments were performed with the readily accessible **2a** (via 1), several successful reactions were obtained with isobenzofurans bearing substituent groups in the benzo or benzyl aromatic ring (i.e., Scheme I, **2b–d**). A variety of dienophiles were used to capture the isobenzofurans, and the results of these experiments are summarized in Table I and Scheme I. Reaction temperatures ranged from 35 °C for the more reactive dienophiles such as maleic anhydride to 80–140 °C for the less reactive dienophiles such as acrylonitrile. In one case, *trans*-1,2-

(1) See, for example: (a) E. Bergmann, *J. Chem. Soc.*, 1147 (1938); (b) J. A. Berson, *J. Am. Chem. Soc.*, **75**, 1240 (1953); (c) M. P. Cava and J. P. Van Meter, *J. Org. Chem.*, **34**, 538 (1969); (d) E. D. Bergmann, Sh. Blumberg, P. Bracha, and Sh. Epstein, *Tetrahedron*, **20**, 195 (1964); (e) A. Etienne, A. Spire, and E. Toromanoff, *Bull. Soc. Chim. Fr.*, 750 (1952).

(2) M. Hamaguchi and T. Ibata, *Chem. Letters*, 287 (1976); R. Faragher and T. L. Gilchrist, *J. Chem. Soc., Perkin Trans. 1*, 336 (1976); A. S. Kende, D. P. Curran, Y. Tsay, and J. E. Mills, *Tetrahedron Lett.*, 3537 (1977); L. Contreras, C. E. Slemon, and D. B. MacLean, *ibid.*, 4237 (1978); H. P. Plaumann, J. G. Smith, and R. Rodrigo, *J. Chem. Soc., Chem. Commun.*, in press.

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

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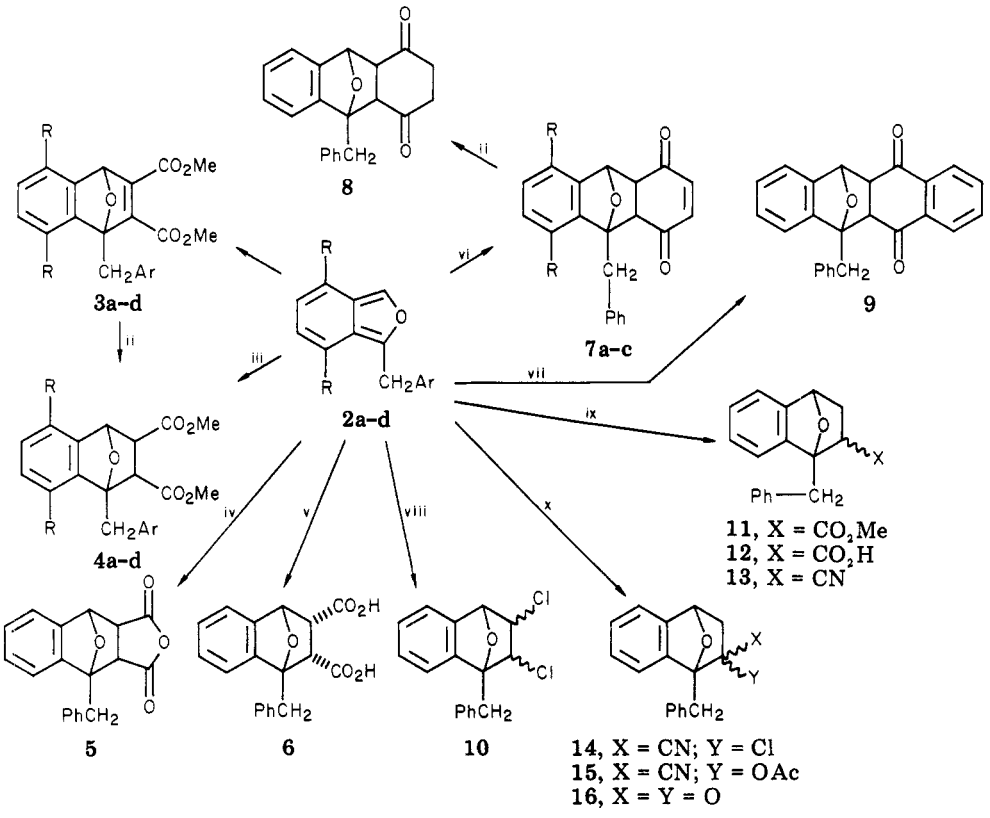
Scheme I. Diels-Alder Reactions with Isobenzofurans[a]



a, R = H; Ar = Ph; b, R = Me; Ar = Ph; c, R = Ar = Ph; d, R = H; Ar = *p*-C_6H_4OMe

[a] i, $MeO_2CC{\equiv}CCO_2Me$; ii, H_2/Pd; iii, dimethyl maleate or fumarate; iv, maleic anhydride; v, maleic acid; vi, *p*-benzoquinone; vii, 1,4-naphthoquinone; viii, *trans*-ClCH=CHCl; ix, $CH_2{=}CHX$; x, $CH_2{=}CXY$

Table I. Diels-Alder Reactions with Isobenzofurans

product	isobenzofuran	dienophile	solvent[a]	% yield	% endo
3a	2a	$MeO_2CC{\equiv}CCO_2Me$	DEE	77	-
trans-4a	2a	*trans*-$MeO_2CCH{=}CHCO_2Me$	C_6H_6	84	-
cis-endo-6	2a	*cis*-$HO_2CCH{=}CHCO_2H$	DEE	92	100
5	2a	maleic anhydride	C_6H_6 or DEE	76	50
cis-4a	2a	*cis*-$MeO_2CCH{=}CHCO_2Me$	toluene	80	75
10	2a	*trans*-ClCH=CHCl	xylene	32	*b*
14	2a	$CH_2{=}C(Cl)CN$	C_6H_6	64	
15	2a	$CH_2{=}C(OAc)CN$	C_6H_6	33	
15	2a	$CH_2{=}C(OAc)CN$	toluene	68	
7a	2a	*p*-benzoquinone	DEE	50	100[c]
9	2a	1,4-naphthoquinone	C_6H_6	78	100[c]
11	2a	$CH_2{=}CHCO_2Me$	toluene	50	65
12	2a	$CH_2{=}CHCOCl$	C_6H_6	80	70
12	2a	$CH_2{=}CHCO_2H$	C_6H_6	54	70
13	2a	$CH_2{=}CHCN$	toluene	76	65
3b	2b	$MeO_2CC{\equiv}CCO_2Me$	DEE	45	
7b	2b	*p*-benzoquinone	DEE	49	100[c]
3c	2c	$MeO_2CC{\equiv}CCO_2Me$	DEE	70	
7c	2c	*p*-benzoquinone	DEE	27	exo[c]
3d	2d	$MeO_2CC{\equiv}CCO_2Me$	C_6H_6	66	

[a] Reactions were run at reflux temperature. [b] Two isomers in the ratio of 77/23 by gas chromatography. [c] *Only* isomer isolated.

dichloroethylene, a sealed-tube reaction at 180 °C was necessary before a reaction occurred.

In most cases, stereochemical assignments in the Diels–Alder adducts were made possible by observing whether or not coupling existed between the bridgehead proton and the proton on the adjacent carbon atom.[4] Generally, the reactions were not highly stereoselective. Mixtures of endo and exo isomers were produced with the endo/exo ratio usually ranging from 1:1 to 2:1. Similar ratios have been reported[5] in reactions of isobenzofuran itself. Two interesting exceptions to this were the ketene equivalents[6] α-chloro- and α-acetoxyacrylonitrile where only one stereo- (and regio-) isomer was detected in each

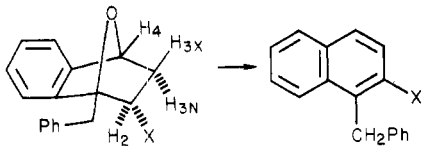
(4) A discussion and prior references are given in L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965).

(5) (a) R. McCulloch, A. R. Rye, and D. Wege, *Tetrahedron Lett.*, 5231 (1969); (b) U. E. Wiersum and W. J. Mijs, *J. Chem. Soc., Chem. Commun.*, 347 (1972); (c) L. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, **43**, 1599 (1965).

(6) A recent review of ketene equivalents has appeared: S. Ranaganathan, D. Ranganathan, and A. K. Mehrotra, *Synthesis*, 289 (1977).

case. This contrasts with a recent report[7] in which stereoisomers were obtained with α-chloroacrylonitrile.

