was added to the reaction mixture, and the reaction was slowly warmed to room temperature followed by heating at reflux for 24 h. The reaction was poured into water (150 mL) and extracted with methylene chloride (50 mL × 3). The combined organic extract was washed with water (50 mL × 3) and a saturated NaCl solution (50 mL) and dried (Na_2SO_4), and the solvent was removed in vacuo. The crude pale brown viscous liquid was flash chromatographed (SiO_2, 400 mesh, 25:75 ether/hexane) to afford vinyl sulfide **85** as a colorless viscous liquid (0.120 g, 79%): ^1H NMR (90 MHz, $CDCl_3$) δ 0.78 (s, 3 H), 0.95 (s, 21 H), 2.25 (s, 3 H), 2.70 (m, 1 H), 3.38 (s, 3 H), 3.62 (s, 1 H), 3.70 (AB q, J_{AB} = 10.00 Hz, 2 H), 4.31 (br s, 1 H), 4.85 (m, 1 H), 4.98 (2 s, 1 H); mass spectrum for $C_{33}H_{60}O_4S\,Si_2$, *m/e* 608 (M^+). Anal. Calcd: C, 65.1; H, 9.87. Found: C, 64.73; H, 10.18.

Saturated α-Ketol Lactol 86. To an ice-cooled solution of vinyl sulfide **75** (0.282 g, 0.462 mmol) in THF (20 mL) was added osmium tetraoxide (0.097 g, 0.50 mmol) in one portion, and the reaction was stirred for 15 min. The reaction mixture was slowly warmed to room temperature and stirred for an additional 4 h. To this reaction mixture was then added a saturated aqueous solution of sodium sulfite (5 mL), and the mixture was stirred for 1 h. The black residue was separated by filtration (Celite), the filtrate was poured into water (100 mL), and the mixture was extracted with ether (50 mL × 3). The combined organic extract was washed with water (50 mL × 2) and a saturated NaCl solution (50 mL) and dried (Na_2SO_4), and the solvent was removed in vacuo. The pale yellow viscous liquid was flash chromatographed (SiO_2, 400 mesh, 25:75 ether/hexane) to yield keto lactol **86** as a white foam (0.23 g, 80%).

Unsaturated α-Keto Lactol 87. To an ice-cooled solution of vinyl sulfide **85** (0.120 g, 0.20 mmol) in THF (10 mL) was added osmium tetraoxide (0.042 g, 0.22 mml) in one portion. The reaction mixture was slowly warmed to room temperature and stirred for 1 h. To the above reaction mixture was then added a saturated solution of Na_2SO_3 (1 mL), and the mixture was stirred for an additional 3 h. The black solid was separated by filtration (Celite), the filtrate was poured into water (100 mL), and the mixture was extracted with ether (50 mL × 3). The combined ether extract was washed with water (50 mL × 3) and a saturated NaCl solution (50 mL) and dried (Na_2SO_4), and the solvent was removed in vacuo. The residual viscous liquid was flash chromatographed (SiO_2, 400 mesh, 25:75 ether/hexane) to produce keto lactol **87** (0.085 g, 72%). Anal. Calcd: C, 64.6; H 9.76. Found: C, 64.23; H, 10.11.

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Supplementary Material Available: Procedures for the syntheses of **4b,c**, **11**, and the C-3 methoxy analogues of **15** and **52–55** and for the borohydride reduction/acylation of **37B**, ^{13}C NMR spectral data for synthesized enones, nitriles, enone esters, lactones, and Baeyer–Villiger lactones, and 470-MHz ^1H NMR spectral data for synthesized lactones and enones (12 pages). Ordering information is given on any current masthead page.

Unsymmetrically Substituted 1,8-Diarylanthracenes[1]

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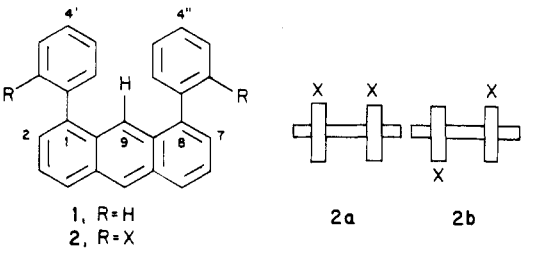
Unsymmetrically substituted 1,8-diarylanthracenes where the aryl rings are *m*-tolyl (**5**), *o*-tolyl (**6**), and 2,3-dimethylphenyl (**7**) have been synthesized; the barriers to aryl ring rotation in these hydrocarbons were found to be 5.3, 10.4, and 16.3 kcal/mol, respectively. Addition of either an acetoxyl (**14**) or a methyl (**15**) substituent at C-9 of the dixylylanthracene gave mixtures of cis and trans isomers that also exhibited rotation of an aryl ring within the temperature range 25–120 °C. X-ray crystal structures for the *cis*- (**14b**) and *trans*- (**14a**) 9-acetoxydixylylanthracenes demonstrated significant distortion in the geometry of the anthracene ring, permitting rotation of the aryl rings with unexpected ease in solutions at temperatures above 100 °C.

Our studies of 1,8-diphenylanthracene (**1**, Scheme I) and its derivatives have provided evidence that these molecules exist largely in conformations with the two phenyl rings approximately parallel and approximately perpendicular to the plane of the anthracene ring.[2,3] Such conformers possess a molecular cavity bounded on the bottom by the anthracene ring and on two sides by phenyl rings. This cavity is of sufficient size to allow reagents to enter and engage in chemical reactions at the bottom of the cavity, namely, at the C-9 position of the anthracene ring.

Scheme I



Consideration of this geometry leads to the conclusion that 1,8-diarylanthracene derivatives **2** with unsymmetrically substituted aryl rings will exist as two geometrical isomers, a cis form (**2a**) and a trans form (**2b**). Furthermore, the trans form **2b** would be composed of two nonsuperimposable mirror images (enantiomers). Resolution of an appropriate set of enantiomers possessing a functional group at C-9 would provide two molecules, each with

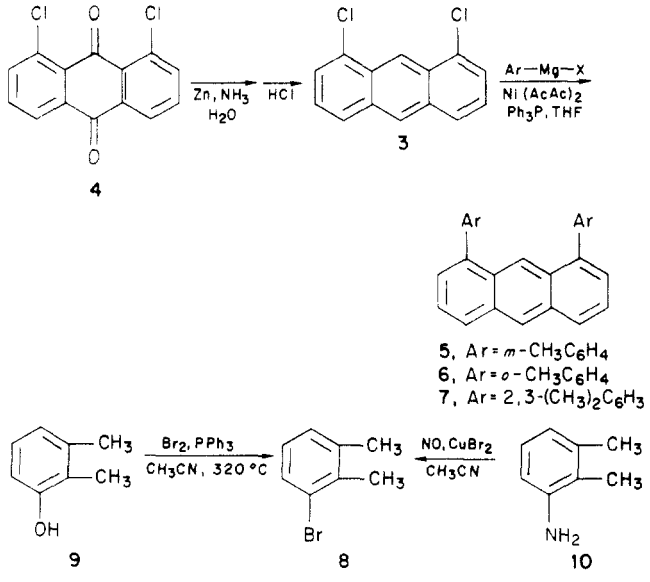
(1) A portion of this research was supported by Public Health Service Grant R01-GM-30735 from the National Institute of General Medical Science. The execution of this research was also aided by Institutional Research Grants from the National Science Foundation for the purchase of a mass spectrometer and an NMR spectrometer.

(2) (a) House, H. O.; Koepsell, D.; Jaeger, W. *J. Org. Chem.* **1973**, *38*, 1167. (b) House, H. O.; Koepsell, D. G.; Campbell, W. *Ibid.* **1972**, *37*, 1003.

(3) House, H. O.; Ghali, N. I.; Haack, J. L.; VanDerveer, D. *J. Org. Chem.* **1980**, *45*, 1807.

0022-3263/86/1951-0921$01.50/0

Scheme II



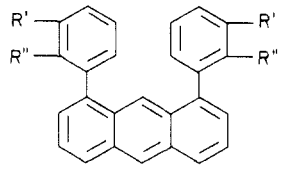
a chiral cavity and a functional group at the bottom of this cavity. Such molecules have the potential to serve as "synthetic enzymes" that could convert achiral substrates to chiral products or could discriminate between the two enantiomers of a racemic substrate.[4]

To explore this possibility we needed information about the rotation barrier for substituted phenyl rings in various 1,8-diarylanthracenes. Since rotation of an aryl ring would both interconvert cis and trans isomers **2a** and **2b** and would also allow racemization of the trans enantiomers, any diarylanthracene that was to be useful as a "synthetic enzyme" would need to have a sufficient barrier to rotation to be configurationally stable at the temperature where it was to be used. In this paper we describe the preparation and properties of several unsymmetrically substituted 1,8-diarylanthracenes that have provided information about the rotation barrier for aryl rings.

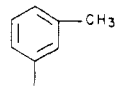
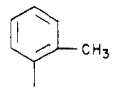
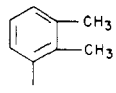
Our syntheses involved several modifications (see Experimental Section) of previous procedures[2,3] in which 1,8-dichloroanthraquinone (**4**) was reduced to 1,8-chloroanthracene (**3**, Scheme II), and this dihalide was coupled with various aryl-Grignard reagents in the presence of a nickel catalyst.[5] A particularly helpful modification involved the addition of a 2:1 molar ratio of Ph_3P and Ni(AcAc)$_2$ to the reaction mixture so that the nickel intermediates could be stabilized as $Ni(PPh_3)_4$ or $NiX_2(PPh_3)_2$.[5] With the present modifications, these syntheses provided very satisfactory routes to the three substituted 1,8-diarylanthracenes **5–7** as well as the parent hydrocarbon **1**.

