Correlation of one carbon with the H_{17a} gives C_{17}, and thus assignment of the remaining H_{17b} is deduced. This proton identification is a good example of the effectiveness of going back and forth between ^1H and ^{13}C identifications through ^1H–^{13}C correlation. Only one methylene carbon remains unassigned in the ^{13}C NMR spectrum and must therefore be C_{18}. The chemical shifts of H_{18a} and H_{18b} are then deduced, and a confirmation of this result is found in the "COSY" spectrum, which shows that H_{18a} and H_{18b} are coupled together and with H_{17b}.

We have demonstrated that, following the procedure described above, it is possible to completely assign ^1H and ^{13}C NMR spectra of a natural product with only 0.1 mmol of material. This procedure is quite reliable, ^1H assignments were often verified a second time through ^1H–^{13}C correlation and, except for the positioning of H_{23}–H_{24}–H_{25} of the pyrrole, no comparison with parent compounds was made. Total 2-D NMR experimentation time (acquisition, computation, and plot of spectra) was 68 h, 14 h for "COSY" correlation (0.1 mmol), and 27 h for each δ–δ ^1H–^{13}C correlation (0.1 mmol).

Experimental Section

Production of X.14547 A. The antibiotic X.14547 A was produced and isolated from a strain of *Streptomyces antibioticus* NRRL 8167 according to ref 7b and 9.

NMR Spectra. All the spectra were recorded on a Brucker WM 400.

COSY. The two-dimensional correlated ^1H NMR experiment was also performed on the Brucker WM 400. The applied pulse sequence was $(\pi/2)$-(t1)-$(\pi/4)$-(FID, t2). The spectral width in F_1 and F_2 was 4000 Hz; the number of data points in F_2 was 2048, and 512 increments were recorded. Before Fourier transformation, the data were multiplied with unshifted sine bell. Zero filling was applied in each dimension. Total acquisition time was 4 h. The $\pi/2$ pulse was 8 μs.

^1H–^{13}C Shift Correlation. The experiment was also performed on the Brucker WM 400. The applied pulse sequence was $(\pi/2, {}^1H)$-$(t_{1/2})$-$(\pi, {}^{13}C)$-$(t_{1/2})$-(τ_1)-$(\pi/2, {}^1H; \pi/2, {}^{13}C)$-$(\tau_2)$-(BB, ^1H; FID, t_2) with $\tau_1 = 0.0033$ s and $\tau_2 = 0.00167$ s. The spectral width in F_1 was 2700 Hz and in F_2, 14 200 Hz; the number of data points in F_2 was 4096, and 256 increments were recorded. Before Fourier transformation, the data wre multiplied with sine-bell shifted $\pi/10$ in F_2, and Lorentz–Gauss in F_1. Zero filling was applied in each dimension. Total acquisition time was 17 h. The $\pi/2$ pulse was 11 μs for ^{13}C, and the decoupler $\pi/2$ pulse for ^1H was 47 μs.

^1H–^{13}C "Long Range" Shift Correlation. Id to ^1H–^{13}C shift correlation, except: $\tau_1 = 0.0417$ s, $\tau_2 = 0.0417$ s; the data were multiplied with sine-bell squared shifted $\pi/6$ in F_1 and $\pi/4$ in F_2 before Fourier transformation.

Registry No. 1, 66513-28-8.

Mechanistic Aspects of the Annelation Reactions of Benzocyclobutenedione Monoketals with Vinyllithium Reagents

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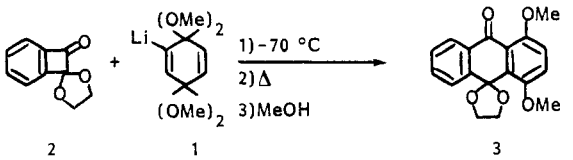
The mechanism of the annelation reaction of vinyllithium reagents with benzocyclobutenedione monoketals has been investigated. The results of these studies strongly support a mechanism involving addition of the organolithium reagent to form the lithium salt of a benzocyclobutenol followed by ring opening and cyclization to produce the tricyclic product. This reaction was examined with benzocyclobutenone and with the ethylene glycol and ethanedithiol monoketals of benzocyclobutenedione as the carbonyl components. The lithio derivatives of the bisketal of 2-bromobenzoquinone, the ethylene glycol ketal of α-bromocyclohexenone, and the ethanedithiol ketal of β-bromocyclohexenone were explored as the organometallic components. These studies have established the major mechanistic aspects and the scope of this annelation reaction.