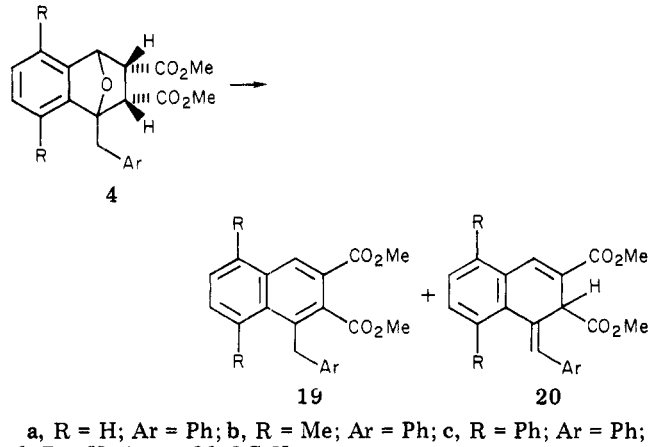
Regioselectivity was high in the case of the unsymmetrical dienophiles examined. In all cases the functionalized carbon of the dienophile bonded to the benzyl-substituted carbon of the diene. Exo and endo isomers were observed and isolated in the cases of **11**, **12**, and **13**. In the case of



11, X = CO_2Me 17, X = CO_2Me
13, X = CN 18, X = CN

exo- and *endo*-**11**, each of the isomers was aromatized to the same compound, methyl 1-benzyl-2-naphthoate (**17**). Treatment of **17** with $Eu(fod)_3$ caused one aromatic proton in the NMR spectrum to shift downfield from the aromatic multiplet and this proton appeared as a doublet, J = 9 Hz. This information placed the carbomethoxy group of **17** at the 2 position *ortho* to the benzyl group. Analysis of the 220-MHz NMR spectra of *exo*- and *endo*-**11** and -**13** along with decoupling experiments established the stereochemistry of these compounds. For example, *endo*-**11** showed a $J_{2,3X}$ of 10 Hz and a $J_{2,3N}$ of 4 Hz while *exo*-**11** showed a $J_{2,3N}$ of 10 Hz ($J_{2,3X}$ could not be obtained). These values agree closely with those obtained from similar isomeric compounds of the norbornenyl system.[8] Similarly, *exo*- and *endo*-**13** were aromatized to the same compound **18** and interconversion of **18** and **17** served to complete the structural elucidation.

Potentially, aromatization of these Diels–Alder adducts by dehydration will lead to substituted naphthalenes and substituted 1,4-anthraquinones. Usually, such dehydrations are effected under strongly acidic conditions.[9a] However, such conditions did not produce characterizable products from the compounds studied here. Catalytic quantities of toluenesulfonic acid in refluxing benzene or toluene were the most generally successful reaction conditions. As has been reported[3] earlier, two dehydration products are formed from **4a**, the expected naphthalene derivative **19a** and a nonnaphthalenic product **20a**. It was



4

19 **20**

a, R = H; Ar = Ph; b, R = Me; Ar = Ph; c, R = Ph; Ar = Ph; d, R = H; Ar = *p*-$MeOC_6H_4$

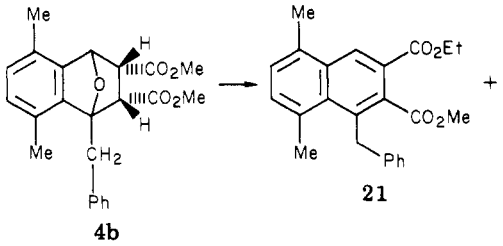
Table II. Dehydration of *endo*-**4a**

conditions	% yield 19	20	ref
H_2SO_4-sulfolane, −55 °C	no product		10
TsOH-benzene, 3 h[a]	84	16	
TsOH-toluene, 3 h[a]	80	20	
MeOH-HCl, 40 h[a]	67	33	3
$FeCl_3$-silica gel, 22 °C, 3 h	50	50	11
P_2S_5-CS_2, 22 °C, 3 days	100	0	1c, 12
Cl_2CHOCH_3-NaI, 22 °C, 1 h	60	40	13
Me_3SiCl-NaI, 22 °C, 0.25 h	60	40	14
Me_3SiCl-NaI, 22 °C, 24 h	90	10	14

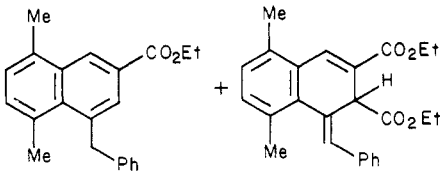
[a] At reflux.

suggested that the increased nonbonded interactions of the three substituent groups which occur on aromatization encourage the alternative dehydration to **20a**. In support of this, when only one substituent was present in addition to the benzyl group (i.e., **11** and **13**) aromatization was uneventful. However, when additional substituents were present (i.e., **3b** and **3c**), *only* products **20b** and **20c** were obtained.

In an attempt to dehydrate **4b** under conditions where the two dehydration products might equilibrate, dehydration was effected in refluxing ethanol containing HCl. While some naphthalene derivative was obtained, extensive ester interchange and some decarboxylation occurred giving **21** and **22**, and the nonnaphthalenic product (**23**) was still produced.



4b **21**



22 **23**

Different methods of aromatization were examined to optimize the formation of the naphthalene product, using **4a** as a model compound. These experiments are summarized in Table II. With one exception (P_2S_5/CS_2), mixtures of **19** and **20** were formed and, generally speaking, the lower the reaction temperature, the greater the amount of **20** formed. One other reagent (Me_3SiCl/NaI) proved of interest since the results showed that it was capable of isomerizing **20** to the naphthalene derivative **19**. This is the only reagent which has been found to effect this isomerization under nonbasic conditions. It also proved useful as an alternative to the acid-catalyzed aromatization in some cases where the latter failed (e.g., **5**) or produced undesired side reactions (e.g., **12** and **28**).

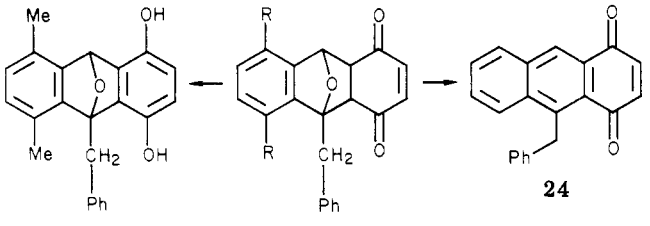
The problem of forming two dehydration products was circumvented when it was realized that under basic conditions the α-H (to the CO_2Me) of **20** would be labile but

(7) S. A. Monti, S. Chen, Y. Yang, S. Yuan, and O. P. Bourgeois, *J. Org. Chem.*, **43**, 4062 (1978).
(8) J. L. Marshall, S. R. Walter, M. Barfield, A. P. Marchand, N. W. Marchand, and A. L. Segre, *Tetrahedron*, **32**, 537 (1976); K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).
(9) (a) See, for example, M. S. Newman and J. A. Cella, *J. Org. Chem.*, **38**, 3482 (1973), and ref 1c and 1d. (b) We are grateful to Dr. P. Confalone of Hoffmann-La Roche Inc. for drawing our attention to this aromatization procedure.
(10) M. S. Newman and V. Lee, *J. Org. Chem.*, **42**, 1478 (1977).
(11) E. Keinan and Y. Mazur, *J. Org. Chem.*, **43**, 1020 (1978).
(12) M. P. Cava and F. M. Scheel, *J. Org. Chem.*, **32**, 1304 (1967).
(13) C. A. Smith and J. B. Grutzner, *J. Org. Chem.*, **41**, 367 (1976).
(14) G. A. Olah, S. C. Narang, B. G. B. Gupta, and R. Malhotra, *J. Org. Chem.*, **44**, 1247 (1979).

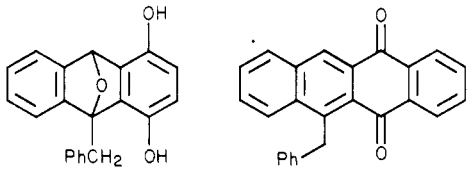
the delocalized anion so formed would be irreversibly protonated at the benzylic carbon to form **19**. Experimentally this was realized by using 1,5-diazabicyclo-[5.4.0]undec-5-ene (DBU) as the base in refluxing benzene. By this combination of dehydration plus isomerization, the substituted naphthalene derivatives **19a–d** were prepared.

Acid-catalyzed aromatization of the carboxylic acid **12** failed. Decarboxylation to 1-benzylnaphthalene was the principal reaction, a result which is not surprising considering the resemblance of **12** to a glycidic acid. While decarboxylation was not eliminated by using Me_3SiCl–NaI, a considerable increase in yield of the aromatized product, 1-benzyl-2-naphthoic acid, was achieved.

Acid-catalyzed aromatization of the quinone Diels–Alder adducts **7** and **9** also failed since complex reaction mixtures results. However, sodium acetate in refluxing methanol[9b] smoothly aromatized **7a** and **9** to **24** and **26**, respectively.



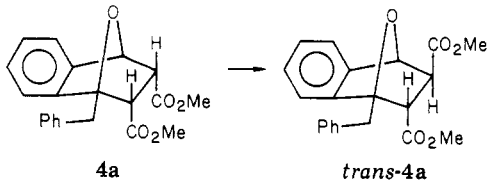
25 7a, R = H; b, R = Me 24



27 26

In contrast, **7b** was isomerized to the hydroquinone **25b**, and **8** was both isomerized and oxidized to **27**. In the case of **7b**, the peri interactions that would exist between the benzyl group and the methyl substituents in the aromatized compound must account for a slower dehydration reaction than with **7a**, and this permits the isomerization to predominate.