Although the aryl halide precursors for Grignard reagents used to prepare anthracenes **5** and **6** were commercially available, it was necessary to prepare the xylyl bromide **8** from either the phenol **9** or the aniline **10**. Conversion of the aniline **10** to the bromide **8** by a conventional procedure involving diazotization in aqueous solution gave a rather poor yield of the bromide (typically 35%) accompanied by comparable amounts of the phenol **9**, a byproduct from solvolysis of the diazonium salt intermediate. This difficulty was avoided by employing an alternative procedure[6] in which the amine was treated with a stoichiometric amount of copper(II) bromide and excess nitric oxide in acetonitrile. This procedure offered a particularly convenient route to the bromide **8**.

Scheme III



rotation barriers

	Energy	coalesc temp	solvent
5, Ar = 	5.3 (0.5) kcal	−55 °C	CD_2Cl_2
6, Ar = 	10.4 (1.0) kcal	124 °C	DMF-d_7
7, Ar = 	16.3 (2.0) kcal	>170 °C	$C_6D_5NO_2$

The energy barriers for rotation of an aryl ring in the diarylanthracenes **5–7**, summarized in Scheme III were determined by standard NMR techniques (see Experimental Section). The data presented include the energies,[7] the solvents used for the NMR measurement, and the estimated coalescence temperatures. The barrier (5.3 kcal/mol) observed for anthracene **5** with no ortho substituent larger than hydrogen was approximately doubled (10.4 kcal) when one *o*-methyl substituent was present. The effective steric bulk of this *o*-methyl substituent was significantly enhanced (16.3 kcal) by the buttressing effect of a second methyl added to the **3** position of each phenyl ring in anthracene **7**. The cis (**2a**) and trans (**2b**) isomers of anthracene **7** were separated by HPLC techniques; these geometrical isomers interconverted only slowly at 25 °C so that reequilibration of solutions of the partially separated isomers was complete after 24 h. These results led us to anticipate that derivatives of the anthracene **7** with an additional hindering substituent larger than hydrogen at C-9 might be sufficiently stable to interconversion to be useful as potential "synthetic enzymes".

Since we have thus far[2,3] found no satisfactory method to effect selective, direct substitution at C-9 in 1,8-diarylanthracenes, we choose an alternative indirect route involving formation of the intermediate quinone **11** that could be selectively reduced to the 9-anthrone **12** (Scheme IV). Although preliminary small-scale experiments suggested that photosensitized oxidation of the dixylylanthracene **7** with oxygen in the presence of methylene blue might be part of a useful route for the formation of the quinone **11**, we were unsuccessful in efforts to use this reaction on a preparative scale.[8] After considerable experimentation with various oxidation procedures, we selected a two-phase oxidation with chromic acid in a water–chlorobenzene mixture that would regularly produce the desired quinone **11** in 50% yield. The major byproduct in this reaction was the keto lactone **13** that we presume was formed via the intramolecular attack of a phenoxy radical on one of the *o*-methyl groups.

(4) For recent reviews of this general concept, see: (a) Tabushi, I. *Tetrahedron* **1984**, *40*, 269–292. (b) Gutsche, C. D. *Acc Chem. Res.* **1983**, *16*, 161–170. (c) Rebek, J., Jr. *Ibid.* **1984**, *17*, 258–264. (d) Cram, D. J. *Science (Washington, D.C.)* **1983**, *219*, 1177–1183. (e) Lehn, J.-M. *Ibid.* **1985**, *227*, 849–856.

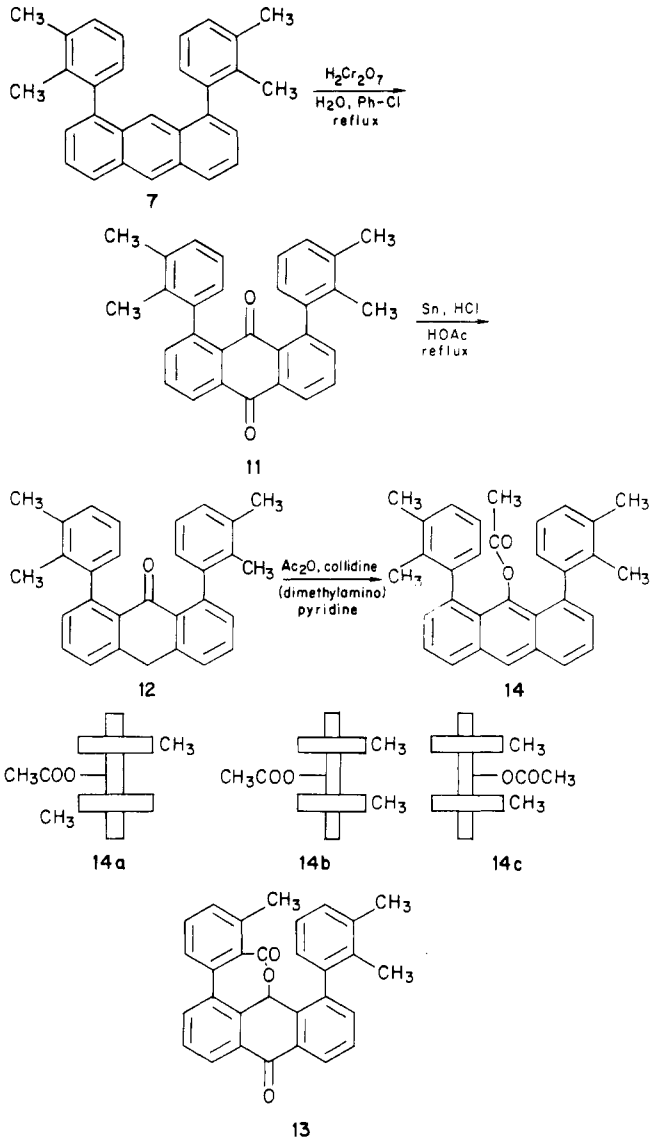
(5) For a recent review of this coupling procedure, see: Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340–348.

(6) (a) Brackman, W.; Smit, P. J. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 857. (b) For a typical procedure to diazotize an anime and convert it to a bromide in aqueous solution, see: Hartwell, J. L. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. 3, p 185.

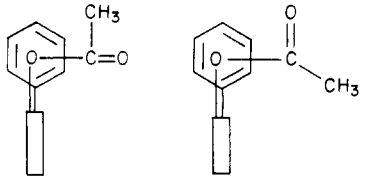
(7) Values in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digit(s).

(8) For a review of this reaction, see: Denny, R. W.; Nickon, A. *Org. React. (N.Y.)* **1973**, *20*, 133–336.

Scheme IV



Reaction of the anthrone **12** with a solution of acetic anhydride in collidine containing a catalytic amount of 4-(dimethylamino)pyridine produced a mixture of three 9-acetoxydixylylanthracenes **14**. Although all three compounds were interconverted when solutions of the products were heated above 100 °C, at room temperature HPLC techniques separated the mixture into the pure trans isomer **14a** and a rapidly equilibrating mixture of the cis isomer **14b** and a second component (minor) tentatively assigned the structure of the cis isomer **14c**. The major components **14a** and **14b** could also be separated from the mixture by recrystallization from a mixture of acetone and chloroform. The structures of these two materials were confirmed by obtaining an X-ray crystal structure for each compound as illustrated in Figures 1 and 2. The NMR spectra of solutions of these materials (see Experimental Section) were fully consistent with the solid state structures.



14b **14d**

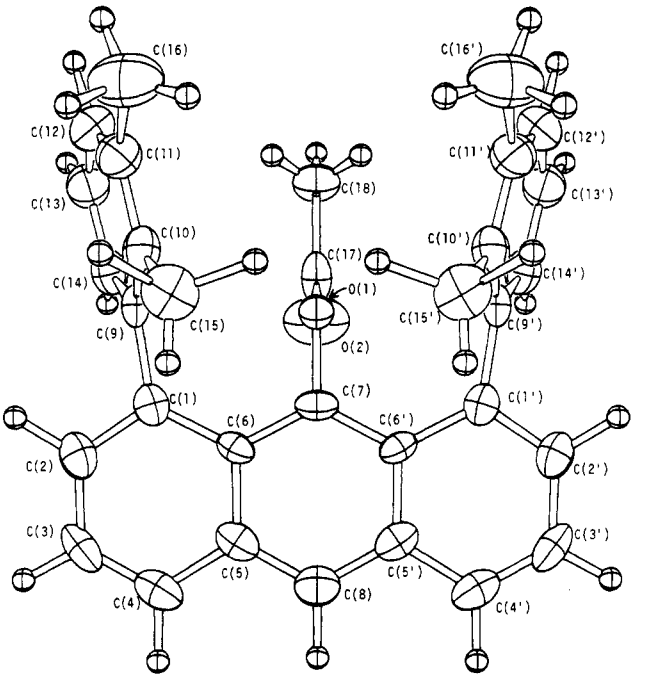


Figure 1. Perspective view of the molecular structure of *anti*-9-acetoxy-*cis*-1,8-dixylylanthracene.