In connection with past synthetic studies, a mild, regiospecific method for the construction of linear polycyclic systems was required. The reaction of a lithiated quinone bisketal, **1**,[1] with a benzocyclobutanedione monoketal, **2**,[2] to form **3**[3] reported in 1979 met this need; this type of



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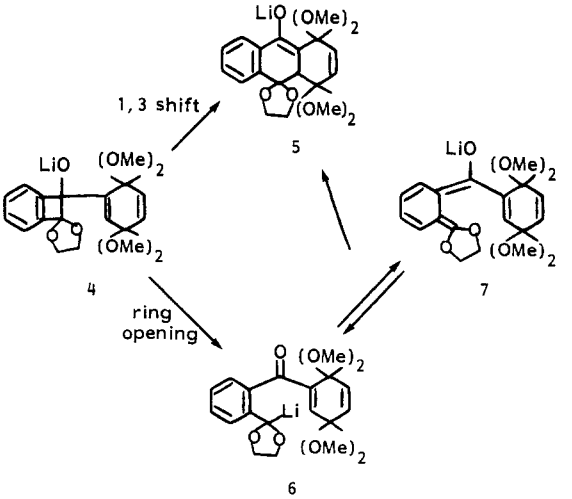
annelation was later employed in the synthesis of 4-demethoxydaunomycinone,[3a] daunomycinone,[3b] and α-citromycinone.[4] Applications to the synthesis of other polycyclic natural products would be facilitated by an understanding of the mechanism of the reaction. The studies reported herein provide this information for the

Scheme I. Mechanistic Possibilities for Annelation



(1) Manning, M. J.; Raynolds, P. W.; Swenton, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 5008. Swenton, J. S.; Jackson, D. K.; Manning, M. J.; Raynolds, P. W. *Ibid.* **1978**, *100*, 6182.

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(3) (a) Jackson, D. K.; Narasimhan, L.; Swenton, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 3989. (b) Swenton, J. S.; Anderson, D. K.; Jackson, D. K.; Narasimhan, L. *J. Org. Chem.* **1981**, *46*, 4825.

(4) Anderson, D. K.; Coburn, C. E.; Haag, A. A.; Swenton, J. S. *Tetrahedron Lett.* **1983**, *24*, 1329.

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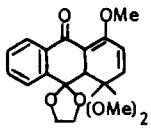
annelation reaction of vinyllithium reagents with protected benzocyclobutenediones.

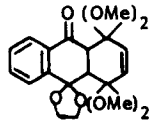
Several mechanistic possibilities were considered. The first step is undoubtedly attack of the organolithium species **1** on the carbonyl group of **2** to produce **4**, which has two obvious pathways available to it. A concerted, anion-accelerated [1,3]-sigmatropic shift[5] could occur, affording **5** directly. A second possibility is ring opening of **4** to form intermediates **6** or **7**, which can cyclize to **5** via a Michael addition or electrocyclic ring closure, respectively (Scheme I). Protonation and aromatization of **5** produces the observed product **3**. The possible intermediates **6** and **7** in the latter mechanistic sequence were of unknown stability. The literature prior to 1979 suggested that organolithium compounds similar to **6** fragmented to ethylene and the corresponding carboxylate under mild conditions.[6a-e] However, it was reported in 1979[6f] that certain conjugated anion salts of this type could be alkylated in high yield. The reaction of **1** with **2** under preparative conditions had always been accomplished by heating the initial −70 °C reaction mixture to reflux temperature. Thus, we first sought to establish whether any isolable intermediates intervened between reactants and annelation product **3**.

Low-Temperature Trapping Studies

When the reaction of **1** with **2** was conducted at −70 °C and quenched at 0 °C, two new products were isolated. One is reasonably stable and is assigned structure **8** on the



8



9

basis of spectroscopic and analytical data. Most informative is the ^{1}H NMR spectrum (200 MHz, C_6D_6), which shows a deshielded aromatic proton, δ 8.07; three other aromatic protons; two vinyl protons as an AB quartet at δ 6.29; the ethylene glycol ketal protons as multiplets; a vinyl methoxy group at δ 3.82; a methine hydrogen at δ 3.66; and two saturated methoxy groups at δ 3.39 and 3.17. The UV (CH_3OH) spectrum of **8** exhibits a maximum at 347 nm (ϵ 11 700) in addition to shoulders at 290 nm (ϵ 7300) and 260 nm (ϵ 10 000). The second product isolated is extremely labile, being converted to **8** on standing under seemingly neutral conditions. On the basis of its conversion to **8** and its ^{1}H NMR spectrum—which shows, in addition to the other expected absorptions, a deshielded aromatic absorption (δ 7.92 m, 1 H), a two-hydrogen AB-quartet in the vinyl region (δ 5.93 $\Delta\nu$ = 20.7 Hz, J = 10.3 Hz), and four saturated methoxy groups (δ 3.61, 3.41, 3.24, and 3.02)—this material is assigned structure **9**. Both **8** and **9** were converted to **3** by reaction with potassium *tert*-butoxide in tetrahydrofuran. Trapping experiments under a variety of conditions afforded no evidence for compounds derived directly from **4**, **6**, or **7**.