The use of sodium acetate to aromatize *endo*-**4a** was also



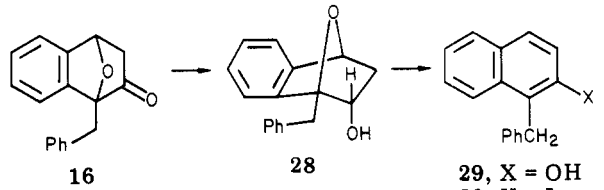
4a *trans*-**4a**

attempted, but in this case only epimerization occurred, producing *trans*-**4a** identical with the major Diels–Alder product from 1-benzylisobenzofuran and dimethyl fumarate. Another isomerization was observed in the case of the maleic anhydride adduct **5** which was converted from the endo to the exo isomer on heating above its melting point. An authentic sample of *exo*-**4a** was prepared by using *exo*-**5**.

In other transformations, hydrogenation of the dimethyl acetylenedicarboxylate adducts **3** to *endo*-**4** has been described[3] in the case of **3a**. Other examples are reported here and, indeed, this was the most convenient way of obtaining **4** since direct preparation using dimethyl maleate gave exo/endo mixtures from which pure products were isolated with difficulty.

The ketene equivalents α-chloro- and α-acetoxyacrylonitrile were intended to provide access to intermediates (i.e., **16**) from which naphthalene derivatives having a simple substitution pattern might be generated. While Diels–Alder adducts **14** and **15** were obtained, hydrolysis of the α-chloroacrylonitrile product (**14**) under a variety of conditions[15] produced nonketonic products. In contrast to reports[6] that the α-acetoxyacrylonitrile adducts require strongly basic conditions for hydrolysis, **15** hydrolyzed readily with sodium sulfide in methanol to **16**. Indeed, judging by the infrared spectrum of the reaction product, more rigorous conditions (KOH–Me_2SO) resulted in hydrolysis of the nitrile group.

Reduction of **16** with lithium aluminum hydride produced the endo alcohol **28**, the stereochemistry being as-



16 **28** **29**, X = OH; **30**, X = I

signed on the basis of the observed coupling constants. Aromatization of this alcohol was accomplished with Me_3SiCl/NaI to give the known 1-benzyl-2-naphthol (**29**) and 1-benzyl-2-iodonaphthalene (**30**). Evidently, conversion of the alcohol **28** to its corresponding iodide is competitive with cleavage of the ether bridge.

In summary, the use of isobenzofurans as transient intermediates offers promise for the synthesis of substituted polycyclic aromatic hydrocarbons. The chief limitation is the aromatization of the initially formed Diels–Alder adducts under acidic conditions. However, the trimethylchlorosilane–sodium iodide reagent has proven a viable alternative and merits further investigation.

Experimental Section

Melting points were measured with a Mel-Temp apparatus in open capillaries and are uncorrected. Infrared spectra were recorded on a Beckman IR-10 spectrometer and NMR spectra were determined on a Varian T-60 spectrometer in deuteriochloroform solutions (unless specified otherwise) with chemical shifts reported in δ units downfield from internal tetramethylsilane. Ultraviolet spectra were recorded on a Beckman Model 35 spectrophotometer. Analyses were performed by MHW Laboratories, Phoenix, AZ. All new compounds gave satisfactory elemental analyses. The 220-MHz spectra were recorded at the Canadian 220-MHz NMR Centre, University of Toronto, Toronto, Ontario.

1-Benzalphthalan (**1**) and its 4,7-dimethyl and 4,7-diphenyl analogues were prepared as previously described.[16] 1-Hydroxy-1-(*p*-methoxybenzyl)phthalan was prepared likewise by the lithium aluminum hydride reduction of 3-(*p*-methoxybenzal)phthalide[17] and dehydrated[16] to 1-(*p*-methoxybenzal)-phthalan: NMR δ 3.77 (s, 3 H, OCH_3), 5.47 (s, 2 H, OCH_2), 5.87 (s, 1 H, vinyl H), 6.7–7.8 (m, 8 H, aromatic H containing AB q at 6.87 and 7.67, J = 8 Hz, P-$CH_3OC_6H_4$).

General Procedure for Diels–Alder Reactions. The hydroxyphthalan or benzalphthalan was dissolved in the selected reaction solvent (100 mL/0.01 mol) and treated with 3 molar equiv of the dienophile. Concentrated HCl (2–3 drops) was added to ensure dehydration of any hydroxyphthalan, and the solution was refluxed under nitrogen for 12–14 h. The solvent was removed and the residue purified by recrystallization or by chromatography. The overall results are summarized in Table I and details of the

(15) P. K. Freeman, D. M. Balls, and D. J. Brown, *J. Org. Chem.*, **33**, 2211 (1968); D. A. Evans, W. L. Scott, and L. K. Truesdale, *Tetrahedron Lett.*, 121 (1972).
(16) J. G. Smith and R. T. Wikman, *Tetrahedron*, **30**, 2603 (1974).
(17) C. D. Gutsche, E. F. Jason, R. S. Coffey, and H. E. Johnson, *J. Am. Chem. Soc.*, **80**, 5756 (1958).

purification and spectral properties of the products follow. In the case of *trans*-1,2-dichloroethylene, 6 molar equiv of the dienophile was used. In the case of *p*-benzoquinone, it was found that reducing the excess of dienophile to 1.5 molar equiv facilitated isolation of the product. Optimization of product yields was not attempted.

With Dimethyl Acetylenedicarboxylate. 1-Benzyl-2,3-bis(carbomethoxy)-1,4-epoxy-1,4-dihydronaphthalene (**3a**) and 1-benzyl-*cis*-*endo*-2,3-bis(carbomethoxy)-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (**4a**) have been reported earlier.[3,18]

1-Benzyl-2,3-bis(carbomethoxy)-1,4-epoxy-5,8-dimethyl-1,4-dihydronaphthalene (3b). The crude product was chromatographed on silica gel with petroleum ether (bp 30–60 °C) graded to petroleum ether containing 10% diethyl ether followed by recrystallization from petroleum ether–diethyl ether: mp 86–86.5 °C; NMR 2.34 and 2.50 (s, 6 H, aromatic CH_3's), 3.72 and 3.81 (s, 6 H, OCH_3), 3.69 and 4.17 (AB q, J = 16 Hz, 2 H, $PhCH_2$), 6.03 (s, 1 H, bridgehead H), 6.82 (s, 2 H, aromatic H), 7.34 (s, 5 H, aromatic H); IR (Nujol) 1755 and 1720 (C=O), 1640, 1310, 1250, 1200, 1100, 980, 970, 800, 790, 710, 690 cm^{-1}.

1-Benzyl-2,3-bis(carbomethoxy)-1,4-epoxy-5,8-diphenyl-1,4-dihydronaphthalene (3c): mp 154–155 °C after recrystallization from ethanol; NMR δ 3.07 and 3.81 (s, 6 H, OCH_3's), 6.08 (s, 1 H, bridgehead H), 6.8–7.7 (m, 17 H, aromatic H); IR (Nujol) 1730 (C=O), 1640, 1310, 1250, 110, 980, 970, 830, 810, 740, 690 cm^{-1}.

2,3-Bis(carbomethoxy)-1,4-epoxy-1-(*p*-methoxybenzyl)-1,4-dihydronaphthalene (3d). The crude product was treated with petroleum ether (bp 30–60 °C) to extract the excess dienophile and the solid recrystallized from ethanol: mp 108–109 °C; NMR δ 3.55 (s, 6 H, ester CH_3's), 3.60 (s, 3 H, ether CH_3), 5.97 (s, 1 H, bridgehead H), 6.7–7.6 (m, 8 H, aromatic H's); IR (Nujol) 1730 and 1710 (C=O), 1520, 1300 (ester C–O), 1240 (ether C–O), 980, 830, 740, 720 cm^{-1}.

With Dimethyl Maleate. These Diels–Alder reactions gave a mixture of *endo*- and *exo*-**4** which was tedious to separate, and excessive reaction times (72 h) were required. Instead, hydrogenation of the dimethyl acetylenedicarboxylate adducts **3** was used to produce *endo*-**4** (vide infra).

With Dimethyl Fumarate. 1-Benzyl-*endo*-2-*exo*-3-bis(carbomethoxy)-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (*trans*-4a). Reaction of **2a** with dimethyl fumarate gave a product consisting of two isomers. Because of overlapping peaks in the NMR spectrum, the ratio of these isomers could not be determined. Recrystallization of the crude product from methanol gave the major isomer which was identical with *trans*-**4a** obtained by isomerization of *endo*-**4a** with sodium acetate.