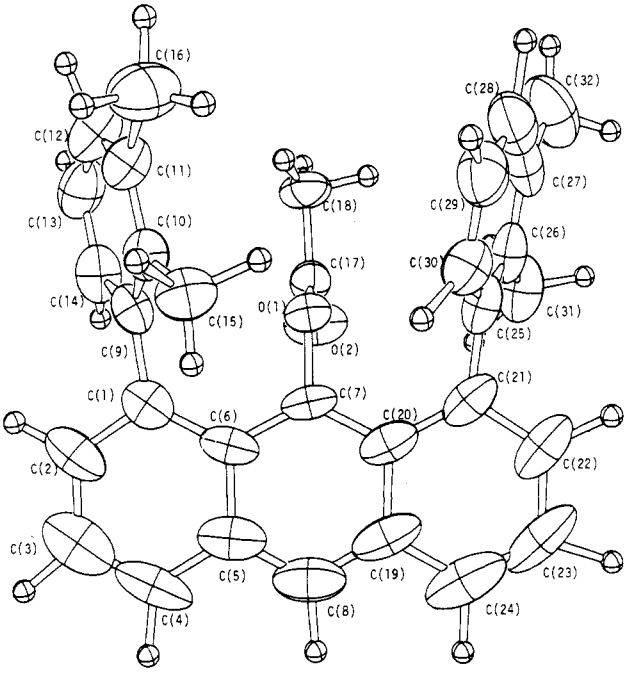
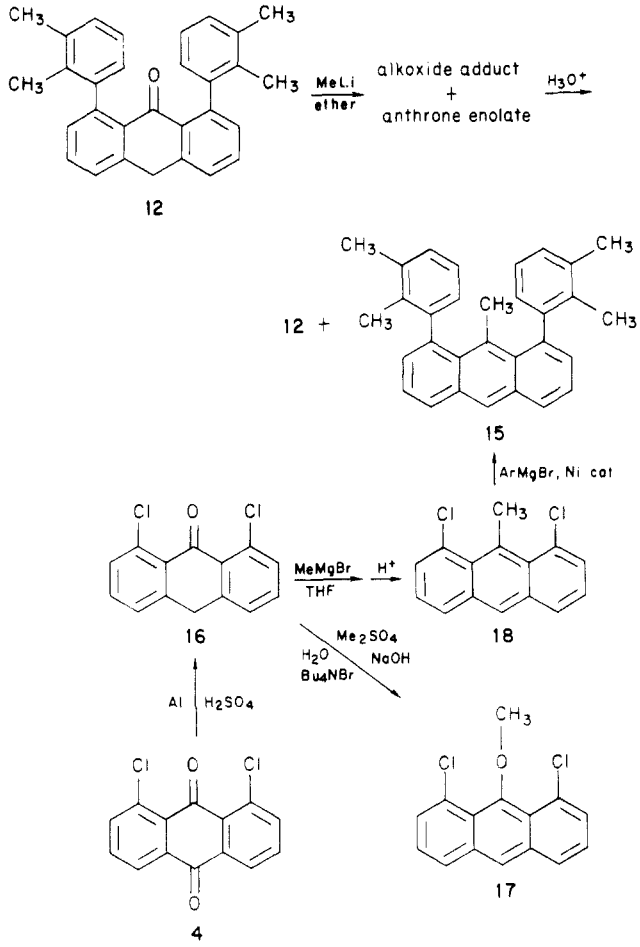


Figure 2. Perspective view of the molecular structure of 9-acetoxy-*trans*-1,8-dixylylanthracene.

The third product, present in solution as about 10% of a rapidly interconverting mixture with **14b**, has NMR absorption compatible with its tentative assignment as the cis-syn acetate **14c**. Presumably the two materials **14b** and **14c** are interconverting either by rotation about the C-9 C–O bond or by an inversion at oxygen involving a transition state with a linear C–O–C bond. Since this linear inversion at divalent oxygen is estimated to have an energy barrier greater than 18 kcal/mol,[9] it seems likely that the

(9) (a) Kessler, H.; Rieker, A.; Rundel, W. *Chem. Commun.* **1968**, 475. (b) Raban, M.; Kenney, G. W. *J. Tetrahedron Lett.* **1969**, 1295. (c) Gordon, A. J.; Gallagher, J. P. *Ibid.* **1970**, 2541. (d) For a review, see: Lambert, J. B. In "Topics in Stereochemistry"; Allinger, N. L., Eliel, E. L., Eds.; Wiley-Interscience: New York, 1971; Vol. 6, pp 19–105.

Scheme V



facile interconversion we are observing should be attributed to rotation and not a linear inversion process. Although we favor structure **14c** for the minor cis isomer present, we cannot exclude the possibility that the minor product has structure represented in part by formula **14d** and is interconverting with **14b** by rotation about the O–CO bond of the ester.

Another dixylylanthracene derivative with a substituent at C-9 was obtained by the reaction of the anthrone **12** with ethereal methyllithium. This reaction formed a mixture of the alkoxide precursor of hydrocarbon **15** (minor) and the enolate of anthrone **12** (major, Scheme V). However, when the crude reaction mixture was acidified, isolated, and treated with methyllithium repeatedly, a reasonable yield of the 9-methyl derivative **15** was obtained. This material proved to be a 2:1 mixture of trans (**15a**) and cis (**15b**) isomers that was interconverting slowly at 25 °C. In an alternative synthetic approach to 9-substituted diarylanthracenes, the dichloro quinone **4** was selectively reduced to the dichloroanthrone **16**. Subsequent methylation with dimethyl sulfate formed the 9-methoxy dichloride **17** and addition of methylmagnesium bromide to the anthrone afforded the 9-methyl dichloride **18**. Efforts to couple the 9-methoxy dichloride **17** with either phenylmagnesium bromide or the Grignard reagent from bromide **8** in the presence of various Ni or Pd catalysts were uniformly unsuccessful. However, reaction of the 9-methyl dichloride **18** with the *o*-xylyl-Grignard reagent in the presence of the catalyst from $Ni(AcAc)_2$ and Ph_3P did form the 9-methyl derivative **15** in low yield.

It is apparent that 1,8-dixylylanthracenes, even with additional substituents at C-9, have relatively low energy barriers to rotation of an aryl ring contrary to our expectation. The reason for the relatively low energy barriers became apparent when the crystal structures (Figures 1 and 2) for the 9-acetates **14a** and **14b** were examined. In both cases the two aryl rings are no longer parallel but are bent away from one another as a result of a series of small distortions in bond lengths and bond angles of the anthracene system. The extent of this distortion may be seen by using crystal structure data to compare the distance between the 4′ and 4″ positions of the two phenyl rings in various derivatives (see structure 1). For the relatively uncongested molecule, 10-bromo-1,8-diphenylanthracene[3] with hydrogen at C-9, the distance is 5.485 Å (the calculated distance with no distortion should be 5.0 Å). The distance found for the *trans*-dixylyl acetate **14a** is 6.468 Å and the even more congested cis isomer **14b** has a distance of 6.833 Å. A view of the *trans*-dixylyl acetate **14a** from above the top edge of the anthracene ring in Figure 3 also provides an indication of the extent of distortion in these molecules. Thus, to achieve a significant increase in the barrier to aryl ring rotation it will be necessary to add substituents that oppose this distortion of the anthracene ring. We believe that addition of substituents at the C-2 and C-7 positions of the anthracene ring should be most effective and plan to explore the preparation and properties of such materials.

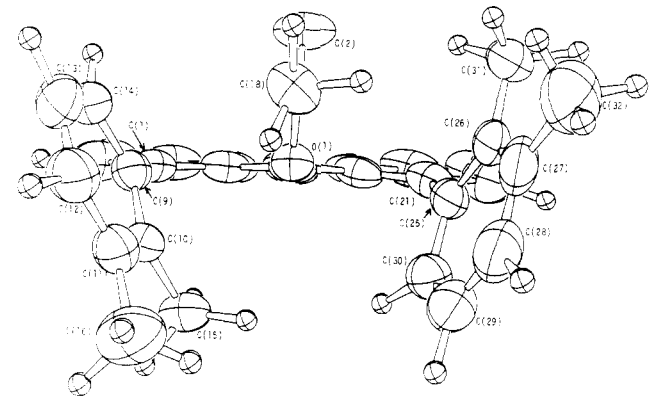


Figure 3. Perspective view of the molecular structure of 9-acetoxy-*trans*-1,8-dixylylanthracene as seen from the edge of the anthracene ring.

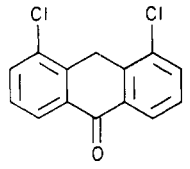
Experimental Section[10]

Preparation of 1,8-Dichloroanthracene (3). The following modifications in earlier directions[2,3] are an improved procedure for the preparation of this dihalide on a large scale. A slurry of 100.0 g (361 mmol) of the quinone **4** in 1.2 L of aqueous 28% NH_3 and 900 mL of H_2O was cooled to 10 °C (ice bath) and then 500 g (7.65 mol) of Zn dust was added, portionwise with stirring during 15 min. The resulting red slurry, which warmed to 30 °C when the cooling bath was removed, was heated to 75 °C on a steam bath and then held at this temperature with stirring for 4 h. During this period the color of the solution changed from red to light brown and a white precipitate separated. The mixture was

(10) All melting points are corrected and all boiling points are uncorrected. Unless otherwise noted, $MgSO_4$ was employed as a drying agent. The IR spectra were determined with a Perkin-Elmer, Model 299, infrared recording spectrophotometer fitted with a grating. The UV spectra were determined with either a Cary, Model 14, or a Perkin-Elmer, Model 202, recording spectrophotometer. The ^1H NMR spectra were determined at 60 MHz with a Varian, Model T-60A, NMR spectrometer or at 300 MHz with a Bruker, Model WM-300, NMR spectrometer. The ^{13}C NMR spectra were determined at 25 MHz with a JEOL, Model PFT-100, NMR spectrometer or at 75 MHz with a Bruker, Model WM-300, NMR spectrometer. The NMR chemical shift values are expressed in δ values (ppm) relative to a Me_4Si internal standard. The mass spectra were obtained with either a Hitachi (Perkin-Elmer), Model RMU-7, or a Varian MAT, Model 112S, mass spectrometer. All reactions involving strong bases or reactive organometallic intermediates were performed under a nitrogen atmosphere.

allowed to stand and cool to room temperature and then the supernatant liquid was filtered from the mixture of white and grey (excess Zn) solids. The filtrate was extracted with two 200-mL portions of CH_2Cl_2 while the solids were separately extracted with several portions of boiling CH_2Cl_2. After the combined extracts had been concentrated, the residual off-white solid (85 g) was suspended in a mixture of 400 mL of aqueous 12 M HCl and 4.4 L of *i*-PrOH. The resulting suspension was refluxed for 3 h during which time all the solid dissolved to give a pale yellow solution. This solution was allowed to cool and stand overnight and then filtered with suction. The collected product was allowed to dry in the air for 2 days to leave 67.65 g (75.7%) of the dichloride **3** as yellow needles, mp 156.5–157 °C. Concentration of the mother liquor to one-third of its original volume followed by cooling, filtration, and drying separated an additional 8.07 g of product (total yield 75.72 g or 84.7%), mp 154–156 °C. This product was identified with previously described material, mp 156–157 °C, by a mmp determination and by comparison of IR and NMR spectra.

