of 1, the rate constant for the formation of 4 exceeds that for 3, in contrast to the neutral form (Figure 4).

Experimental Section

A. Quantitative Analysis. A multicomponent spectrophotometric assay procedure was employed for the determinations of the concentrations of 1, 3, and 4.[10] The hydrolyzed solutions of 1 were buffered to pH 2 (where 1 is completely stable to further hydrolysis). Extraction with chloroform was carried out to remove 3 and 4. The chloroform extract was evaporated to dryness under reduced pressure and the residue redissolved in pH 4.5 acetate buffer. The concentrations of 3 and 4 were then determined by a two-component assay from the absorption at 356 and 445 nm. The concentration of 1 was determined, using the aqueous layer, from its absorption at 385 nm.

B. Thin-Layer Chromatography. TLC was carried out on 250-μm cellulose plates (Whatman CC41) and the following solvent systems were used: (a) 50:30:2:18 1-butanol-1-propanol-acetic acid-water; (b) 40:10:50 (organic phase) 1-butanol-acetic acid-water. TLC was also carried out on silica gel G (Merck) with 70:20:10 1-butanol-ethanol-water as the solvent system. Flavins were detected by their characteristic fluorescence emission under UV (370 nm) excitation.

Registry No. 1, 4250-90-2; 3, 1086-80-2; 4, 1088-56-8.

Isolation and Structure of the Oxidized Diels-Alder Adducts of Certain Styrenes and 1,4-Naphthoquinone

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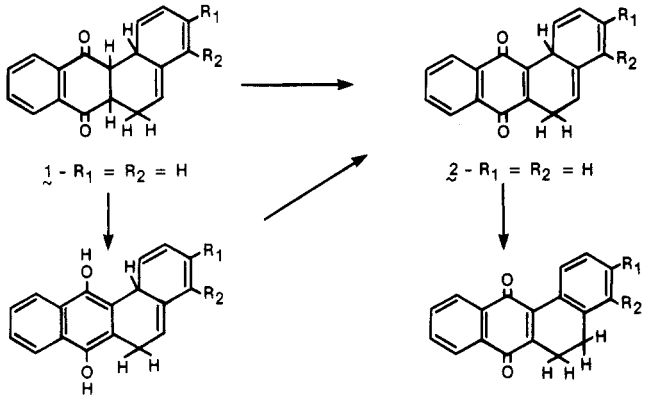
The production of substituted benz[*a*]anthracene-7,12-diones via the Diels-Alder reaction between styrenes and 1,4-naphthoquinones has been demonstrated.[1] The two oxidation steps needed to furnish the benz[*a*]-anthracene-7,12-diones from the Diels-Alder adducts would be "expected" to occur from the intermediates shown below as 1, **1a**, and 2.



1 - $R_1 = R_2 = H$

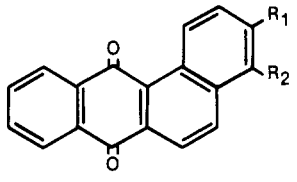
2 - $R_1 = R_2 = H$

1a - $R_1 = R_2 = H$

2a - $R_1 = R_2 = H$
3 - $R_1 = R_2 = OMe$
5 - $R_1 = OMe, R_2 = H$

The type of isomerism of 1 to **1a** has been well documented,[2] and spectral evidence has suggested this in the case of the 4-chloro isomer.[1] The structure of the product of oxidation of 1 or **1a**, however, was not determined. We felt the prolonged heating required to overcome the sluggish styrene reactivity made possible the rearrangement of 2 to the 5,6-dihydro isomer **2a**.

After a toluene solution of 2,3-dimethoxystyrene,[3] 1,4-naphthoquinone, chloranil, and catalytic amounts of trichloroacetic acid[4] was heated at 105 °C for 2 weeks, the product mixture was chromatographed on a silica gel column (benzene/hexane gradient) to yield 5,6-dihydro-3,4-dimethoxybenz[*a*]anthracene-7,12-dione (**3**; mp 173-175 °C, 15%) and 3,4-dimethoxybenz[*a*]anthracene-7,12-dione (**4**; mp 210-211 °C, 12%). Compound **4** was



4 - $R_1 = R_2 = OMe$
6 - $R_1 = OMe, R_2 = H$

identified by its mass spectrum, its IR spectrum, and its complex proton NMR spectrum,[5] which exhibited a doublet (J = 9.7 Hz) at δ 9.49 for H_1[6] and lacked meta coupling (J = 2 Hz). The absence of this meta coupling indicated substitution at the 3-position. Compound **3** was qualitatively identified by its mass spectrum and its proton NMR spectrum which showed an unresolved signal at δ 2.9 whose integral corresponded to four protons. Treatment of compound **3** with oxygen in alcoholic KOH produced **4**, mp 210-211 °C.