With Maleic Anhydride. 1-Benzyl-1,4-epoxy-1,2,3,4-tetrahydro-2,3-naphthalic Anhydride (5). Treatment of the crude product (50% endo) with diethyl ether at 10 °C gave a solid: mp 125–160 °C; NMR δ 3.2–4.2 (m, 4 H, $PhCH_2$ and CHC(O)'s), 5.67 (s, bridgehead H, exo isomer), 5.80 (d, J = 4 Hz, bridgehead H, endo isomer) (total 1 H, endo/exo $\approx$ 2/1), 7.1–7.6 (m, 9 H, aromatic H); IR (KBr) 1860 and 1770 (anhydride C=O), 1450, 1270, 1220, 1060, 910, 750 cm^{-1}.

With Maleic Acid. 1-Benzyl-1,4-epoxy-1,2,3,4-tetrahydro-*cis*-*endo*-2,3-naphthalenedicarboxylic acid (6). Crude **6** was recrystallized from acetonitrile: mp 182–183 °C dec; NMR (CD_3CN) δ 3.21 (d, J = 11 Hz, 1 H), 3.63 (s, 2 H, $PhCH_2$), 3.65 (dd, J = 11 Hz, J' = 5 Hz), 5.46 (d, J = 5 Hz, 1 H, bridgehead H), 5.8 (br s, 2 H, CO_2H), 7.2–7.7 (m, 9 H, aromatic H); IR (Nujol) 3100 (br, COOH), 1730 (C=O), 1680 (br, C=O), 1410, 1230, 1220, 760 cm^{-1}.

With *p*-Benzoquinone. 9-Benzyl-9,10-epoxy-*exo*-4a,9,*exo*-9a,10-tetrahydro-1,4-anthraquinone (7a): yellow solid from ethanol: mp 158–158.5 °C; NMR δ 3.15 (d, J = 10 Hz, 1 H) and 3.52 (dd, J_1 = 10 Hz, J_2 = 5 Hz, 1 H, ring juncture H's), 3.60 and 3.88 (AB q, J = 14 Hz, 2 H, $PhCH_2$), 5.35 (d, J = 5 Hz, 1 H, bridgehead H), 5.97 (s, 2 H, vinylic H's), 7.0–7.7 (m, 9 H, aromatic H); IR ($CHCl_3$) 3010, 1670 (C=O), 1290, 1270, 980 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 227 (4.01), 257 (3.23) nm.

9-Benzyl-9,10-epoxy-*exo*-4a,9,*exo*-9a,10-tetrahydro-5,8-dimethyl-1,4-anthraquinone (7b): yellow solid from ethanol: mp 116–117 °C; NMR δ 2.15 and 2.23 (2 s, 6 H, CH_3's), 3.12 (d, J = 9 Hz) and 3.42 (dd, J = 9 Hz, J' = 5 Hz) (total 2 H, ring juncture H's), 3.69 and 4.05 (AB q, J = 14 Hz, 2 H, $PhCH_2$), 5.70 (d, J = 5 Hz, 1 H, bridgehead H), 5.98 (s, 2 H, vinyl H), 6.84 (s, 2 H, aromatic H), 7.2–7.7 (m, 5 H, CH_2Ph); IR (Nujol) 3010, 1670 (C=O), 1500, 1290, 990, 880 cm^{-1}.

9-Benzyl-9,10-epoxy-*endo*-4a,9,*endo*-9a,10-tetrahydro-5,8-diphenyl-1,4-anthraquinone (7c) precipitated during refluxing. The yellow solid was filtered and recrystallized from ethanol: mp 178–179 °C dec; NMR δ 3.0–3.6 (m, 4 H, $PhCH_2$ and ring juncture H's), 5.83 (s, 1 H, bridgehead H), 6.4–7.6 (m, 19 H, vinyl and aromatic H's); IR (Nujol) 1680 (C=O), 1290, 1150, 820, 750, 710, 690 cm^{-1}.

The filtrate from **7c** was evaporated and the residue chromatographed on silica gel with petroleum ether (30–60 °C) graded to diethyl ether. No additional **7c** was isolated, but 40% of the starting material was recovered as 1-benzal-4,7-diphenylphthalan.

With 1,4-Naphthoquinone. 6-Benzyl-6,11-epoxy-6,11-dihydro-5,12-naphthacenedione (9): light yellow solid from ethanol, mp 172.5–173 °C; NMR δ 3.3–3.8 (m, C(O)CHCHC(O)) overlapping 3.68 and 3.98 (AB q, J = 14 Hz, $PhCH_2$) (total 4 H), 5.78 (d, J = 5 Hz, 1 H, bridgehead H), 6.8–8.0 (m, 13 H, aromatic H); IR (Nujol) 1680 (C=O), 1600, 1270 (br), 980, 970, 900, 840 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 227 (4.47), 251 (3.99), 308 (3.08) nm.

With *trans*-1,2-Dichloroethylene. 1-Benzyl-*trans*-2,3-dichloro-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (10). 10 had mp 108–118 °C after recrystallization from ethanol. Gas chromatography (5 ft × $^1/_8$ in. column, 3% SE-52 on Chromosorb W 100–120 mesh, column temperature 160 °C) showed two compounds (A and B) in the ratio of 77:23 (A:B) and with relative retention times 1.0:1.2 (A:B). GC/MS on this material gave identical spectra for these two diastereomers; m/e (relative intensity) 271 (31), 270 (17), 269 (88, M^+ – Cl), 209 (19), 208 (100), 207 (67), 179 (44), 178 (58), 115 (34). NMR was interpreted as two overlapping spectra: major isomer A, δ 3.55 (s, $PhCH_2$), 3.78 (d, J = 3 Hz, endo H), 4.02 (d, J = 3 Hz, exo H), 5.27 (s, bridgehead H), 6.8–7.4 (m, aromatic H); minor isomer B, δ 3.60 and 3.67 (central peaks of AB q, $PhCH_2$), 3.88 (d, J = 3 Hz, endo H), 4.55 (q, J = 4 Hz, J' = 3 Hz, exo H), 5.32 (d, J = 4 Hz, bridgehead H), 6.8–7.4 (m, aromatic H); IR (KBr) 1495, 1450, 1230, 980, 950, 810, 760, 730, 700 cm^{-1}.

With Methyl Acrylate. 1-Benzyl-2-(carbomethoxy)-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (11). The crude product from 5.5 g (0.024 mol) of **1** and 6.25 g (0.073 mol) of methyl acrylate was dissolved in 8 mL of diethyl ether and 1 mL of ethanol added. After the mixture was cooled overnight at −10 °C, 1.4 g (20%) of material separated, mp 113–131 °C. Recrystallization from ethanol gave *exo*-**11**: 1.05 g (15%); mp 138–140 °C; NMR (220 MHz) δ 1.69 (q, 1 H, H_{3N}, $J_{3N,3X}$ = 12 Hz, $J_{2,3N}$ = 10 Hz), 2.4–2.9 (m, 2 H, H_{3x} and H_2), 3.33 and 3.70 (AB q, 2 H, J = 16 Hz, $PhCH_2$), 3.74 (s, 3 H, CO_2CH_3), 5.50 (d, 1 H, J = 4 Hz, H_4), 7.0–7.7 (m, 9 H, aromatic H); IR (Nujol) 1740 (C=O), 1460, 1360, 1190, 1170, 970, 750, 700 cm^{-1}.

The filtrate from the crude *exo*-**11** was concentrated and the residue crystallized by dissolving it in ethanol and cooling to −10 °C. This solid was recrystallized twice from ethanol to give 2.1 g (30%) of *endo*-**11**: mp 88–90 °C; NMR (220 MHz) δ 1.87 (q, 1 H, H_{3N}, $J_{3N,3X}$ = 12 Hz, $J_{2,3N}$ = 4 Hz), 2.26 (2 q, 1 H, H_{3X}, $J_{3X,4}$ = 5 Hz, $J_{3N,3X}$ = 12 Hz, $J_{2,3X}$ = 10 Hz), 3.0 (q, 1 H, H_2, $J_{2,3X}$ = 10 Hz, $J_{2,3N}$ = 4 Hz), 3.56 (s, 3 H, CO_2CH_3), 3.62 and 3.82 (AB q, 2 H, J = 14 Hz, $PhCH_2$), 5.33 (d, 1 H, J = 5 Hz, H_4), 7.0–7.5 (m, 9 H, aromatic H); IR (Nujol) 1740 (C=O), 1340, 1200, 1180, 990, 950, 765, 705 cm^{-1}.

With Acrylic Acid. 1-Benzyl-1,4-epoxy-1,2,3,4-tetrahydro-2-naphthoic acid (12). The crude reaction mixture on treatment with diethyl ether gave an insoluble solid rich in *exo*-**12**. This was recrystallized from chloroform to give *exo*-**12**: mp 203–205 °C dec; NMR (acetone-d_6) δ 1.18 (q, 1 H, H_{3N}, $J_{3N,3X}$ = 12 Hz, $J_{2,3N}$ = 10 Hz), 1.8–2.4 (m, 2 H, H_{3X} and H_2), 2.92 and 3.32 (AB q, 2 H, J = 14 Hz, $PhCH_2$), 4.96 (d, 1 H, J = 5 Hz, bridgehead H), 6.3–7.0 (m, 9 H, aromatic H); IR (Nujol) 3250 (OH), 1720 and 1680 (C=O), 1400, 1160 (br), 990, 970, 950, 760, 750, 710, 690 cm^{-1}.