Preparation of 1,8-Dichloro-9-methoxyanthracene (17). In a modification of a previously described reduction procedure,[3] 100 g (361 mmol) of the quinone **4** was dissolved in 1.1 L of concentrated sulfuric acid with vigorous mechanical stirring. Then 30.0 g (1.11 mol) of Al powder was added and the mixture was stirred for 8 h while the temperature of the mixture was maintained at 25–30 °C by intermittent use of a cold water bath. The resulting yellow suspension was poured onto 3 L of ice and, after standing for 30 min, was filtered. The residual brown solid was extracted with eight 150-mL portions of CH_2Cl_2 and the combined extracts were washed with aqueous $NaHCO_3$, dried, and concentrated. The resulting tan solid (86.6 g or 90%) could be analyzed for the amounts of isomeric anthrones **16** (major) and **19** (minor) by examining the NMR signals ($CDCl_3$) for the benzylic methylene groups (δ 4.23 for anthrone **19** and δ 4.16 for anthrone **16**). Recrystallization from a CH_2Cl_2–hexane mixture very efficiently separated 82.3 g (86%) of the anthrone **16** as tan needles, mp 166–168 °C, that were identified with the previously described sample, mp 167–168 °C, by comparison of IR and NMR spectra.



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To a solution of 160 g (4.0 mol) of NaOH and 7.1 g (22 mmol) of $(n\text{-Bu})_4NBr$ (a phase-transfer agent) in 500 mL of H_2O was added, dropwise and with vigorous stirring during 1 h, a solution of 20.0 g (76 mmol) of the anthrone **16** and 38 g (300 mmol) of dimethyl sulfate in 400 mL of CH_2Cl_2. The resulting mixture was stirred at 25 °C for an additional 2 h and then partitioned between water and CH_2Cl_2. The combined organic layers were dried and concentrated to leave 17.55 g (83%) of the crude methoxy dichloride **17** as a dark yellow-orange powder, mp 167–170 °C. Recrystallization from an acetone–chloroform mixture afforded 17.05 g (81%) of the methoxy derivative **17** as bright yellow prisms, mp 170–171 °C. A 2.00-g sample of the product was chromatographed on silica gel with a methylene chloride–hexane eluent (1:4 v/v) and the appropriate fractions were combined and recrystallized from a chloroform–acetone mixture to separate 1.80 g of the pure methyl ether **17**, mp 172–173 °C. The spectral properties follow: IR ($CHCl_3$), no absorption corresponding to OH or C=O groups in the 3-μm or 6-μm region; ^1H NMR (60 MHz, $CDCl_3$) δ 8.22 (1 H, s, aryl CH), 7.2–7.9 (6 H, m, aryl CH), 3.92 (3 H, s, methoxyl); ^{13}C NMR [$CDCl_3$, multiplicity determined by a DEPT (Distortionless Enhancement by Polarization Transfer)], 153.6 (s), 134.2 (2 C, s), 129.3 (2 C, s), 129.1 (2 C, d), 127.8 (2 C, d), 125.5 (2 C, d), 124.1 (d), 122.9 (2 C, s), 65.0 ppm (q); mass spectrum, *m/e* (relative intensity), 278 (51), 276 (82, M^+), 263 (65), 261 (100), 235 (16), 233 (24), 163 (18); UV maxima, nm (cyclohexane, ϵ), 260 (123 000), 347 (3090), 365 (6520), 385 (10 100), 402 (shoulder, 6030), 407 (8750).

Anal. Calcd for $C_{15}H_{10}Cl_2O$: C, 65.01; H, 3.64; Cl, 25.58. Found: C, 65.10; H, 3.68; Cl, 25.56.

Preparation of 1,8-Di-*o*-tolylanthracene (6). A solution of 94.9 g (0.75 mol) of *o*-chlorotoluene and 5.0 mL of 1,2-dibromoethane (to clean Mg surface) in ca. 600 mL of THF was added, dropwise and with stirring during 1 h, to 19.45 g (0.80 mol) of Mg turnings. After the addition was complete, the reaction mixture was refluxed for 15 h and then cooled. Analysis[11] of an aliquot of the solution (total volume 680 mL) indicated the concentration of the aryl-Grignard reagent to be 0.50 M corresponding to a 45% yield. This Grignard reagent solution (680 mL or 340 mmol) was added, dropwise and with stirring during 1 h, to a solution of 20.0 g (72.2 mmol) of the dichloride **3**, 100 mg (0.39 mmol) of nickel(II) acetylacetonate, and 205 mg (0.78 mmol) of Ph_3P in 200 mL of anhydrous THF.

During this addition a cold water bath was used periodically to keep the temperature of the reaction mixture below 50 °C. The resulting black (colloidal Ni) reaction mixture was stirred overnight (10 h) at 25 °C and then quenched with aqueous 3 M HCl and partitioned between water and methylene chloride. The organic phase was dried and concentrated to leave 26.1 g of crude product as a brown liquid. The product was crystallized from a methylene chloride–acetone mixture to separate 15.6 g (54%) of the hydrocarbon **6** as an off-white powder, mp 189–196 °C. A 2.00-g sample of this material was recrystallized again to separate 1.12 g of the pure hydrocarbon **6** as fine colorless needles, mp 200–201 °C: IR ($CHCl_3$), no absorption attributable to OH or C=O groups in the 3- or 6-μm regions; ^1H NMR (60 MHz, CCl_4) δ 7.0–8.6 (16 H, m, aryl CH), 1.92, and 1.89 (6 H, 2 s, Me groups and cis and trans isomers); ^{13}C NMR ($CDCl_3$, multiplicity on off-resonance decoupling) (double peaks for cis and trans isomers present are listed together), 140.3 and 140.2 (2 C, s), 139.7 (2 C, s), 136.5 and 136.3 (2 C, s), 131.62 and 131.57 (2 C, s), 130.7 and 130.6 (2 C, s), 130.12 and 130.10 (2 C, d), 129.6 and 129.4 (2 C, d), 127.4 and 127.3 (4 C, d), 126.5 and 126.4 (1 C, d), 125.53 and 125.48 (2 C, d), 125.3 and 125.2 (2 C, d), 125.1 (2 C, d), 124.2 and 124.0 (1 C, d), 19.9 ppm (2 C, q); mass spectrum, *m/e* (relative intensity), 359 (30), 358 (100, M^+), 357 (20), 343 (12), 265 (12), 252 (6), 170 (15), 101 (6); UV maxima, nm (cyclohexane, ϵ), 243 (48 100), 249 (86 700), 254 (123 000), 261 (136 000), 332 (3240), 349 (6630), 366 (10 100), 386 (8890). When this product was subjected to HPLC analysis employing a 0.46 × 25 cm column packed with 10-μm silica gel and eluted with hexane, only a single peak (13.98 min) was observed for the two equilibrating isomers present.

Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.82; H, 6.17.

NMR Study of the Equilibration of the Two Stereoisomers of 1,8-Di-*o*-tolylanthracene (6). The ^1H NMR (300 MHz) of the hydrocarbon **6** in $CDCl_3$ at 35 °C exhibited peaks at δ 7.07–8.51 (16 H, m, aryl CH), 1.90, and 1.87 (6 H, 2 s, Me groups of cis and trans isomers) with a peak area ratio of ca. 1:1 for the two Me peaks. The ^1H NMR (300 MHz) of a 0.010 M solution of the hydrocarbon **6** in DMF-d_7 at 35 °C exhibited corresponding peaks at δ 7.12–8.77, 1.919, and 1.903 with a Me peak area ratio of ca. 1:1. The solution in DMF-d_7 was measured at each of the following temperatures: 373, 383, 393, 403, and 413 K. At each temperature below the estimated coalescence temperature (397 K), the chemical shifts and peak widths at half height for each of the Me peaks was measured. The spectrum measured in DMF-d_7 at 35 °C was used to measure the separation between Me peak A (571.22 Hz) and Me peak B (576.06 Hz) in the "nonexchange" limit. Using standard relationships,[14] a computer program was written to simulate the spectra of the two Me groups for various preexchange lifetimes, τ and various mole fractions[14c] of the two isomers responsible for peaks A and B. At each temperature these two quantities were varied to obtain the best match between the simulated and observed spectra. The values for τ (in ms) and the mole fraction of the isomer exhibiting peak A at various temperatures were 373 K, 125 and 0.51; 383 K, 91 and

(11) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.
(12) Cachin, M.; Wahl, H. *C. R. Acad. Sci., Ser. B* **1957**, *244*, 783.
(13) Blanchard, A. A. *Inorg. Synth.* **1946**, *2*, 126.
(14) (a) Gutowsky, H. S.; Holm, C. H. *J. Phys. Chem.* **1956**, *25*, 1228. (b) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. "High-Resolution Nuclear Magnetic Resonance"; McGraw-Hill: New York, 1959; pp 218–224. (c) Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: Philadelphia, 1977; pp 252–259.