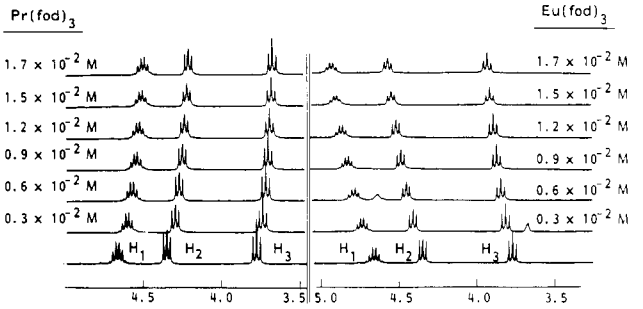
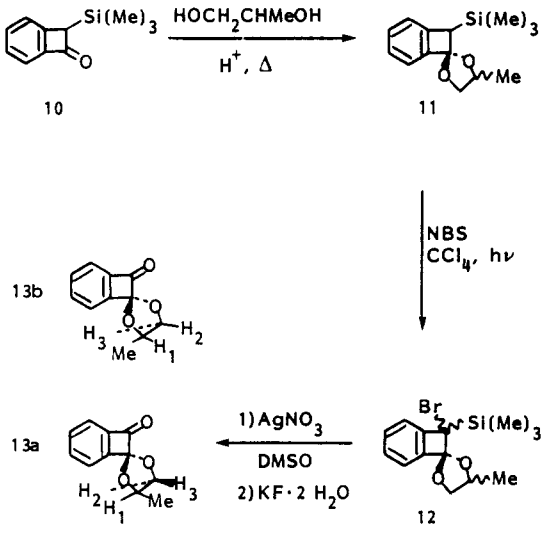


Figure 1. Representative 300-MHz ^{1}H NMR spectra of **13b** as a function of $Pr(fod)_3$ and $Eu(fod)_3$ concentration.

Scheme II. Synthesis of 13a and 13b



Stereochemical Studies

While the trapping experiments did not furnish evidence on the two basic mechanistic possibilities considered, stereochemical studies could provide more definitive information. The benzocyclobutenedione monoketals of 1,2-propanediol, **13a** and **13b**, were prepared as outlined in Scheme II from the readily available (trimethylsilyl)-benzocyclobutenone[7] **10**. The two products were separated by medium-pressure chromatography, and their relative stereochemistry was assigned as follows. The 300-MHz ^{1}H NMR spectra of **13a** and **13b** are quite similar, showing, in addition to the aromatic protons and the methyl groups ($\sim\delta$ 1.4, d, J = 6 Hz), a methine hydrogen as a multiplet ($\sim\delta$ 4.6), one methylene hydrogen as a doublet of doublets ($\sim\delta$ 4.3), and the second methylene hydrogen as a pseudotriplet ($\sim\delta$ 3.8) (Figure 1). The lowest field multiplet of each diastereomer collapsed to a clean doublet of doublets (J = 6, 6 Hz) on irradiation of the methyl resonance, confirming its assignment as the methine proton. Irradiation of the methyl signal also led to enhancement (10–20%) of this multiplet ($\sim\delta$ 4.6) and the higher field pseudotriplet ($\sim\delta$ 3.8). Since the nuclear Overhauser enhancement (NOE) is a function of distance from the irradiated proton,[8] the pseudotriplet must be the meth-

(5) (a) Franzus, B.; Scheinbaum, M. L.; Waters, D. L.; Bowlin, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 1241. (b) Thies, R. W.; Seitz, E. P. *J. Chem. Soc., Chem. Commun.* **1976**, 846. (c) Wilson, S. R.; Mao, D. T. *Tetrahedron Lett.* **1977**, 2559. (d) Wilson, S. R.; Mao, D. T. *J. Chem. Soc., Chem. Commun.* **1978**, 479. (e) Thies, R. W.; Seitz, E. P. *J. Org. Chem.* **1978**, *43*, 1050. (f) Miyashi, T.; Hazato, A.; Mukai, T. *J. Am. Chem. Soc.* **1982**, *104*, 891. (g) Zoeckler, M. T.; Carpenter, B. K. *Ibid.* **1981**, *103*, 766. (h) Danheiser, R. L.; Martinez-Davila, C.; Sard, H. *Tetrahedron* **1981**, *37*, 3943. (i) Cohen, T.; Bhupathy, M.; Matz, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 520.

(6) (a) Wharton, P. S.; Hiegel, G. A.; Ramaswami, G. *J. Org. Chem.* **1964**, *29*, 2441. (b) Berlin, K. D.; Rathore, B. S.; Peterson, M. *Ibid.* **1965**, *30*, 226. (c) Hines, J. N.; Peagram, M. J.; Whitham, G. H.; Wright, M. *J. Chem. Soc., Chem. Commun.* **1968**, 1593. (d) Hines, J. N.; Peagram, M. J.; Thomas, E. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2332. (e) Klemer, A.; Rodemeyer, G. *Chem. Ber.* **1974**, *107*, 2612. (f) Meyers, A. I.; Campbell, A. L. *Tetrahedron Lett.* **1979**, 4155.

(7) Chenard, B. L.; Slapak, C.; Anderson, D. K.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1981**, 179.

(8) Pasto, D. J.; Johnson, C. R. "Laboratory Text for Organic Chemistry"; Prentice-Hall Inc.: Englewood Cliffs, NJ, 1979; p 231.