The ether-soluble portion of the crude reaction product was recrystallized twice from 1:1 ethanol/water to give *endo*-**12**: mp

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146–149 °C; NMR δ 1.77 (q, 1 H, H_{3N}, $J_{3N,3X}$ = 12 Hz, $J_{2,3N}$ = 5 Hz), 2.23 (t of d, 1 H, H_{3X}), 3.01 (q, 1 H, H_2, $J_{2,3X}$ = 10 Hz), 3.54 and 3.85 (AB q, 2 H, J = 14 Hz, PhC**H**$_2$), 5.31 (d, 1 H, bridgehead H_4, $J_{3X,4}$ = 5 Hz), 6.9–7.5 (m, 9 H, aromatic H), 10.12 (s, 1 H, CO_2H); IR (nujol) ~3000 (br, OH), 1710 and 1690 (C=O), 1240, 1220, 990, 950, 750, 700 cm^{-1}.

With Acrylonitrile. 1-Benzyl-2-cyano-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (13). The crude product (2.65 g) from 2.2 g (0.0096 mol) of 1 and 3.5 g (0.065 mol) of acrylonitrile was chromatographed on 100 g of silica gel with benzene containing 5% ethyl acetate as eluting solvent. The first material to elute was *endo*-**13** (0.2 g, 8%) followed by a mixture of *endo*- and *exo*-**13** (0.80 g, 32%) and finally *exo*-**13** (0.9 g, 36%).

The crude *endo*-**13** was recrystallized three times from ethanol: mp 103–109 °C; NMR (220 MHz) δ 1.62 (q, 1 H, H_{3N}, $J_{3N,3X}$ = 11.5 Hz, $J_{2,3N}$ = 4 Hz), 2.43 (2 overlapping q, 1 H, H_{3X}, $J_{3N,3X}$ = 11.5 Hz, $J_{3X,4}$ = 5 Hz, $J_{2,3X}$ = 10 Hz), 2.80 (q, 1 H, H_2, $J_{2,3N}$ = 4 Hz, $J_{2,3X}$ = 10 Hz), 3.60 (s, 2 H, PhC**H**$_2$), 5.40 (d, 1 H, $J_{3X,4}$ = 5 Hz), 7.2–7.7 (m, 9 H, aromatic H); IR ($CHCl_3$) 2240 (C≡N), 1500, 1470, 1460, 1370, 1270, 1260, 990, 950, 820, 700 cm^{-1}.

The crude *exo*-**13** was recrystallized from ethanol to give an analytical sample: mp 101–104 °C; NMR (220 MHz) δ 1.97 (q, 1 H, H_{3N}, $J_{3N,3X}$ = 12 Hz, $J_{2,3N}$ = 8.5 Hz), 2.52 (2 overlapping t, 1 H, $J_{3X,4}$ = 5 Hz, $J_{3N,3X}$ = 12 Hz, $J_{2,3X}$ = 4.5 Hz), 2.67 (q, 1 H, H_2, $J_{2,3N}$ = 8.5 Hz, $J_{2,3X}$ = 4.5 Hz), 3.73 and 3.88 (AB q, 2 H, J = 16 Hz, PhC**H**$_2$), 5.50 (d, 1 H, $J_{3X,4}$ = 5 Hz, H_4), 6.9–7.5 (m, 9 H, aromatic H); IR ($CHCl_3$) 2240 (C≡N), 1500, 1470, 1460, 1000, 980, 960, 700 cm^{-1}.

With α-Chloroacrylonitrile. 1-Benzyl-2-chloro-2-cyano-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (14). The crude reaction product was dissolved in diethyl ether and on cooling to 0 °C **14** crystallized: mp 99–100 °C; NMR δ 1.89 (d, J = 13 Hz, 1 H, endo H), 3.19 (dd, J = 13 Hz, J = 6 Hz, 1 H, exo H), 3.66 and 3.94 (AB q, J = 15 Hz, 2 H, PhC**H**$_2$), 5.42 (d, J = 6 Hz, 1 H, bridgehead H), 7–7.5 (m, 9 H, aromatic H); IR ($CHCl_3$) 3020, 2250 (C≡N), 1500, 1470, 1460, 1360, 990, 950, 860, 840, 700 cm^{-1}.

With α-Acetoxyacrylonitrile. 2-Acetoxy-1-benzyl-2-cyano-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (15). The crude product was recrystallized from ethanol to give **15**: mp 181–182 °C; NMR δ 1.78 (d, J = 14 Hz, 1 H, endo H), 1.83 (s, 3 H, CH_3C=O), 3.17 (dd, J = 14 Hz, J′ = 6 Hz, 1 H, exo H), 3.70 and 3.98 (AB q, J = 14 Hz, 2 H, PhC**H**$_2$), 5.42 (d, J = 6 Hz, 1 H, bridgehead H), 7.0–7.6 (m, 9 H, aromatic H); IR ($CHCl_3$) 2240 (w, C≡N), 1760 (C=O), 1370, 1190, 1050, 700 cm^{-1}.

Hydrogenation of Dimethyl Acetylenedicarboxylate Adducts. Hydrogenation of **3b–d** was effected at 20 °C and 50 psi hydrogen with 5% Pd on charcoal as catalyst (100 mg/g of compound) and ethyl acetate as solvent.

1-Benzyl-2,3-*cis*-*endo*-bis(carbomethoxy)-1,4-epoxy-1,2,3,4-tetrahydro-5,8-dimethylnaphthalene (*endo*-4b): 86% yield after recrystallization from hexane–diethyl ether; mp 120–121 °C; NMR δ 2.33 and 2.43 (2 s, 6 H, aromatic CH_3), 3.2–3.8 (m, C**H**CO_2CH_3) overlapping 3.47 and 3.57 (2 s, CO_2CH_3, total 8 H), 5.27 and 5.60 (AB q, J = 16 Hz, 2 H, PhC**H**$_2$), 5.47 (d, 1 H, J = 4 Hz, bridgehead H), 6.93 (s, 2 H), and 7.33 (s, 5 H) (aromatic H); IR ($CHCl_3$) 2960, 1750 (C=O), 1500, 1440, 1270, 1170 (br) cm^{-1}.

1-Benzyl-2,3-*cis*-*endo*-bis(carbomethoxy)-1,4-epoxy-1,2,3,4-tetrahydro-5,8-diphenylnaphthalene (*endo*-4c): 88% yield after recrystallization from ethanol; mp 224–225 °C; NMR δ 3.20 and 3.60 (2 s, CO_2CH_3), 3.0–3.9 (m, PhC**H**$_2$ and C**H**CO_2CH_3) overlapping 3.20 and 3.60 (2 s, CO_2CH_3)(10 H), 5.80 (d, J = 4 Hz, 1 H, bridgehead H), 7.1–7.8 (m, 17 H, aromatic H); IR ($CHCl_3$) 2960, 1750 (C=O), 1480, 1440, 1180 cm^{-1}.

***endo*-4d:** 87% yield after recrystallization from ethanol; mp 109–110 °C; NMR δ 3.1–3.8 (m, Ar**CH**$_2$ and 2 CH), 3.43 and 3.47 (s, CO_2CH_3), 3.77 (s, OCH_3) (total 13 H), 5.38 (d, 1 H, J = 5 Hz, bridgehead H), 6.83 and 7.23 (AB q, J = 8 Hz) and 7.0–7.4 (m) (total 8 H, aromatic H); IR (Nujol) 1750 (C=O), 1510, 1330, 1250, 1200, 1030, 810, 750 cm^{-1}.

The same hydrogenation conditions were used to convert the quinone Diels–Alder adduct **7a** to its dihydro derivative **9-benzyl-9,10-epoxy-2,3,*exo*-4a,9,*exo*-9a,10-hexahydro-1,4-naphthoquinone (8)** in 91% yield after recrystallization from ethanol: mp 159.5–160 °C; NMR δ 1.0–1.6 (m, 2 H) and 2.0–2.5 (m, 2 H) (C(O)CH_2CH_2C(O)), 2.9–3.6 (m, 2 H, C(O)CHCHC(O)), 3.58 and 3.91 (AB q, J = 14 Hz, 2 H, PhC**H**$_2$), 5.65 (d, J = 6 Hz, 1 H, bridgehead H), 7.1–7.6 (m, 9 H, aromatic H); IR (KBr) 1705 and 1690 (C=O), 1430, 1300, 1265, 1050, 970, 810, 750, 695 cm^{-1}.

Aromatization of Quinone Adducts. The Diels–Alder adducts **7a** and **9** were aromatized by refluxing 1 g of compound with 100 mg of anhydrous sodium acetate in 30 mL of methanol under nitrogen for 16 h.