0.52; 393 K, 62 and 0.51. From these data the Arrhenius activation energy for the interconversion of the two isomers was calculated to be 10.4 (ca. 1.0)[7] kcal/mol.

Preparation of 1,8-Di-*m*-tolylanthracene (5). A solution of 20.0 g (0.117 mol) of *m*-bromotoluene in 150 mL of THF was added, dropwise and with stirring during 1 h, to 5.0 g (0.020 mol) of Mg turnings with cooling to maintain the reaction temperature at 25 °C. After the addition was complete, the mixture was refluxed for 1 h and then cooled to room temperature. Analysis[11] of an aliquot of the reaction solution (total volume 155 mL) indicated the concentration of Grignard reagent to be 0.62 M corresponding to an 82% yield. The Grignard reagent solution (155 mL or 95.9 mmol) was added, dropwise and with stirring during 1 h, to a solution of 4.76 g (19.2 mmol) of the dichloride **3**, 50 mg (0.20 mmol) of nickel(II) acetylacetonate, and 102 mg (0.39 mmol) of Ph_3P in 50 mL of THF. The resulting black (colloidal Ni) mixture was refluxed for 2 h and then poured into 50 mL of aqueous 3 M HCl and partitioned between water and CH_2Cl_2. The organic layer was dried and concentrated to leave 6.2 g of light tan solid. Recrystallization from a $CHCl_3$–acetone mixture afforded 5.91 g (86.0%) of the hydrocarbon **5** as a colorless powder, mp 128–129 °C: IR ($CHCl_3$), no absorption corresponding to OH or C=O groups in the 3- or 6-μm region; ^1H NMR (60 MHz, $CDCl_3$) δ 8.46 (1 H, s, aryl CH), 8.73 (1 H, s, aryl CH), 7.2–8.1 (14 H, m, aryl CH), 2.32 (6 H, s, Me); ^{13}C NMR [$CDCl_3$, multiplicity determined by a DEPT], 140.7 (2 C, s), 140.5 (2 C, s), 137.5 (2 C, s), 131.9 (2 C, s), 130.6 (2 C, s), 130.1 (2 C, d), 127.9 (2 C, d), 127.8 (2 C, d), 127.5 (2 C, d), 127.1 (2 C, d), 126.7 (1 C, d), 126.0 (2 C, d), 125.2 (2 C, d), 124.0 (1 C, d), 21.4 ppm (2 C, q); mass spectrum, *m/e* (relative intensity) 359 (31), 358 (100, M^+), 342 (5.6), 327 (2.9), 265 (1.9), 252 (2.0), 179 (4.1), 163 (4.2); UV maxima, nm (cyclohexane, ε), 257 (shoulder, 81 100), 263 (151 000), 340 (4120), 358 (7460), 375 (10 800), 395 (9260).

Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.68; H, 6.31.

NMR Study of the Equilibration of the Two Stereoisomers of 1,8-Di-*m*-tolylanthracene (5). The ^1H NMR (300 MHz) of the hydrocarbon **5** in CD_2Cl_2 at 27 °C exhibited a single peak at δ 2.38 for the 6 H atoms of the methyl groups in the rapidly equilibrating cis and trans isomers. The ^1H NMR (300 MHz) of a 0.010 M solution of the hydrocarbon **5** in CD_2Cl_2 was cooled slowly and spectra were obtained at the following temperatures: 260, 250, 240, 235, 230, 225, 220, 215, 210, 205, and 200 K. Line broadening became a sufficiently serious problem below 200 K to prevent collection of data below this temperature. At each temperature below the estimated coalescence temperature (218 K), the chemical shifts, peak widths at half height, and "depth of valley" for each of the Me peaks was measured. The spectrum measured 200 K was used to measure the separation between Me peak A (703.90 Hz) and Me peak B (724.50 Hz) in the "slow-exchange" limit. Previously described techniques were used to simulate the spectra of the two Me groups for various preexchange lifetimes, τ, and various mole fractions[14c] of the two isomers responsible for peaks A and B. The values for τ (in ms) and the mole fraction of the isomer exhibiting peak A at various temperatures were 200 K, 46.8 and 0.427; 205 K, 39.4 and 0.405; 210 K, 29.4 and 0.394; 215 K, 21.3 and 0.390; 220 K, 13.7 and 0.390. From these data the Arrhenius activation energy for the interconversion of the two isomers was calculated to be 5.3 (ca. 0.5)[7] kcal/mol.

Preparation of 1,8-Diphenylanthracene (1). This procedure differs from that described earlier[3] in the addition of a relatively small amount of Ph_3P to help keep the Ni(0) species in solution. To a solution of 80.0 g (289 mmol) of the dichloride **3**, 818 mg (3.12 mmol) of Ph_3P, and 400 mg (1.56 mmol) of $Ni(acac)_2$ in 750 mL of THF was added, dropwise and with stirring during 2 h, 850 mL of a THF solution containing[11] 1.12 mol of PhMgBr. During the addition the temperature of the reaction mixture was maintained below 50 °C by intermittent cooling with a water bath. The resulting black colored reaction mixture (colloidal Ni) was stirred at 25 °C for an additional 10 h and then quenched by the addition of 150 mL of aqueous 3 M HCl. The reaction mixture was partitioned between water and CH_2Cl_2 and the organic layer was dried and concentrated to leave 92.5 g of the crude product as a brown solid, mp 170–182 °C. Recrystallization from a CH_2Cl_2–hexane mixture separated 79.16 g (83%) of the hydrocarbon **1** as colorless needles, mp 191–193 °C. This material was identified with a previously described sample (mp 191.5–193 °C) by a mmp determination and by comparison of IR and NMR spectra.

Preparation of 2,3-Dimethylbromobenzene (8). A. From the Aniline 10. Following a general procedure described previously,[6a] a cold (0 °C) slurry of 268.2 g (1.20 mol) of $CuBr_2$ in 1.5 L of acetonitrile was saturated with NO.[13] Then the ice cooling bath was replaced with a dry ice–CCl_4 bath, and a solution of 145.3 g (1.20 mol) of the aniline **10** in 300 mL of acetonitrile was added, dropwise and with stirring during 20 min. The resulting mixture was allowed to warm to 25 °C with stirring during the next 1.5 h while a slow stream of NO was continually passed through the solution. The resulting mixture was allowed to stand overnight and then it was poured into 2.5 L of water and extracted with five 200-mL portions of pentane. After the combined organic extracts had been washed with aqueous 10% NaOH and with aqueous NaCl, they were dried and then decolorized by filtration through a short column of alumina. The resulting pentane solution was distilled to separate 162.1 g (73%) of the bromide **8** as a colorless liquid, bp 101–103 °C (20 mm); n^{25}_D 1.5576. Redistillation through a Vigreux column afforded a sample of the xylyl bromide **8** as a colorless liquid with the same boiling point, n^{25}_D 1.5588 [lit.[12] n^{25}_D 1.5605]: NMR (neat) δ 6.5–7.5 (3 H, m, aryl CH), 2.15 (3 H, s, methyl), and 2.02 (3 H, s, methyl); IR (CCl_4), no bands in the 3- or 6-μm regions attributable to OH or C=O.

In a typical experiment involving diazotization of the aniline **10** in aqueous solution,[6d] a cold (0–3 °C) solution of 30.3 g (250 mmol) of the aniline **10** and 49 g (500 mmol) of sulfuric acid in 200 mL of water was treated with a solution of 17.5 g (250 mmol) of $NaNO_2$ in 30 mL of water while the temperature was kept at 0–3 °C by addition of ice and external cooling. This solution of the diazonium salt was added, slowly and with stirring, to a cold (0 °C) solution of 80 g (560 mmol) of CuBr in 180 mL of aqueous 48% HBr. The resulting solution was allowed to warm to 25 °C and then it was steam distilled. The bromide **8**, isolated from the steam distillate in the usual way, amounted to 16.0 g (34.5%), bp 210–214 °C, n^{25}_D 1.5721; the other major product present in the crude reaction mixture was the phenol **9**.

B. From the Phenol 9. Following a general procedure for the conversion of phenols to aryl bromides,[15] 176 g (1.1 mol) of Br_2 was added, dropwise and with stirring during 1.5 h, to a cold (0 °C) suspension of 288 g (1.1 mol) of Ph_3P in 250 mL of acetonitrile. After the resulting suspension had been stirred in an ice bath for an additional 30 min, a solution of 122.2 g (1.0 mol) of the phenol **9** in 125 mL of acetonitrile was added, dropwise and with stirring during 30 min. Then the slurry was allowed to warm to 25 °C and stirring was continued for 48 h. The acetonitrile was removed by distillation under reduced pressure (water aspirator) and the temperature of the residue in the stillpot was rapidly raised to 320 °C (voluminous evolution of HBr occurred at ca. 300 °C) resulting in distillation of the crude product, by 200–225 °C. The crude liquid product was washed successively with aqueous 20% NaOH and with aqueous NaCl and these aqueous washes were each extracted with pentane. The combined organic phases were dried, decolorized by filtration through a short column of alumina, and distilled to separate 76.6 g (41.1%) of the bromide **8**, bp 212–214 °C; n^{25}_D 1.5585.