Table I. Slopes from Plots of Chemical Shift Changes of Ketal and Methyl Protons in 13a and 13b vs. Concentration of Lanthanide Shift Reagents[10]

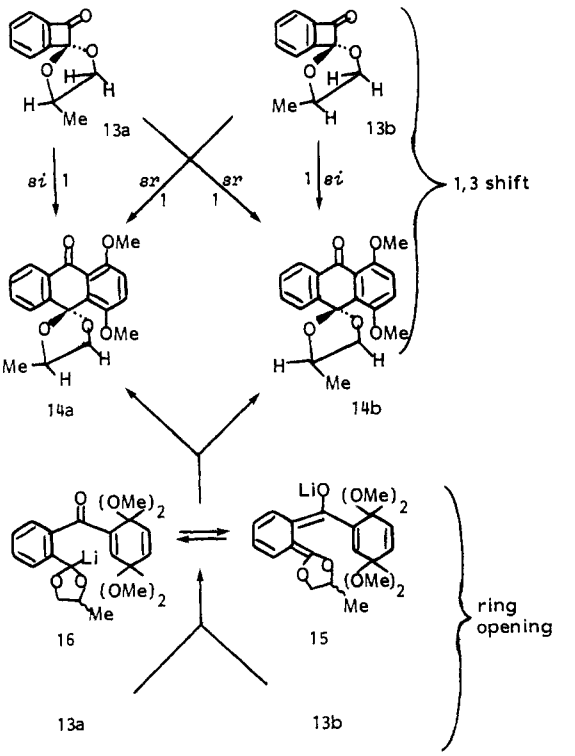
		slope	
	hydrogen	Eu(fod)$_3$	Pr(fod)$_3$
13a	H_1	-0.21	0.16
	H_2	-0.20	0.12
	H_3	-0.34	0.20
	CH_3	-0.19	0.13
13b	H_1	-0.20	0.15
	H_2	-0.17	0.13
	H_3	-0.13	0.09
	CH_3	-0.07	0.06

ylene proton syn to the methyl group.

After assignment of the ketal protons, lanthanide shift reagent studies could be used to determine the relative stereochemistry of **13a** and **13b**. The lanthanide shift reagents employed were the tris-octahedral europium and praseodymium complexes of 2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dione [Eu(fod)$_3$ and Pr(fod)$_3$]. In these experiments, standard solutions of the shift reagents were added to NMR samples of **13a** and **13b**, and the effects on the chemical shifts of the ketal and the methyl group protons were recorded. A representative series of spectra for **13b** are given in Figure 1, and the complete data are presented in Table I.[9] Several points must be established before the shift data can be reasonably interpreted. First, the site of complexation is assumed to be the carbonyl oxygen of **13a** and **13b** since the carbonyl group complexes stronger than an ether oxygen.[10] Second, the pseudocontact mechanism is assumed for the induced shift, and finally the lanthanide ion is assumed to complex on the less hindered side of the carbonyl group. These considerations, which are discussed thoroughly in the supplementary material section, lead to the conclusion that those ketal substituents on the same side as the carbonyl group will experience a greater shift than substituents away from the carbonyl group. In comparing **13a** and **13b**, **13a** showed the larger chemical shift changes for the methylene proton syn to the methyl group, H_3, and the methyl group; this diastereomer was assigned the stereochemistry with these two groups on the side of the carbonyl. For **13b**, relatively larger chemical shift changes were recorded for H_2 (the proton anti to the methyl group) and H_1 (the methine proton); this isomer was then assigned the stereochemistry shown.

With the two diastereomeric benzocyclobutenedione monoketals available in pure form, the stereochemical outcome of their annelation with 1 could be examined. Scheme III depicts the predicted stereochemical course of the two proposed mechanistic possibilities. If the reaction proceeds via ring-opened intermediates **15** or **16**, both **13a** and **13b** will produce the same mixture of diastereomeric products, **14a** and **14b**, provided bond rotation is faster than ring closure. If the reaction instead proceeds via the concerted 1,3 sigmatropic shift, different results would be predicted. The stereochemical course allowed by the Woodward–Hoffmann rules[11] is that involving suprafacial

Scheme III. Stereochemical Outcome of Two Proposed Mechanisms



migration along the allyl portion of the molecule and inversion of the migrating center (*si*). However, it has been demonstrated that suprafacial migration with retention of the migrating center (*sr*), although not formally allowed by the Woodward–Hoffmann rules, can occur in a concerted fashion and may be favored over a nonconcerted pathway by subjacent orbital stabilization.[12] If both the *sr* and *si* concerted pathways are operating in the reaction of **13a** or **13b** with 1, a mixture of **14a** and **14b** could be obtained from either pure starting material. However, one would not expect to obtain the same product mixture from both **13a** and **13b** except through coincidence. It has been proposed that in some cases diastereomeric reactants can follow different concerted reaction paths,[5g-i,13] but they do not tend to produce the same product ratios. This change in preferred mechanism is usually observed when there is steric hindrance impeding the reaction of one diastereomer via the allowed, concerted pathway.[13,14]

Reaction of 1 with pure **13a** and **13b**, or with a 1:1 mixture of the two compounds, gave a 1:1.5 mixture of two diastereomeric products as determined by high-pressure liquid chromatography. The products were characterized as the expected **14a** and **14b** by standard methods, but their relative stereochemistry was not established. These results do not rigorously eliminate the concerted mechanism, but do strongly disfavor it. To yield the same ratio of products via two concerted mechanisms, each diastereomer would have to react by a different major concerted reaction pathway to the same extent.