9-Benzyl-1,4-anthraquinone (24): 90% yield after recrystallization from ether; mp 180–183 °C; NMR δ 5.17 (s, 2 H, PhC**H**$_2$), 7.0 (s, 2 H, H_2 and H_3), 7.1–8.1 (m, 9 H, aromatic H), 8.71 (s, 1 H, H_{10}); IR (KBr) 1670 and 1655 (C=O), 1610, 1500, 1420, 1280, 850, 750, 720 cm^{-1}; UV (MeOH) λ_{max} (log ε) 234 (5.02), 267 (4.16), 283 (4.12), 295 (4.11), 371 (3.52), 406 (3.66) nm.

6-Benzyl-5,12-naphthacenedione (26): 76% yield after recrystallization from ethanol as a yellow solid; mp 210–212 °C; NMR δ 5.20 (s, 2 H, PhC**H**$_2$), 7.32 (s, 5 H, **Ph**CH$_2$) 7.3–8.5 (m, 8 H, aromatic H), 8.88 (s, 1 H, H); IR ($CHCl_3$) 1670 (C=O), 1600, 1580, 1420, 1340, 1270, 990, 915, 690 cm^{-1}; UV (MeOH) λ_{max} (log ε) 237 (4.93), 242 (4.92), 273 (sh, 4.71), 282 (4.74), 293 (4.78), 391 (3.77) nm.

Isomerization of Quinone Adducts. The same procedure as described for **7a** and **9** was employed with **7b** to give 9-benzyl-9,10-epoxy-9,10-dihydro-1,4-dihydroxy-5,8-dimethylanthracene (**25**). **25** was purified by dissolving in methanol, filtering from some insoluble tar, diluting with 10 volumes of water, and cooling to 0 °C to give a tan solid: mp dec >160 °C; NMR (CD_3CN) δ 1.90 and 2.00 (s, 6 H, CH_3's), 3.54 and 4.02 (AB q, J = 14 Hz, 2 H, PhC**H**$_2$), 5.80 (s, 1 H, bridgehead H), 5.95 (s, 2 H, aromatic H), 6.30 (s, 2 H, aromatic H), 6.8–7.3 (m, 5 H, CH_2C_6**H**$_5$), 6.1 (br s, 2 H, OH); IR (Nujol) 3300 and 3200 (br, OH), 1500, 1280, 1200, 870, 810, 800, 750, 700 cm^{-1}.

In the case of **8**, ethanol was used in place of methanol (in which no reaction occurred). The product, 9-benzyl-9,10-epoxy-9,10-dihydro-1,4-dihydroxyanthracene (**27**), was obtained in 82% yield after recrystallization from water–30% ethanol: mp 185–187 °C dec; NMR (CD_3CN) δ 3.92 and 4.19 (AB q, 2 H, J = 15 Hz, PhC**H**$_2$), 6.16 (s, 1 H, bridgehead H), 6.40 (s, 2 H, "hydroquinone" aromatic H), 6.80 (br s, 2 H, OH, exchanges with D_2O), 6.9–7.7 (m, 9 H, aromatic H); IR (KBr) 3300 (br, OH), 1490, 1430, 1275, 1225, 750, 700, 690 cm^{-1}; UV (MeOH) λ_{max} (log ε) 301 (3.65) nm.

Isomerization of 4a to give *trans*-4a. *endo*-**4a** (1 g, 2.8 mmol) was dissolved in 100 mL of methanol containing 1 g (0.012 mol) of sodium acetate for 20 h. The solution was diluted with 200 mL of water and extracted with chloroform, and the extracts were dried ($MgSO_4$) and evaporated to dryness. The residue, 0.94 g, mp 134–136 °C, was recrystallized from methanol to give 0.88 g (88%) of *trans*-**4a**; mp 135–136 °C; NMR δ 3.13 (d, J = 4 Hz, 1 H, C**H**CO_2CH_3), 3.53 (s plus m, 4 H, CO_2CH_3 and C**H**CO_2CH_3), 3.70 (s, 3 H, CO_2CH_3), 3.77 (s, 2 H, PhC**H**$_2$), 5.63 (s, 1 H, bridgehead H), 7–7.6 (m, 9 H, aromatic H); IR (Nujol) 1750 and 1740 (C=O), 1310, 1220, 1010, 990, 770, 710 cm^{-1}.

***exo*-5 and *exo*-4a.** The Diels–Alder adduct of 1-benzylisobenzofuran and maleic anhydride (1:1 exo/endo mixture) was heated under nitrogen at 200 °C for 5 min. The resulting gum crystallized on treatment with chloroform to give *exo*-**5** (80% yield): NMR δ 3.19 and 3.35 (AB q, 2 H, C(O)CHCHC(O)), 3.59 and 3.91 (AB q, 2 H, J = 17 Hz, PhC**H**$_2$), 5.80 (s, 1 H, bridgehead H), 7.0–7.5 (m, 9 H, aromatic H). The anhydride was characterized by converting it to the dimethyl ester. After the anhydride was dissolved in methanol (20 °C, 24 h), the solution was treated with excess diazomethane. Evaporation of the solvent and chromatography on silica gel with benzene as the eluting solvent gave *exo*-**4a**: mp 88–91 °C; NMR δ 2.85 and 3.15 (AB q, 2 H, J = 10 Hz, C(O)CHCHC(O)), 3.52 (s, 2 H, PhC**H**$_2$), 3.73 (s, 6 H, CO_2CH_3), 5.9 (s, 1 H, bridgehead H), 6.9–7.5 (m, 9 H, aromatic H); IR (Nujol) 1740 (C=O), 1330, 1230, 1200, 960, 750, 700 cm^{-1}.

Dehydration of Diels–Alder Adducts. Acid-catalyzed dehydration was effected by refluxing a solution of 1 g of compound and 0.1 g of *p*-toluenesulfonic acid monohydrate in 25 mL of toluene under nitrogen for 2–4 h. The reaction product was isolated by washing the solution with water, drying, evaporating the solvent, and recrystallizing the residue.

Dehydration of *endo*-**4a** to a mixture of dimethyl 1-benzyl-2,3-naphthalenedioate (**19a**) and dimethyl 1-benzal-1,2-dihydro-2,3-naphthalenedioate (**20a**) has been described[3] and the results are included in Table II.

Dehydration of *endo*-**4b** produced dimethyl 1-benzal-1,2-dihydro-5,8-dimethyl-2,3-naphthalenedioate (**20b**) in 79% yield after recrystallization from ethanol: mp 147–148 °C; NMR δ 2.43 and 2.50 (2 s, 6 H, aromatic CH_3), 3.63 and 3.77 (2 s, 6 H, ester CH_3), 5.10 (s, 1 H, $CHCO_2CH_3$), 6.77 (s, 1 H, PhC**H**=C), 7.0–7.8 (m, 7 H, aromatic H), 7.9 (s, 1 H, C**H**=CCO_2Me); IR ($CHCl_3$) 1730 and 1710 (C=O), 1440, 1260, 1230, 905 cm^{-1}.

Dehydration of *endo*-**4c** gave a 90% yield of dimethyl 1-benzal-1,2-dihydro-5,8-diphenyl-2,3-naphthalenedioate (**20c**) after recrystallization from ethanol: mp 158.5–159 °C; NMR δ 3.70 and 3.80 (2 s, 6 H, CO_2CH_3), 5.03 (s, 1 H, $CHCO_2Me$), 6.4 (s, 1 H, PhC**H**=C), 7.0–7.8 (m, 20 H, aromatic H); IR ($CHCl_3$) 1730 and 1710 (C=O), 1470, 1440, 1240 (br), 700 cm^{-1}.

Dehydration of *endo*-**11** gave a 65% yield of methyl 1-benzyl-2-naphthoate (**17**) after recrystallization from ethanol: mp 75–77 °C; NMR δ 3.90 (s, 3 H, CO_2CH_3), 4.88 (s, 2 H, $PhCH_2$), 7.18 (s, 5 H, CH_2**Ph**), 7.3–8.3 (m, 6 H, aromatic H); IR (Nujol) 1725 (C=O), 1280, 1240, 1000, 770, 740 cm^{-1}.

Similarly *exo*-**11** produced the same product, mp 74–76 °C, mixture mp 75–77 °C.

Addition of $Eu(fod)_3$ to the NMR sample of **17** caused a single aromatic proton to be shifted downfield from the aromatic multiplet. This proton appeared as a doublet, J = 9 Hz.

The crude reaction mixture from the Diels–Alder reaction which contained *endo*- and *exo*-**13** was dehydrated as described above. The resulting reaction mixture was chromatographed on silica gel to give a 60% yield of 1-benzyl-2-naphthonitrile (**18**), mp 75–80 °C. Two recrystallizations from ethanol gave the analytical sample: mp 81–82 °C; NMR δ 4.73 (s, 2 H, $PhCH_2$), 7.23 (s, 5 H, CH_2**Ph**), 7.4–8.3 (m, 6 H, aromatic H); IR (Nujol) 2210 (C≡N), 1470, 810, 750, 740, 710, 690 cm^{-1}.