Preparation of 1,8-Bis(2,3-dimethylphenyl)anthracene (7). A solution of 150.0 g (0.81 mol) of 2,3-dimethylbromobenzene in 1.0 L of THF was added, dropwise and with stirring during 5 h, to 23.09 (0.95 mol) of Mg turnings. During the addition, the temperature of the reaction mixture was kept at 25–30 °C by intermittent cooling with a water bath. After the addition was complete, the reaction mixture was allowed to stir overnight and then analyzed.[11] The solution (total volume 1.23 L) was 0.52 M in Grignard reagent corresponding to a 80% yield. This solution of Grignard reagent (0.648 mol) was added, dropwise and with stirring during 3 h, to a refluxing solution of 32.19 g (0.130 mol) of the dichloride **3**, 250 mg (0.96 mmol) of $Ni(acac)_2$, and 505 mg (1.92 mmol) of Ph_3P in 500 mL of THF. After the addition was complete, the black (colloidal Ni) reaction mixture was refluxed

(15) Typical procedures for the conversion of a phenol to an aryl bromide are given by Schaefer, J. P.; Higgins, J. *J. Org. Chem.* **1967**, *32*, 1607.

for an additional 3 h, stirred at 25 °C for 10 h, and then quenched by the addition of excess aqueous 3 M HCl. The reaction mixture was partitioned between water and CH_2Cl_2 and the combined organic layers were dried and concentrated. The residual brown solid (44 g, mp 201–210 °C) was recrystallized from a CH_2Cl_2–acetone mixture to separate 35.05 g of the hydrocarbon **7**; concentration of the mother liquors afforded an additional 6.45 g (total yield 41.50 g or 83%), mp 219–220 °C. The spectral properties of the hydrocarbon **7** (a slowly equilibrating mixture of cis and trans isomers) follow: IR ($CHCl_3$), no OH or C=O absorption in the 3- or 6-μm regions; ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.8–8.6 (14 H, m, aryl CH), 2.17 and 2.25 (6 H, pair of singlets, Me groups of two isomers), 1.67 and 1.75 (6 H, pair of singlets, Me groups of two isomers); ^{13}C NMR ($CDCl_3$, multiplicity on off-resonance decoupling, pairs of peaks for cis and trans isomers listed together) 141.1 and 140.9 (s, 2 C), 139.9 (s, 2 C), 136.6 and 136.1 (s, 2 C), 135.2 and 134.7 (s, 2 C), 131.5 and 131.4 (s, 2 C), 130.9 and 130.6 (s, 2 C), 128.7 (d, 2 C), 128.1 and 128.0 (d, 2 C), 127.2 (d, 2 C), 126.3 (d), 125.3 and 125.2 (d, 2 C), 125.1 and 125.0 (d, 2 C), 124.91 and 124.89 (d, 2 C), 124.5 (d), 20.3 and 20.2 (q, 2 C), 17.0 and 16.7 ppm (q, 2 C); mass spectrum, *m/e* (relative intensity) 387 (33), 386 (100, M^+), 371 (13), 193 (9), 170 (8), 169 (8); UV maxima, nm (cyclohexane, ϵ), 253 (shoulder, 76 700), 260 (114 000), 332 (3310), 348 (6670), 366 (10 200), 386 (8980). HPLC analysis of this sample employing a 0.46 × 25 cm column packed with 10-μm silica gel and eluted with an ether–hexane mixture (1:99 v/v) showed two well-resolved peaks for the two isomers with retention times of 9.86 and 12.70 min. The relative areas for the two peaks varied from ca. 1:3 immediately after preparation of the solution to ca. 2:1 after the solution had been allowed to stand for 24 h. Similar changes in area were observed in the pairs of Me peaks in the NMR spectrum.

Anal. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 92.90; H, 6.95.

NMR Study of the Equilibration of the Two Diastereoisomers of 1,8-Bis(2,3-dimethylphenyl)anthracene (7). The ^{1}H NMR (300 MHz) spectrum of the hydrocarbon **7** as a 0.010 M solution in nitrobenzene-d_5 at 27 °C exhibited peaks at δ 6.89–8.53 (14 H, m, aryl CH), 2.08 and 2.19 (6 H, s, Me groups of two isomers), and 1.68 and 1.75 (6 H, s, Me groups of two isomers). Each of the sets of Me peaks exhibited an area ratio of 5:4 (high field:low field) at 27 °C. ^{1}H NMR spectra (300 MHz) of this solution were obtained at the following temperatures: 413, 423, 433, 438, and 443 K. Instrumental limitations prevented us from collecting data above this temperature; at this upper temperature limit each of the pairs of methyl peaks had broadened but had not yet coalesced. As the temperature was raised from 27 °C to 170 °C (443 K) the peak separation changed from 22.99 Hz to 18.15 Hz for the higher field pair of peaks and from 31.94 Hz to 22.94 Hz for the lower field pair of peaks. At each temperature studied, the chemical shift differences, the peak widths at half height, and the "depth of valley" for each pair of Me peaks was measured. The spectrum measured at 27 °C (300 K) was used to measure the "slow-exchange" limit; the higher field pair of methyl groups were located at 503.57 Hz (A) and 526.47 Hz (B) and the lower field pair of methyl groups were at 624.98 Hz (A) and 656.92 Hz (B). Previously described techniques were used to simulate the spectra of each pair of methyl groups for various preexchange lifetimes, τ, and various mole fractions[14c] of the two isomers responsible for each pair of peaks. The values for τ (in ms) and the mole fraction of the isomer exhibiting peak A of the higher field pair of methyl peaks at various temperatures were 413 K, 90.2 and 0.477; 423 K, 50.0 and 0.456; 433 K, 35.2 and 0.4597; 438 K, 31.03 and 0.4594; 443 K, 27.52 and 0.4617. The values for τ (in ms) and the mole fraction of the isomer exhibiting peak A of the lower field pair of methyl peaks at various temperatures were 413 K, 91.1 and 0.4547; 423 K, 55.8 and 0.4612; 433 K, 31.73 and 0.4622; 438 K, 26.42 and 0.4619; 443 K, 23.54 and 0.4633. From these data the average Arrhenius activation energy for the interconversion of the two isomers was calculated to be 16.3 (ca. 2.0)[7] kcal/mol.

Preparation of 1,8-Bis(2,3-dimethylphenyl)-9,10-anthraquinone (11). A mixture of 20.0 g (51.8 mmol) of the 1,8-dixylylanthracene **7**, 80.0 g (272 mmol) of potassium dichromate, 500 mL of chlorobenzene, 250 mL of water, 200 mL of HOAc, and 50 mL of concentrated sulfuric acid was refluxed with stirring for 10 days. After the resulting mixture had been cooled and extracted with three 100-mL portions of CH_2Cl_2, the combined organic extracts were washed with water, dried, and concentrated to leave 20.5 g of dark yellow solid, mp 235–260 °C. This crude product was chromatographed on silica gel with CH_2Cl_2–hexane eluent (1:1 v/v) to separate early fractions containing the quinone **11** and later fractions containing the more polar oxidation product, lactone **13**. The very polar products were not eluted from the chromatography column.

Concentration of the appropriate early chromatography fractions and subsequent recrystallization from a $CHCl_3$–acetone mixture separated 11.2 g (52.1%) of the anthraquinone **11** as a yellow solid, mp 269.5–270.5 °C. The spectral properties of the quinone **11** follow: IR ($CHCl_3$) 1674 cm^{-1} (quinone C=O); ^{1}H NMR (60 MHz, $CDCl_3$) δ 8.3–8.5 (2 H, m, aryl CH), 6.8–7.9 (10 H, m, aryl, CH), and 4 methyl signals (ca. 3 H each corresponding to two isomers) at 2.25, 2.23, 1.95, and 1.88; ^{13}C NMR ($CDCl_3$, multiplicity measurement prevented by insolubility of sample, the number of peaks observed suggests that the material is a mixture of cis and trans isomers) 184.6, 184.0, 143.2, 140.8, 140.4, 137.5, 137.4, 136.5, 134.5, 134.2, 134.0, 133.9, 133.4, 133.1, 132.1, 131.8, 128.8, 128.7, 126.9, 126.2, 126.1, 125.8, 124.9, 124.8, 20.4, 17.0, 16.9 ppm; mass spectrum, *m/e* (relative intensity) 417 (15), 416 (46, M^+), 401 (74), 399 (42), 398 (100), 383 (15), 369 (5), 208 (14), 193 (11), 179 (11), 178 (15), 165 (7); UV maxima, nm (cyclohexane, ϵ), 258 (51 000), 332 (4200).

Anal. Calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.54; H, 5.89.