To rule out the simultaneous operation of two concerted mechanisms, the reaction of a second vinyllithium species

(9) (a) Rondeau, R.; Sievers, R. E. *Anal. Chem.* **1973**, *45*, 2145. (b) Sievers, R. E., Ed. "NMR Shift Reagents"; Academic Press: New York, 1973; p 230.

(10) Sanders, J. K. M.; Williams, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 641.

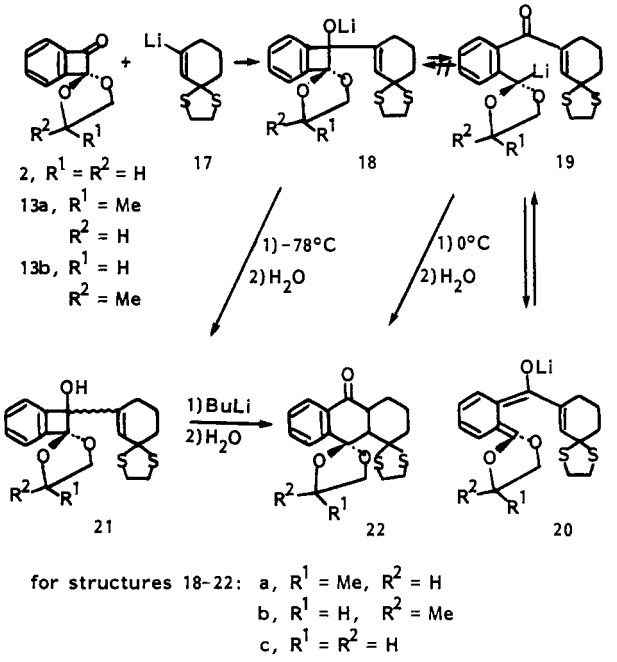
(11) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395. Hoffmann, R.; Woodward, R. B. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.

(12) (a) Berson, J. A. *Acc. Chem. Res.* **1972**, *5*, 406. (b) Berson, J. A.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 8917.

(13) (a) Roth, W. R.; Friedrich, A. *Tetrahedron Lett.* **1969**, 2607. (b) Berson, J. A.; Holder, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 2037.

(14) Marchand, A.; Lehr, R. "Organic Chemistry", *35-1*; Academic Press: New York, 1977; p 33.

Scheme IV. Reaction of 17 with Benzocyclobutenedione Monoketals



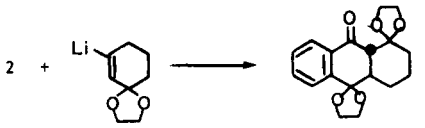
with **13a** and **13b** was required. Reaction of 17[15] with **2** gave **21c** or **22c**, depending on the length of reaction (Scheme IV). This same reaction, when conducted with **13a** and **13b** either individually or as a mixture, gave a 2.2:1 mixture of the diastereomeric products **22a** and **22b** as determined by 200-MHz ^{1}H NMR. This result makes the operation of two simultaneous concerted mechanisms for the annelation reaction exceedingly unlikely.

A final complication in the interpretation of these stereochemical studies is possible equilibration of intermediates **18a** and **18b** prior to rearrangement to form the annelation product. This could arise if a rapid, reversible equilibrium were established between **18** and **19**, followed by a slow reaction to give the annelation product, e.g., **18** $\rightleftharpoons$ **19** $\rightarrow$ **22**. The following set of experiments tends to rule out this possibility. Reaction of **17** with a mixture of **13a** and **13b** for a shorter period than utilized previously gave a mixture of **21a,b** and **22a,b**. The presence of four diastereomers of **21a,b** was evident from the four methyl doublets in the ^{1}H NMR 200-MHz spectrum of the material isolated by chromatography. However, when **17** was reacted with **13b** and the benzocyclobutenol fraction was isolated, the ^{1}H NMR spectrum showed the presence of only two diastereomers of **21a,b**. Had a rapid equilibration (via some process such as **18** $\rightleftharpoons$ **19**) occurred prior to the annelation step, reaction of **17** with **13b** would have given **21a,b** as a mixture of four diastereomers rather than the mixture of two diastereomers observed.

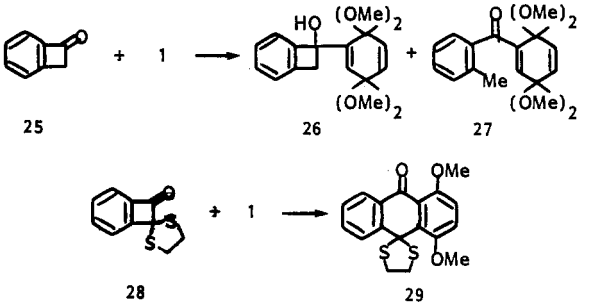
Summary

Evidence has been provided through stereochemical studies and trapping experiments that the annelation exemplified by the reaction of **1** with **2** proceeds via a mechanism involving irreversible ring opening of the benzocyclobutenoxide anion to form intermediates such as **6** or **7** (Scheme I), which then cyclize to form the observed product. For this type of reaction, there is no evidence that an anion-accelerated concerted [1,3]-shift mechanism is important.