The naphthonitrile **18** was converted to the ester **17** by heating it in methanol saturated with hydrogen chloride (10 h, 80–90 °C, sealed tube). The product had spectroscopic properties identical with those of **17** and showed no depression of melting point after mixing with **17**.

A solution of 1.0 g of **12** (3.6 mmol, 80% endo) in 25 mL of toluene containing 0.15 g of toluenesulfonic acid monohydrate was refluxed under nitrogen for 1 h. The yellow solution was extracted with dilute aqueous potassium carbonate solution, and then the toluene was removed under vacuum. The residue was chromatographed on silica gel by eluting with 1:1 benzene/petroleum ether to give 0.58 g (74%) of 1-benzylnaphthalene: mp 56–59 °C (lit.[19] 58–59 °C); NMR δ 4.33 (s, 2 H, $PhCH_2$), 7.0–8.0 (m, 12 H, aromatic H); IR (film) 1600, 1510, 1490, 1450, 1400, 780, 760, 700, 680 cm^{-1}.

The potassium carbonate extract on acidification deposited 0.16 g (17%) of 1-benzyl-2-naphthoic acid: mp 193–197 °C after recrystallization from toluene; NMR (acetone-d_6) δ 4.37 (s, 2 H, $PhCH_2$), 6.57 (s, 5 H, **Ph**CH_2), 6.7–7.6 (m, 7 H, aromatic H and CO_2H); IR (Nujol) ~3000 (br, OH), 1680 (C=O), 1470, 1280, 1250, 770, 750, 730, 710 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.68; H, 5.41.

Aromatization Using Trimethylsilyl Chloride and Sodium Iodide. The literature procedure[14] was used in all cases. **12** (endo/exo mixture, 1.0 g, 3.6 mmol) after treatment for 4 h at 22 °C with 1.07 g of sodium iodide and 0.78 g of trimethylsilyl chloride in 10 mL of acetonitrile gave 0.93 g of crude reaction mixture. This was separated by base extraction into 0.65 g of 1-benzyl-2-naphthoic acid (66%), mp 175–190 °C, and 0.30 g of 1-benzylnaphthalene, both identified by comparison of their spectral properties with those of authentic samples.

5 (endo/exo mixture, 0.3 g, 1 mmol) was refluxed with 0.3 of sodium iodide and 0.25 mL of trimethylsilyl chloride in 5 mL of acetonitrile for 24 h (no reaction occurred at 22 °C). Addition of ether caused 0.21 g (74%) of 1-benzyl-2,3-naphthalenedicarboxylic anhydride to precipitate.

An analytical sample was obtained by recrystallization from toluene: mp 192–194 °C; NMR δ 5.07 (s, 2 H, $PhCH_2$), 7.27 (s, 5 H, **Ph**CH_2), 7.6–8.4 (m, 4 H, aromatic H), 8.50 (s, 1 H, H_4); IR (Nujol) 1850 and 1780 (C=O), 1250, 1210, 1170, 1140, 920, 910, 770, 740, 700 cm^{-1}. Anal. Calcd for $C_{19}H_{12}O_3$: C, 79.16; H, 4.20. Found: C, 78.95; H, 4.34.

***endo*-28** (0.57 g, 2.3 mmol) was treated for 1 h at 22 °C with a solution of 0.68 g of sodium iodide and 0.49 g of trimethylsilyl chloride in 10 mL of acetonitrile. The crude reaction product, 0.50 g, was chromatographed on silica gel with benzene as eluant to give 0.18 g (25%) of 1-benzyl-2-iodonaphthalene (**30**): mp 58–61 °C; NMR δ 4.27 (s, 2 H, $PhCH_2$), 7.0–8.0 (m, 11 H, aromatic H); IR (Nujol) 1500, 1250, 780, 760, 720, 690 cm^{-1}. After this, 0.23 g (40%) of 1-benzyl-2-naphthol (**29**) eluted: mp 108–109 °C (after recrystallization from benzene) (lit.[20] mp 111–112 °C); NMR ($CDCl_3$) δ 4.42 (s, 2 H, $PhCH_2$), 4.90 (s, 1 H, OH), 6.9–8.0 (m, 11 H, aromatic H); IR (Nujol) 3420 (OH), 1500, 1490, 1430, 1270, 1230, 980, 810, 800, 750, 710 cm^{-1}.

Forced Dehydration of 4b. The Diels–Alder adduct *endo*-**4b** (2.0 g, 5.3 mmol) was refluxed for 16 h under nitrogen in a solution of 300 mL of ethanol and 10 mL of concentrated HCl. The reaction product was treated with ether and water and the ether layer was separated, washed with water, dried ($MgSO_4$), and evaporated. The residue (1.80 g) was chromatographed on 100 g of silica gel by eluting with benzene graded to benzene plus 5% diethyl ether. In order of elution, there were obtained the following:

Ethyl 4-benzyl-5,8-dimethyl-2-naphthoate (22): 510 mg (30%); mp 94.5–95 °C (after recrystallization from ethanol); NMR δ 1.45 (t, J = 7 Hz, 3 H, CH_3CH_2O), 2.77 (br s, 6 H, aromatic CH_3), 4.47 (q, J = 7 Hz, 2 H, CH_3CH_2O), 4.77 (s, 2 H, $PhCH_2$), 6.8-7.4 (m, 7 H, aromatic H), 7.95 (d, J = 2 Hz, 1 H, H_6), 8.78 (d, J = 2 Hz, 1 H, H_8); IR ($CHCl_3$) 1710 (C=O), 1280, 1250, 1160, 1140, 1030 cm^{-1}.

Diethyl 1-benzal-1,2-dihydro-5,8-dimethyl-2,3-naphthalenedioate (23): 491 mg (24%); mp 96.5–97 °C (after recrystallization from ethanol); NMR δ 1.13 and 1.27 (overlapping t, J = 7 Hz, 6 H, OCH_2CH_3), 2.43 and 2.50 (2 s, 6 H, aromatic CH_3), 4.11 and 4.23 (overlapping q, J = 7 Hz, 4 H, OCH_2CH_3), 5.08 (s, 1 H, $CHCO_2Et$), 6.73 (s, 1 H, PhC**H**=C), 6.9–7.8 (m, 7 H, aromatic H), 7.87 (s, 1 H C**H**=CCO_2Et); IR ($CHCl_3$) 1725 and 1700 (C=O), 1480, 1455, 1370, 1230 (br), 1020, 900 cm^{-1}.

1-Benzyl-2(or 3)-(carbethoxy)-3(or 2)-(carbomethoxy)-5,8-dimethylnaphthalene (21): 496 mg (25%); mp 116–117 °C (after recrystallization from ethanol); NMR δ 1.43 (t, J = 7 Hz, 3 H, OCH_2CH_3), 2.73 (br s, 6 H, aromatic CH_3), 3.73 (s, 3 H, OCH_3), 4.45 (q, J = 7 Hz, 2 H, OCH_2CH_3), 4.75 (s, 2 H, $PhCH_2$), 6.7–7.4 (m, 7 H, aromatic H), 8.85 (s, 1 H, H_4); IR ($CHCl_3$) 1720 (C=O), 1450, 1440, 1285, 1160, 1120, 1020, 900 cm^{-1}.

Isomerization of Dehydrated Diels–Alder Adducts. Those dehydrated Diels–Alder adducts which contained substantial amounts of the nonnaphthalenic product were isomerized to the naphthalene derivative by refluxing them in benzene under nitrogen in the presence of 20–25% w/w 1,5-diazabicyclo[5.4.0]-undec-5-ene (DBU) for 1 h. After the benzene solution was washed with water, the benzene was evaporated and the product recrystallized.

The dehydration product (TsOH catalyzed) of *endo*-**4a** consisting of 67% **19a** and 33% **20a** was converted entirely to **19a** (NMR of crude product). Recrystallization from methanol gave an 80% yield of **19a** (based on **4a**), mp 100–102 °C (lit.[3] mp 101.5–102.5 °C).

The dehydration product of *endo*-**4b** (i.e., **20b**) was isomerized to dimethyl 1-benzyl-5,8-dimethyl-2,3-naphthalenedioate (**19b**) by DBU. After recrystallization from methanol, **19b** was obtained in 78% yield (based on **4b**): mp 141–142 °C; NMR δ 2.75 (br s, 6 H, aromatic CH_3's), 4.1 and 4.33 (s, 6 H, CO_2CH_3), 4.77 (s, 2 H, $PhCH_2$), 6.8–7.4 (m, 7 H, aromatic H), 8.8 (s, 1 H, aromatic H_4); IR (Nujol) 1720 (C=O), 1430, 1270, 1240, 1220, 770, 710 cm^{-1}.