Concentration of the appropriate later chromatographic fractions followed by recrystallization from a $CHCl_3$–ether mixture afforded 4.3 g (19%) of the keto lactone **13** as fine colorless needles, mp 261.8–262.5 °C. The spectral properties of the product follow: IR ($CHCl_3$), 1720 (γ-lactone), 1666 cm^{-1} (conjugated ketone); ^{1}H NMR (60 MHz, $CDCl_3$) δ 8.3–8.5 (2 H, m, aryl CH), 6.7–7.9 (10 H, m, aryl CH), 5.95 (1 H, s, benzylic CH-O), three 3 H singlets (aryl methyl) at 2.38, 2.15, 2.08; ^{13}C NMR ($CDCl_3$, multiplicity determined by DEPT), 182.8 (s), 167.1 (s), 144.4 (s), 139.5 (s), 138.7 (s, 2C), 137.6 (s), 136.8 (s), 136.5 (s), 135.8 (s), 135.5 (d), 133.9 (s), 133.6 (d), 132.0 (s), 131.2 (d), 131.0 (d), 130.1 (d, 2 C), 129.7 (d), 129.5 (d), 129.1 (s), 127.5 (d), 126.9 (d), 126.3 (d), 125.6 (d), 124.8 (d), 67.3 (d), 20.6 (q), 20.5 (q), 17.3 ppm (q); mass spectrum, *m/e* (relative intensity) 431 (21), 430 (81, M^+), 412 (47), 386 (29), 385 (23), 369 (39), 51 (24), 49 (100); UV maxima, nm (cyclohexane, ϵ), 230 (31 800), 248 (24 500), 283 (shoulder, 12 500), with intense end absorption (22 200 at 210 nm).

Anal. Calcd for $C_{30}H_{22}O_3$: C, 83.70; H, 5.15. Found: C, 83.46; H, 5.30.

Preparation of 1,8-Bis(2,3-dimethylphenyl)-9-anthrone (12). To a refluxing mixture of 10.0 g (24.0 mmol) of the dixylyl quinone **11**, 10.0 g (84.3 mmol) of grannular tin, and 300 mL of HOAc was added, dropwise and with stirring during 2 h, a solution of 80 mL of aqueous 12 M HCl in HOAc. The resulting pale yellow solution was refluxed with stirring for an additional hour during which time some colorless precipitate formed. The resulting slurry was poured into an ice–water mixture and the crude product was collected on a filter. The crude anthrone **12** amounted to 9.6 g (98%) of off-white powder, mp 207–218 °C dec. The material was chromatographed on silica gel with a CH_2Cl_2–hexane eluent (2:3 v/v) to separate 0.4 g (5%) of the diarylanthracene **7** in the early fractions. Later fractions were combined and recrystallized from a $CHCl_3$–ether mixture to separate 8.60 g (89%) of the pure anthrone **12** as a colorless powder, mp 226.5–227.5 °C: IR ($CHCl_3$) 1670 cm^{-1} (conjugated C=O); ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.8–7.5 (12 H, m, aryl CH), 4.28 (2 H, s, methylene), 2.20 (6 H, s, Me), 1.95 (3 H, s, Me), 1.83 (3 H, s, Me); ^{13}C NMR ($CDCl_3$, multiplicity determined by a DEPT), both the cis and trans isomers are present in this sample) 187.2 (1 C, s) 185.7 (1 C, s), 142.8 (1 C, s), 142.5 (1 C, s), 141.7 (1 C, s), 141.1 (1 C, s), 139.7 (1 C, s), 139.5 (1 C, s), 136.1 (1 C, s), 135.9 (2 C, s), 134.0 (1 C, s), 133.6 (2 C, s), 133.4 (1 C, s), 133.3 (1 C, s), 130.7 (1 C, d), 130.3 (1 C, d), 130.1 (1 C, d), 130.0 (1 C, d), 128.2 (2 C, d), 127.1 (1 C, d), 126.7 (1 C, d), 126.4 (1 C, d), 126.0 (1 C, d), 124.5 (1 C, d), 124.3 (1 C, d), 34.4 (1 C, t), 34.3 (1 C, t), 20.4 (2 C, q), 17.1 (1 C, q), 17.0 ppm (1 C, q); mass spectrum, *m/e* (relative intensity) 403 (10), 402 (33, M^+), 388 (31), 387 (96), 385 (46), 384 (100), 370 (17), 369 (39), 355 (8), 353 (8), 282 (11), 279 (16), 201 (17), 193 (12), 186 (15), 185 (14),

178 (29); UV maxima, nm (cyclohexane, ϵ), 304 (shoulder, 10500), 260 (26900).

Anal. Calcd for $C_{30}H_{26}O$: C, 89.51; H, 6.51. Found: C, 89.85; H, 6.66.

Preparation of the 9-Acetoxy-1,8-dixylylanthracenes 14. To a slurry of 2.00 g (4.97 mmol) of the anthrone **12** in 30 mL of collidine was added 10 mL of acetic anhydride and 0.20 g (1.63 mmol) of 4-(dimethylamino)pyridine. The resulting mixture was heated to 95 °C for 15 min during which time the suspension first changed to a clear solution and then a colorless precipitate formed. The reaction mixture was poured into cold aqueous HCl and the resulting mixture was extracted with CH_2Cl_2. The organic layer was dried and concentrated to leave a brown viscous liquid that was triturated with acetone. The residual pale brown solid (1.95 g) was extracted with 15 mL of chloroform to leave 0.60 g of mixture of the cis acetates **14b** and **14c**, mp 310–315 °C. The soluble material from this extraction was concentrated and chromatographed on silica gel with a hexane–CH_2Cl_2 eluent (1:1 v/v) to separate early fractions containing (NMR analysis) the minor cis acetate **14c**, middle fractions containing the trans acetate **14a**, and late fractions containing the major cis acetate **14b**. Within an hour the early and late fractions each contained an equilibrium mixture of the cis acetates **14b** and **14c**, yield 0.21 g (total yield 0.81 g or 37%) of pale yellow powder, mp 315–316 °C. The middle chromatographic fractions were concentrated to separate 0.48 g (22%) of the trans acetate **14a** as a yellow powder, mp 314.5–316 °C. Since all the isomers **14** interconvert readily when heated above 100 °C, the final melting point of any sample is the melting point of the high melting cis isomer **14b**. This cis (**14b**) and trans (**14a**) acetates could each be recrystallized from a warm mixture of acetone and $CHCl_3$ without cis–trans isomerization. Recrystallization of the cis material separated the more abundant (and less soluble) acetate **14b** as colorless needles, mp 315–316 °C, while recrystallization of the trans isomer gave the product **14a** as pale yellow prisms, mp 315–316 °C.

The spectral properties of the cis isomer **14b** (a mixture of **14b** and **14c** in solution) follow: IR (KBr pellet) 1760 cm^{-1} (acetate C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.50 (1 H, s, aryl CH), 8.00 (2 H, d, J = 8.5 Hz, aryl CH), 7.44 (2 H, d of d, J = 6.8 and 8.5 Hz, aryl CH), 6.9–7.2 (8 H, m, aryl CH), 2.29 and 2.23 (6 H, 2 s in ratio 9:1, aryl Me), 1.88 and 1.87 (6 H, 2 s in ratio 1:9, aryl Me), 0.22 and 0.12 (3 H, 2 s in ratio 1:9, acetate Me); mass spectrum, m/e (relative intensity) 444 (9.2, M^+), 403 (34), 402 (100), 386 (9.2), 370 (4.1), 369 (4.1), 43 (6.6); UV maxima, nm (cyclohexane, ϵ), 257 (shoulder, 64100), 264 (95300), 326 (shoulder, 1410), 345 (3170), 358 (6210), 376 (9740), 397 (8500).

Anal. Calcd for $C_{32}H_{28}O_2$: C, 86.45; H, 6.35. Found: C, 86.33; H, 6.36.

The spectral properties of the trans isomer **14a** follow: IR ($CHCl_3$), 1760 cm^{-1} (acetate C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.52 (1 H, s, aryl CH), 8.03 (2 H, d of d, J = 3 and 7 Hz, aryl CH), 7.47 (2 H, m, aryl CH), 7.0–7.2 (8 H, m, aryl CH), 2.31 (3 H, s, aryl Me), 2.28 (3 H, s, aryl Me), 1.99 (3 H, s, aryl Me), 1.87 (3 H, s, aryl Me), 0.24 (3 H, s, acetate Me); mass spectrum, m/e (relative intensity) 444 (9.7, M^+), 403 (33), 402 (100), 386 (11), 43 (22); UV maxima, nm (cyclohexane, ϵ), 258 (shoulder, 81500), 264 (117000), 327 (shoulder, 1570), 347 (3460), 360 (7100), 378 (10900), 400 (9500); ^{13}C NMR [$CDCl_3$, multiplicity determined by a DEPT] 170.3 (s), 143.8 (s), 143.5 (s), 142.7 (s), 137.5 (s), 137.0 (s), 136.7 (s), 136.2 (s), 135.7 (s), 133.7 (s), 132.9 (s), 132.3 (s), 130.2 (d), 130.1 (d), 128.5 (d), 128.3 (d), 128.2 (d), 128.03 (d), 127.96 (d), 127.1 (d), 126.5 (d), 125.1 (s), 124.9 (d), 124.6 (d), 124.3 (d), 123.8 (d), 123.6 (s), 20.5 (q), 20.3 (q), 17.3 (q), 17.2 (q), 16.6 ppm (q).

Anal. Calcd for $C_{32}H_{28}O_2$: C, 86.45; H, 6.35. Found: C, 86.48; H, 6.36.