When 3-methoxystyrene[3] replaced 2,3-dimethoxystyrene under similar conditions, column chromatography as above afforded 5,6-dihydro-3-methoxybenz[*a*]anthracene-7,12-dione (**5**; mp 148-149 °C, 21%) and 3-methoxybenz[*a*]-anthracene-7,12-dione [**6**; mp 168-169 °C (lit.[7] mp 169-169.5 °C), 19%]. Compound **5** was identified as a dihydro intermediate by its mass spectrum and its proton NMR spectrum which showed an unresolved four-proton resonance signal at δ 2.78. Compound **5** was converted in oxygenated alcoholic KOH to **6**, mp 167.5-169.0 °C.

To determine the structure of the dihydro intermediates, ^{13}C NMR spectra and off-resonance decoupled spectra were taken. Assignment of aromatic resonances was made by single-frequency decoupling. Proton NMR assignments used in the single-frequency decoupling experiments were based on published assignments in 9,10-anthraquinone[5] and benz[*a*]anthracene-7,12-dione.[6] Nonprotonated carbon resonances were identified by their lower intensity. Assignments are shown in Table I.

In both cases the structures such as **2** possess a methylene carbon and methine carbon while the **2a**-like structures contain two methylene carbon atoms. The off-resonance multiplicities for the carbon atoms in the

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Table I. ^{13}C Chemical Shifts (ppm from Me_4Si in $CDCl_3$)

compd[a]	C-1	C-2	C-3	C-4	C-5[b]	C-6[b]	C-7	C-8[b]	C-9	C-10	C-11[b]	C-12
3[c]	125.7, d	109.5, d	154.2, s	145.2, s	20.5, t	18.8, t	183.9, s	126.9, d	133.1, d	133.1, d	126.4, d	184.3, s
5	131.6, d	111.5, d	160.6, s	113.5, d	27.6, t	20.8, t	183.8, s	125.5, d	133.0, d	133.0, d	126.3, d	184.2, s

[a] The resonances of the bridgehead carbon atoms were not assigned but are listed as follows. Compound 3: 122.9, 131.9, 132.8, 133.0, 138.7, 141.5 ppm. Compound 5: 122.1, 131.8, 132.6, 138.4, 140.9, 140.9 ppm. [b] The 5- and 6-carbon atoms and the 8- and 11-carbon atoms were not unambiguously assigned. [c] Multiplicities in the off-resonance decoupled spectra are given below each chemical shift.

alkyl region are both triplets, dictating that two methylene carbons are present. These data exclude structures related to **2** and firmly establish structures such as **2a**.

In neither instance was a dihydro compound found which had a structure represented by **2**. It was evident that under the reaction conditions virtually complete conversion of **2** to **2a** was occurring.

Experimental Section

All melting points were determined by using a Fisher-Johns hot-stage apparatus and are uncorrected. Low-resolution mass spectra were taken on a Finnigan 3300 mass spectrometer equipped with a Finnigan 6000 data system. High-resolution mass spectra were obtained from a VG Micromass ZAB-2F mass spectrometer equipped with a VG 2000 data system. Magnetic resonance spectra were taken on a Varian XL-100 spectrometer using $CDCl_3$ (0.5% Me_4Si) as solvent, while IR spectra were obtained on a Perkin-Elmer 467 spectrophotometer as KBr pellets. Microanalyses were performed by Galbraith Laboratories.