The dehydration product of *endo*-**4c** (i.e., **20c**) was isomerized to dimethyl 1-benzyl-5,8-diphenyl-2,3-naphthalenedioate (**19c**) by DBU. Recrystallization from methanol gave a 73% yield of **19c**: mp 169–171 °C; NMR δ 3.67 and 3.83 (s, 6 H, CO_2CH_3's), 4.1 (s, 2 H, $PhCH_2$), 6.2–7.6 (m, 17 H, aromatic H), 8.37 (s, 1 H, aromatic H_4); IR (Nujol) 1730 and 1720 (C=O), 1430, 1260, 1130, 720, 690, 680 cm^{-1}.

endo-**4d** dehydrated by using MeOH/HCl[3] formed a product consisting of 60% dimethyl 1-(*p*-methoxybenzyl)-2,3-naphthalenedioate (**19d**) and 40% dimethyl 1,2-dihydro-1-(*p*-

(19) Lange's Handbook of Chemistry, 12th ed., J. A. Dean, Ed., entry no. 817, Table 7-4.

(20) J. W. Cornforth, R. H. Cornforth, and R. Robinson, *J. Chem. Soc.*, 682 (1942).

methoxybenzal)-2,3-naphthalenedioate (**20d**). This mixture was converted to **19d** after a DBU isomerization. Recrystallization from methanol gave an 82% yield (based on **4d**) of **19d**: mp 85–86 °C; NMR δ 3.73 (s, 3 H, $C_6H_4OCH_3$), 3.93 and 3.98 (s, 6 H, CO_2CH_3), 4.4 (s, 2 H, $ArCH_2$), 6.78 and 7.13 (AB q, 4 H, $C_6H_4OCH_3$), 7.4–8.2 (m, 4 H, aromatic H), 8.62 (s, 1 H, aromatic H_4); IR (Nujol) 1735 and 1720 (C=O), 1300, 1270, 1240, 1130, 1030, 1020, 980, 790, 770, 750 cm^{-1}.

1-Benzyl-1,4-epoxy-3,4-dihydro-2(1*H*)-naphthalenone (16). The acetoxynitrile **15** (500 mg, 1.56 mmol) was dissolved in 25 mL of ethanol containing 500 mg of hydrated sodium sulfide and the solution was refluxed for 12 h. The ethanol was removed, the residue dissolved in ether and water, and the ether layer washed with water and dried ($MgSO_4$). Removal of the solvent gave 240 mg of residue. Recrystallization from ethanol gave 205 mg (52%) of **16**: mp 129–130 °C; NMR δ 2.02 (d, J = 16 Hz, 1 H, endo H), 2.61 (dd, J = 5 Hz, J' = 16 Hz, 1 H, exo H), 3.52 (s, 2 H, $PhCH_2$), 5.64 (d, J = 5 Hz, 1 H, bridgehead H), 7.0–7.6 (m, 9 H, aromatic H); IR ($CHCl_3$) 1760 (C=O), 1500, 1470, 1460, 1050, 690 cm^{-1}.

Reduction of 16 to give 1-Benzyl-1,4-epoxy-1,2,3,4-tetrahydro-*endo*-3-hydroxynaphthalene (28). The ketone **16** (2.0 g, 8 mmol) was reduced by refluxing for 12 h in 250 mL of ether containing 0.50 g (13 mmol) of lithium aluminum hydride. After hydrolysis of the mixture with water, the ether layer was separated and dried ($MgSO_4$) and the solvent removed. The residue was recrystallized from petroleum ether to give 1.9 g (94%) of **28**: mp 86.5–88 °C; NMR δ 0.72 (d, J = 10 Hz, 1 H, OH), 1.03 (dd, 1 H, H_{3N}, $J_{2,3N}$ = 2.5 Hz, $J_{3N,3X}$ = 12 Hz), 2.27–2.75 (m, 1 H, H_{3X}), 3.5 (s, 2 H, $PhCH_2$), 4.5 (t d, 1 H, H_2, $J_{2,3N}$ = 2.5 Hz, $J_{2,3X}$ = 10 Hz, $J_{2,OH}$ = 10 Hz), 5.2 (d, 1 H, H_4, $J_{3X,4}$ = 5.5 Hz), 6.9–7.4 (m, 9 H, aromatic H); IR (Nujol) 3580 (OH), 1055, 730, 670 cm^{-1}.

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Registry No. **1**, 29539-19-3; **1**, 4,7-dimethyl derivative, 54537-61-0; **1**, 4,7-diphenyl derivative, 54537-64-3; **1**, *p*-methoxy derivative, 64421-15-4; **2a**, 61200-14-4; **2b**, 73194-82-8; **2c**, 73194-83-9; **2d**, 73194-84-0; **3a**, 52540-39-3; **3b**, 73194-85-1; **3c**, 73198-05-7; **3d**, 73194-86-2; *endo*-**4a**, 52540-40-6; *exo*-**4a**, 73245-10-0; *trans*-**4a**, 73245-11-1; **4b**, 73194-87-3; **4c**, 73194-88-4; **4d**, 73194-89-5; *exo*-**5**, 73194-90-8; *endo*-**5**, 73245-12-2; **6**, 73194-91-9; **7a**, 73194-92-0; **7b**, 73194-93-1; **7c**, 73194-94-2; **8**, 73194-95-3; **9**, 73194-96-4; **10**, isomer 1, 73194-97-5; **10**, isomer 2, 73245-13-3; *exo*-**11**, 73194-98-6; *endo*-**11**, 73245-14-4; *exo*-**12**, 73194-99-7; *endo*-**12**, 73245-15-5; *exo*-**13**, 73245-16-6; *endo*-**13**, 73194-59-9; **14**, 73194-60-2; **15**, 73194-61-3; **16**, 73194-62-4; **17**, 73194-63-5; **18**, 73194-64-6; **19a**, 52540-41-7; **19b**, 73194-65-7; **19c**, 73194-66-8; **19d**, 73194-67-9; **20a**, 52540-42-8; **20b**, 73194-68-0; **20c**, 73194-69-1; **20d**, 73194-70-4; **21**, 73200-44-9; **22**, 73194-71-5; **23**, 73194-72-6; **24**, 73194-73-7; **25**, 73194-74-8; **26**, 73194-75-9; **27**, 73194-76-0; **28**, 73194-77-1; **29**, 36441-31-3; **30**, 73194-78-2; 1-hydroxy-1-(*p*-methoxybenzyl)phthalan, 73194-79-3; 3-(*p*-methoxybenzal)phthalide, 4767-61-7; dimethyl acetylenedicarboxylate, 762-42-5; dimethyl maleate, 624-48-6; dimethyl fumarate, 624-49-7; maleic anhydride, 108-31-6; maleic acid, 110-16-7; *p*-benzoquinone, 106-51-4; 1,4-naphthoquinone, 130-15-4; *trans*-1,2-dichloroethylene, 156-60-5; methyl acrylate, 96-33-3; acrylic acid, 79-10-7; acrylonitrile, 107-13-1; α-chloroacrylonitrile, 920-37-6; α-acetoxyacrylonitrile, 3061-65-2; 1-benzylnaphthalene, 611-45-0; 1-benzyl-2-naphthoic acid, 73194-80-6; 1-benzyl-2,3-naphthalenedicarboxylic anhydride, 73194-81-7; acryloyl chloride, 814-68-6.

Synthetic Utility of 3,5,5-Trialkoxy-1,2,4-trichlorocyclopentadiene Diels–Alder Adducts in the Preparation of Highly Substituted Aromatic Quinones

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The Diels–Alder reaction of 3,5,5-trialkoxy-1,2,4-trichlorocyclopentadienes with various dienophiles leads to chloro enol ether adducts that can be used synthetically in several ways. When aromatic products are possible, a trifluoroacetic acid (TFA) initiated rearrangement reaction occurs in which quinones having chloro, alkoxy, and carboalkoxy substituents result. If aromatic products are precluded, normal hydrolysis of the chloro enol ether occurs. In TFA these reactions are exclusively initiated by endo protonation of the chloro enol ether moiety.

The exploitative use of 3,5,5-trimethoxy-1,2,4-trichlorocyclopentadiene (**1**) as a starting material for organic synthesis has been minimal.[1] This is despite the fact that it is a reactive diene in Diels–Alder reactions whose adducts can potentially lead by subsequent selective unmasking to two different carbonyl functions of widely different reactivity. In addition, there are reactive alkyl chloride functions which can be utilized as precursors to other important functional groups of interest. Our recent synthesis of a versatile anthracyclinone precursor analogue is an apt example of the aforementioned methodology.[2] In this paper we hope to show that this same methodology can lead to further types of structural units of potential interest.

The preparation of **1** was first performed by McBee and co-workers,[3] who studied the reaction of methoxide ion with hexachlorocyclopentadiene to produce **2**. This was then converted by excess methoxide ion into **1**. These workers proposed the wrong structure for **1**, but this was rectified by the studies of Chang,[4] MacKenzie,[5] and Johnson[6] in later years. These latter investigations have led to precise experimental procedures that allow for the optimum preparation of diene **1** in substantial amounts, thus providing for its ready accessibility in predictable yields and form.

The Diels–Alder reaction of diene **1** with various dienophiles has been shown to yield the expected endo product under mild conditions.[1-7] Selective acid hydrolysis of the

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