Three different types of vinyl organolithium reagents have been reacted with **2** to afford tricyclic products: **1**, **17** (Scheme IV), and **23**.[16]



The assignment of the trans ring junction stereochemistry for **24** is based on the large coupling constant (d, J = 12.8 Hz) for the methine hydrogen adjacent to the carbonyl group and should be considered tentative. Although a variety of vinyllithium components react successfully in the annelation reactions, the nature of the benzocyclobutenone appears to be quite restricted. Benzocyclobutenedione[2] does not react with **1** to yield the respective anthraquinone.[1] Benzocyclobutenone[17] reacts with **1** to yield a mixture of the benzocyclobutenol **26** and ring-opened product **27**, but no tricyclic annelation product. The only other benzocyclobutenone derivative found to undergo successful annelation was the ethanedithiol monoketal of



benzocyclobutenedione **28**, which produced **29** in 46% yield.[18] It seems that the intermediate from opening of the benzocyclobutenoxide ring must be reactive enough to effect the final cyclization reaction. Intermediates of the required reactivity are those resulting from vinyllithium addition to **2**, **13**, or **28**.

These reported annelation reactions comprise a convergent method of assembling polycyclic ring systems under mild conditions and should complement the well-known thermal variants of benzocyclobutene intramolecular annelation reactions. Products from our annelation reaction have interesting synthetic possibilities since the carbonyl groups of the product are often chemically differentiated. For example, the three carbonyl groups of **22** are present in three different forms and in principle can be selectively functionalized in a number of different sequences.

Experimental Section[19]

5-Methoxyspiro[anthracene-9(8a*H*),2′-[1,3]dioxolane]-8,10-dione 8-(Dimethyl acetal) and 4a,9a-Dihydrospiro[anthracene-9(4*H*),2′-[1,3]dioxolane]-1,4,10-trione, 1,4-Bis(dimethyl acetal) (8 and 9). A solution of 3,3,6,6-tetramethoxy-1-bromocyclohexa-1,4-diene (0.087 g, 0.31 mmol) in THF (4 mL) under argon was cooled to −78 °C, and 1.68 M *n*-BuLi in hexane (200 μL, 0.34 mmol) was added slowly. After stirring for 20 min, **2** (0.045 g, 0.26 mmol) was added. Stirring was continued for 20 min at −78 °C and then for 40 min at 0 °C. After addition of 5% $NaHCO_3$ (2 mL), the layers were separated and the organic phase was worked up as usual to afford a crude yellow oil, which was chromatographed on neutral activity III alumina (1 × 15 cm

(15) Shih, C.; Swenton, J. S. *J. Org. Chem.* **1982**, *47*, 2825.

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(17) Cava, M. P.; Margold, D.; Muth, K. *J. Org. Chem.* **1964**, *29*, 2947 and references cited therein.

(18) We thank Dr. D. K. Anderson for performing this experiment.

column, 25% EtOAc/PE as eluant). Elution proceeded as follows: 40 mL, nil; 80 mL, 0.09 g of a yellow oil, which was crystallized from Et_2O to give 38% of **8** (0.033 g) as a white solid [mp 160–162 °C; IR (KBr) 1668 (s), 1410 (m), 1290 (m), 1245 (s), 1238 (s), 1202 (m), 1163 (m), 1136 (s), 1105 (m), 1060 (s), 1040 (m), 950 (s), 775 (s); ^1H NMR (200 MHz, $CDCl_3$) δ 8.09–8.05 (m, 1 H), 7.49–7.42 (m, 3 H), 6.29 (center of AB, $\Delta\nu$ = 58.4 Hz, J = 10.4 Hz, 2 H), 4.32–4.25 (m, 2 H), 3.96–3.90 (m, 2 H), 3.82 (s, 3 H), 3.66 (s, 1 H), 3.39 (s, 3 H), 3.17 (s, 3 H); exact mass calcd for $C_{19}H_{20}O_6$ m/e 344.1260, obsd 344.1259]. Anal. Calcd for $C_{19}H_{20}O_6$: C, 66.3; H, 5.9. Found: C, 65.7; H, 5.8.

From the mother liquor above was obtained 18% of **9** (0.017 g) as a very labile crystalline yellow solid, mp 132–134 °C. This compound was converted to **8** very easily, but an ^1H NMR spectrum (80 MHz, C_6D_6) of crude (ca. 90% pure) material was obtained: δ 7.94–7.89 (m, 1 H), 7.33–7.24 (m, 3 H), 5.93 (center of AB, $\Delta\nu$ = 20.7 Hz, J = 10.3 Hz, 2 H), 4.16–3.95 (m, 2 H), 3.78–3.65 (m, 3 H), overlapping absorptions with strong singlets at 3.61, 3.41, 3.24, and 3.02 and apparently one component of a doublet at 3.45 (total 12–14 H), 1.27 (d, J = 11.4 Hz, 1 H). This last signal may be from an impurity.