Preparation of 5,6-Dihydro-3,4-dimethoxybenz[*a*]anthracene-7,12-dione (3) and 3,4-Dimethoxybenz[*a*]anthracene-7,12-dione (4). To 12 mL of toluene were added 400 mg (2.5 mmol) of 1,4-naphthoquinone, 610 mg (2.5 mmol) of chloranil, 1.5 g (9.1 mmol) of 2,3-dimethoxystyrene, and 30 mg of trichloroacetic acid. This mixture was heated in a 105 °C oil bath until no naphthoquinone could be observed by TLC on silica gel GF plates with benzene as the developing solvent (14 days). The mixture was then chromatographed on a Silicar CC-7 (Mallinckrodt) column employing a 20–50% benzene–hexane gradient as the eluting solvent system. The first red band yielded 95 mg (12%) of **4** as red crystals, mp 209–211 °C. Sublimation yielded analytically pure **4**: mp 210–211 °C; IR 1662 cm^{-1} (C=O), 1589, 1480, 1328, 1311, 1284, 1271, 1225, 1088; NMR δ 9.49 (d, J = 9.7 Hz, 1 H), 8.64–7.47 (m, aromatic, 7 H), 4.07 (s, 3 H), 4.02 (s, 3 H). Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.37; H, 4.36.

The second red band yielded 120 mg (15%) of **3**: mp 173–175 °C; NMR δ 7.28–6.60 (m, aromatic, 6 H), 3.94 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 2.88 (br s, 4 H); mass spectroscopic molecular weight 320.1028 (calcd for $C_{20}H_{16}O_4$, 320.1049). Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.98; H, 5.03. Found: C, 75.26; H, 4.84.

Preparation of 5,6-Dihydro-3-methoxybenz[*a*]anthracene-7,12-dione (5) and 3-Methoxybenz[*a*]anthracene-7,12-dione (6). The same conditions as above were used, with 3-methoxystyrene being substituted for 2,3-dimethoxystyrene and the reaction time being 12 days. Column chromatography employing a 10–30% benzene–hexane gradient yielded as the first major red band 137 mg (19%) of **6**, mp 168–169 °C (lit.[7] mp 169–169.5 °C).

The second band afforded 152 mg (21%) of **5**: mp 148–149 °C; NMR δ 8.25–6.74 (m, aromatic, 7 H), 3.82 (s, 3 H, OCH_3), 2.78 (s, 4 H); mass spectroscopic molecular weight 290.0934 (calcd for $C_{19}H_{14}O_3$, 290.0941).

Conversion of Compound 3 to Compound 4. Oxygen was slowly bubbled for 3 h through a suspension of 75 mg of compound **3** in 25 mL of 5% ethanolic KOH. After neutralization with concentrated hydrochloric acid, the solvent was removed by evaporation and the crude material sublimed to afford 66 mg (89%) of **4**, mp 210–211 °C.

Conversion of Compound 5 to Compound 6. With use of the identical procedure as above, 70 mg of **5** gave 60 mg (87%) of **6**, mp 168–169 °C.

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Registry No. **3**, 72428-42-3; **4**, 72428-43-4; **5**, 72428-44-5; **6**, 63216-11-5; 1,4-naphthoquinone, 130-15-4; 2,3-dimethoxystyrene, 17055-36-6; 3-methoxystyrene, 626-20-0.

Isomerization of Internal Triple Bonds of Alkyn-1-ols with Sodium Hydride in 1,3-Diaminopropane[1]

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The "acetylenic zipper" reaction[2,3] offers a unique method for effecting the functionalization of the end of a long hydrocarbon chain. The reaction, which involves the base-mediated isomerization of an alkyne with an internal triple bond to the terminal alkyne, has been performed on both unsubstituted alkynes and alkyn-1-ols. The latter give ω-hydroxy alkynes:

$$HO(CH_2)_mC{\equiv}C(CH_2)_nH \rightarrow HO(CH_2)_{m+n}C{\equiv}CH$$

The mechanism is thought[2,4] to involve a random-walk process in which a series of allene–alkyne interconversions take place along the carbon chain until the terminal acetylide salt is formed.

The reaction is particularly useful in the synthesis of pheromones[5] and of long-chain fatty acid derivatives.[6] For instance, Pabon et al.[6] have obtained the 22-carbon acetylenic alcohol 21-docosyn-1-ol from 11-docosyn-1-ol in 87% yield—a transformation that involves a *minimum* of ten intermediate alkyn-1-ols.

We have experienced experimental difficulties using the "acetylenic zipper" reaction in work directed toward the synthesis of fatty acid derivatives. We, and others,[7] have encountered serious foaming problems in preparing the isomerization reagent, potassium 3-aminopropylamide

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