Preparation of 9-Methyl-1,8-dichloroanthracene (18). A cold (0 °C) solution of 15.00 g (57.0 mmol) of the anthrone **16** in 300 mL of THF was added, dropwise and with stirring during 30 min, to 50 mL (85 mmol) of a cold (0 °C) 1.70 M solution of MeMgBr in THF. The resulting deep red solution was stirred at 0 °C for 1 h and then hydrolyzed by the addition of aqueous 3 M HCl and extracted with CH_2Cl_2. After the organic extract had been washed with aqueous NaCl, dried, and concentrated, the residual off-white solid (14.1 g, mp 101–110 °C) was suspended in a solution of 1.0 mL of aqueous 12 M HCl in 100 mL of HOAc and the suspension was refluxed for 5 h. The mixture was partitioned between water and CH_2Cl_2 and the organic extract was washed successively with aqueous $NaHCO_3$ and with aqueous NaCl and then dried and concentrated. Recrystallization from a $CHCl_3$–acetone mixture afforded 9.3 g (63%) of the dichloride **18** as yellow prisms, mp 125.5–127 °C (lit.[16] mp 127 °C); IR ($CHCl_3$) no absorption corresponding to OH or C=O groups in the 3- or 6-μm region; ^1H NMR (60 MHz, $CDCl_3$) δ 7.1–8.1 (7 H, m, aryl CH), 3.35 (3 H, s, aryl Me); ^{13}C NMR [$CDCl_3$, multiplicity determined by a DEPT], 133.8 (1 C, s), 133.1 (2 C, s), 131.4 (2 C, s), 131.2 (2 C, s), 129.3 (2 C, d), 128.0 (2 C, d), 126.3 (2 C, d), 124.8 (2 C, d), 26.8 ppm (1 C, q); mass spectrum, m/e (relative intensity) 264 (12, M^+), 262 (63, M^+), 260 (100, M^+), 227 (23), 225 (72), 189 (60), 95 (45), 94 (43); UV maxima, nm (cyclohexane, ϵ), 263 (113,000), 335 (shoulder, 1300), 350 (2610), 369 (5240), 389 (8090), 412 (6640).

Preparation of the 9-Methyl-1,8-dixylylanthracene 15. A. From the Anthrone 12. To a cold (0 °C) solution of 2.00 g (4.97 mmol) of the dixylylanthrone **12** in 80 mL of THF was added, dropwise with stirring and cooling during 30 min, 2.7 mL of an ethereal solution containing[11] 5.13 mmol of MeLi. After the resulting orange solution (contains the enolate of anthrone **12**) had been stirred at 0 °C for 1 h, it was acidified with aqueous 3 M HCl and the final two-phase mixture was refluxed for 30 min. Then the mixture was partitioned between water and CH_2Cl_2 and the organic layer was washed with aqueous NaCl, dried, and concentrated. The residual yellow solid (2.2 g) contained (TLC analysis) a mixture of the anthrone **12** (major) and the anthracene **15** (minor). The crude product was subjected to the same addition–dehydration procedure two more times employing 2.0-mL and 1.5-mL portions of ethereal MeLi. The resulting crude product, 1.9 g of yellow solid, was chromatographed on silica gel with hexane–CH_2Cl_2 eluents (4:1 and 1:1 v/v). Combination and concentration of the appropriate early fractions followed by recrystallization from an acetone–$CHCl_3$ mixture separated 0.82 g (41%) of the anthracene **15** as a pale yellow solid, mp 214–215 °C. Combination of the appropriate later chromatographic fractions afforded 0.98 g (49%) of the starting anthrone **12**, mp 228–229 °C.

The anthracene **15**, a slowly equilibrating mixture of trans (**15a**) and cis (**15b**) isomers, has the following spectral properties: IR ($CHCl_3$) no absorption corresponding to OH or C=O groups in the 3- or 6-μm region; ^1H NMR (300 MHz, $CDCl_3$) δ 8.39 (1 H, s, aryl CH), 7.96 (2 H, d, J = 8.4 Hz, aryl CH), 7.40–7.45 (2 H, m, aryl CH), 6.96–7.08 (6 H, m, aryl CH), 2.28 (6 H, s, aryl Me), 1.96 and 1.95 (6 H total, 2 s, cis and trans aryl Me), 1.49 and 1.59 (3 H total, two s in ratio 1:2, cis and trans aryl Me); mass spectrum, m/e (relative intensity) 401 (32), 400 (88, M^+), 386 (35), 385 (100), 370 (26), 369 (18); UV maxima, nm (cyclohexane, ϵ), 262 (shoulder, 62500), 270 (86600), 350 (2740), 370 (5530), 390 (8510), 410 (7140).

Analysis of the mixture of stereoisomeric anthracenes **15** by HPLC employing a 120-cm column packed with 10-μm silica gel and eluted with an ether–hexane eluent (1:1200 v/v) showed two partially resolved peaks (75.06 and 79.13 min). The area ratio for these peaks varied from 3.5:1 immediately after a solution of the sample had been prepared to 1.8:1 after the solution had been allowed to stand for 48 h.

Anal. Calcd for $C_{31}H_{28}$: C, 92.95; H, 7.05. Found: C, 92.77; H, 7.08.

B. From the Dichloride 18. To a refluxing solution of 3.00 g (11.5 mmol) of the dichloride **18**, 25 mg (0.10 mmol) of $Ni(acac)_2$, and 50 mg (0.20 mmol) of Ph_3P in 100 mL of THF was added, dropwise and with stirring during 1 h, 110 mL of a THF solution containing 57.2 mmol of the Grignard reagent from 2,3-dimethylbromobenzene (**8**). The resulting dark brown reaction mixture was refluxed for an additional 4 h and then hydrolyzed by the addition of aqueous 3 M HCl and extracted with CH_2Cl_2. After the organic extract had been dried and concentrated, the residual brown liquid (3.2 g) was chromatographed on silica gel employing various mixtures of hexane and CH_2Cl_2 as eluents. The appropriate fractions were combined and recrystallized from an acetone–chloroform mixture to separate 1.29 g (28.1%) of the anthracene **15** as a yellow powder, mp 213.5–215 °C, that was

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identified with the previously described sample by comparison of NMR spectra and by a mmp determination.

Crystal Structure of *anti*-9-Acetoxy-*cis*-1,8-bis(2,3-dimethylphenyl)anthracene (14b). A crystal of the acetate **14b** was mounted and data were collected by procedures described in the supplementary material. The crystal belonged to the orthorhombic system and the data collected were consistent only with space groups *Pnma* or $Pna2_1$ (No. 62 or 33).[17] The crystal was centrosymmetric. Assuming the space group *Pnma*, a successful refinement was obtained. From a total of 2195 reflections collected in a complete octant of data, 1415 were accepted as statistically above background. In the data refinement, described in the supplementary material, 178 parameters were varied for the 1415 observations. The full-matrix least-squares refinement converged at $R = 0.0897$ and $R_w = 0.0744$. A perspective view of the acetate **14b** is presented in Figure 1. Lists of the final atomic coordinates and the bond distances and angles are available in the supplementary material as Tables 1 and 2.

Crystal Structure of 9-Acetoxy-*trans*-1,8-bis(2,3-dimethylphenyl)anthracene (14a). A crystal of the acetate **14a** was mounted and data were collected by procedures described in the supplementary material. The crystal belonged to the monoclinic system and the data collected were consistent only with space group $P2_1/c$ (No. 14).[17] From a total of 4249 reflections collected in a complete quadrant of data, 2594 were accepted as statistically above background. In the data refinement, described in the supplementary material, 335 parameters were varied for the 2594 observations. The full-matrix least-squares refinement converged at $R = 0.0789$ and $R_w = 0.0686$. A perspective view of the acetate **14a** is presented in Figure 2. Lists of the final atomic coordinates and the bond distances and angles are available in the supplementary material as Tables 3 and 4.

Supplementary Material Available: Descriptions of the determination of crystal structures for the trans acetate **14a** and the cis acetate **14b**, including tables of atomic coordinates for each compound (10 pages). Ordering information is given on any current masthead page.

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Notes

Polymers as Reagents and Catalysts. 12. Side Chain Bromination of Aromatic Molecules with a Bromine Complex of Poly(styrene-*co*-4-vinylpyridine)

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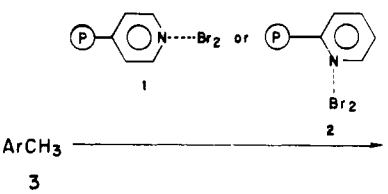
Polymer beads have found a wide range of uses in organic chemistry and can be chemically transformed so that they can act as reagents or catalysts, while the chemical reactivity of the reagent attached to the polymer backbone can also be changed.[1]

Free-radical introduction of halogens into alkanes is one of the most important methods for their functionalization.[2-5]

N-bromosuccinimide is one of the reagents often used for free-radical introduction of bromine into organic molecules, but the mechanism of bromination still seems to be an open question.[6-10]

Table I. The Effect of Reagent, Structure of the Organic Molecule, and Reaction Conditions on Side Chain Bromination



	conversion of 3, %			
	reagent 1		reagent 2	
$ArCH_3$	DBP[a]	hν[b]	DBP[a]	hν[b]
methylbenzene	96	70	87	40.5
1-methylnaphthalene	91	31	78	23.5
2-methylnaphthalene	87	22.5	71.5	23

[a] Conversions were determined by ^1H NMR, 20 mL of CCl_4, 1 mmol of $ArCH_3$, 1 g of **1** or **2**, 4-h reflux, 6 mg of DBP. [b] 10 mL of CCl_4, 1 mmol of $ArCH_3$, 1 g of **1** or **2**, 3-h irradiation with 125-W HPQ lamp.

Cross-linked polystyrene beads have usually been used for the preparation of reagents and catalysts, while cross-linked poly(vinylpyridine) or cross-linked copolymers of styrene and vinylpyridine have received much less attention, in spite of the fact that pyridine has wide application in organic synthesis by itself or in conjuction with other reagents. It has been demonstrated that a cross-linked copolymer of 4-vinylpyridine with styrene gave various types of complexes with halogens,[11,12] and its bromine complexes have been found to be able to introduce bromine into alkenes stereospecifically.[13] We now report our investigations of the reactivity of the bromine

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