When the reaction was carried out as described above except for being stirred at 0 °C for 1 h rather than 40 min, **8** was obtained in 63% yield with no **9** isolated.

Conversion of 5-Methoxyspiro[anthracene-9(8a*H*),2′-[1,3]dioxolane]-8,10-dione, 8-(Dimethyl acetal) (8) to 1,4-Dimethoxyspiro[anthracene-9(10*H*),2′-[1,3]dioxolan]-10-one (3). A solution of **8** (5 mg) in THF (4 mL) was treated with potassium *tert*-butoxide (2 mg) and stirred for 3 h at room temperature. Addition of CH_3OH and workup in the usual manner gave 4 mg (89%) of crystalline **3**.

Trimethyl(4′-methylspiro[bicyclo[4.2.0]octa-1,3,5-triene-7,2′-[1,3]dioxolan]-8-yl)silane (11). A solution containing the (trimethylsilyl)benzocyclobutenone **10** (4.0 g, 21 mmol), distilled propylene glycol (5.1 mL, 70 mmol), and anhydrous *p*-toluenesulfonic acid (150 mg, 0.87 mmol) in dry benzene (200 mL) was heated to reflux with azeotropic removal of water. The reaction was monitored by GLC (5 ft × $^1/_8$ in. column of 3% FFAP on Chromosorb G at 125 °C). After 14 h at reflux, a 5% aqueous NaOH solution (30 mL) and water (60 mL) were added to the room-temperature reaction mixture. The layers were separated, and the organic layer was washed with water (30 mL) and brine (30 mL) and then dried through anhydrous $CaSO_4$. Removal of solvent yielded a light yellow oil, which was distilled through a short-path distillation apparatus to give 96% of **11** (5.0 g) as a light yellow oil: bp 76–82 °C/0.2 mm; IR (neat) 2940 (s), 2920 (s), 2850 (s), 1450 (m), 1240 (m), 835 (m); ^1H NMR ($CDCl_3$, 200 MHz) δ 7.22–7.02 (m, 4 H), 4.48–4.07 (m, 2 H), 3.68–3.27 (m, 2 H), 1.40–1.29 (m, 3 H), 0.07–0.02 (m, 9 H); exact mass calcd for $C_{14}H_{20}O_2Si$ m/e 248.1233, obsd 248.1230. Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.70; H, 8.12. Found: C, 67.61; H, 8.07.

(8-Bromo-4′-methylspiro[bicyclo[4.2.0]octa-1,3,5-triene-7,2′-[1,3]dioxolan]-8-yl)trimethylsilane (12). A suspension of **11** (5.8 g, 23 mmol) and *N*-bromosuccinimide (4.5 g, 25 mmol) in CCl_4 (125 mL) was heated to reflux under a static nitrogen atmosphere with concomitant irradiation by a 200-W incandescent bulb. After 30 min the reaction was judged complete, and the mixture was cooled to room temperature and poured into a cold 5% aqueous $NaHCO_3$ solution (60 mL). The layers were separated, and the aqueous layer was extracted with CCl_4 (2 × 30 mL). The combined organic phases were washed with brine (30 mL) and dried through anhydrous $CaSO_4$. Removal of solvent yielded 8.5 g of a crude yellow oil, which was used without further purification.

To obtain a pure sample of the diastereomers for analysis, crude material (0.5 g) was placed on a Florisil column (2 × 12 cm) and eluted with 3% Et_2O/PE. Product decomposition on the column was evident. Elution proceeded as follows: 0–15 mL, nil; 25–50 mL, 0.2 g of a light green oil [^1H NMR (CCl_4, 90 MHz), 7.4–6.9 (m, 4 H), 4.3–3.2 (m, 3 H), 1.35–1.05 (m, 3 H), 0.1–0 (m, 9 H); exact mass calcd for $C_{14}H_{19}O_2SiBr$ m/e 326.0332, obsd 326.0346].

4′-Methylspiro[bicyclo[4.2.0]octa-1,3,5-triene-7,2′-[1,3]dioxolan]-8-ones (13a/13b). A solution of silver nitrate (4.4 g, 26 mmol) and dry Me_2SO (45 mL) was heated to 60 °C under a static nitrogen atmosphere, the crude bromosilylcyclobutenone ketal **12** (3.8 g, 11.6 mmol) was added, and the solution was stirred for 6 h at 60 °C. A yellow precipitate formed immediately following the addition of **12**. After the reaction mixture cooled to room temperature, potassium fluoride dihydrate (1.8 g, 19 mmol) was added, and the mixture was stirred for 1 h. During this time, the mixture became black. The suspension was filtered through a Celite pad, which was washed with CH_2Cl_2 (40 mL). The filtrate was washed with water (3 × 50 mL) and brine (50 mL) and dried through anhydrous Na_2SO_4. Removal of solvent yielded an orange oil, which was placed on a Florisil column (2 × 12 cm) and eluted with 20% Et_2O/PE. Elution proceeded as follows: 0–30 mL, nil; 30–80 mL, 0.75 g (33% over the ketalization/bromination/oxidation steps) of a mixture of **13a** and **13b** as a colorless oil [IR (neat) 2970 (m), 1770 (s), 1345 (m), 1265 (s), 1140 (m), 1050 (m), 1035 (s), 1005 (s), 870 (m), 750 (s); exact mass calcd for $C_{11}H_{10}O_3$ m/e 190.0630, obsd 190.0608]. Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.47; H, 5.30. Found: C, 68.80; H, 5.42.

Purification of 13a from 13b. The mixture of two diastereomers (1.2 g) was placed on a Merck Lobar silica gel MPLC column (size B) and eluted with benzene. The elution proceeded as follows: 0–1.5 L, nil; 1.5–2.3 L, 120 mg of **13a**, the diastereomer with higher R_f; 2.3–3.4 L, 400 mg of a mixture of **13a** and **13b**; 3.4–4.5 L, 280 mg of **13b**, the diastereomer with the lower R_f, for a 67% recovery of material. The columns were monitored by silica gel TLC in which the plates were eluted twice in benzene. The material from the first and last fractions off the column were placed on EM silica gel preparative TLC plates and eluted with benzene (3×). The upper two-thirds (94 mg) of the band from **13a** and the lower two-thirds (150 mg) of the band from **13b** were collected. All other material was recycled through another MPLC column. The fractions from the preparative TLC plates were shown to be free of the other diastereomer by 300-MHz ^1H NMR but contained minor impurities and so were molecularly distilled (1 mm, 85–100 °C) to give pure samples, higher R_f diastereomer, **13a** [^1H NMR (300 MHz, $CDCl_3$) δ 7.78–7.74 (m, 1 H), 7.67–7.57 (m, 3 H), 4.64–4.53 (m, 1 H), 4.36 (d of d, J = 7, 7 Hz, 1 H), 3.84 (d of d, J = 7, 7 Hz, 1 H), 1.43 (d, J = 6.2 Hz, 3 H)] and lower R_f diastereomer, **13b** [^1H NMR (300 MHz, $CDCl_3$) δ 7.79–7.75 (m, 1 H), 7.67–7.57 (m, 3 H), 4.70–4.63 (m, 1 H), 4.35 (d of d, J = 7, 7 Hz, 1 H), 3.76 (d of d, J = 7, 7 Hz, 1 H), 1.45 (d, J = 6.2 Hz, 3 H)].

Lanthanide Shift Reagent Studies. Standard solutions of 0.294 M $Eu(fod)_3$ and 0.291 M $Pr(fod)_3$ in $CDCl_3$ were prepared. ^1H NMR samples containing pure **13a** (1.65×10^{-5} mol) in $CDCl_3$ (1 mL) and pure **13b** (1.24×10^{-5} mol) in $CDCl_3$ (1 mL) were prepared, and their spectra were recorded. The standard $Eu(fod)_3$ solution was added to each sample in 10-μL increments, and the spectrum was recorded after each addition. Second samples of pure **13a** and **13b** were prepared as above, and the standard $Pr(fod)_3$ solution was added in 10-μL increments.

1,4-Dimethoxy-4′-methylspiro[anthracene-9(10*H*),2′-[1,3]dioxolan]-10-ones (14a and 14b). A solution of 3,3,6,6-tetramethoxy-1-bromo-1,4-cyclohexadiene (0.14 g, 0.50 mmol) in dry THF (5 mL) was prepared under a static argon atmosphere. The solution was cooled to −78 °C, and a 1.58 M solution (350

(19) All melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 283-B grating spectrophotometer and are reported in cm^{-1}. ^1H NMR spectra were taken with a Varian EM-390 (90 MHz) and Bruker WP-200 (200 MHz) or Bruker (300 MHz) instruments. Chemical shifts are reported in ppm downfield (δ) from tetramethylsilane. Mass spectra and exact mass measurements were obtained by Mr. C. R. Weisenberger on a Consolidated Electronics MS-9 double-focusing mass spectrometer. Analytical samples were determined by Scandinavian Microanalytical Laboratory, Herlev, Denmark. Silica gel was from E. Merck Co., and florisil was from J. T. Baker Chemical Co. The following abbreviations were used throughout the experimental section: Me_2SO (dimethyl sulfoxide), *n*-BuLi (*n*-butyllithium), Et_2O (diethyl ether), PE (petroleum ether, 35–60 °C), EtOAc (ethyl acetate), and THF (tetrahydrofuran). Butyllithiums were titrated at −78 °C in tetrahydrofuran with triphenylmethane/hexamethylphosphoramide as indicator. Solvents were dried by distillation from calcium hydride, calcium sulfate, or sodium. Tetrahydrofuran was distilled from benzophenone ketyl and then dried with *n*-butyllithium in hexane as follows: 1–2 mg of triphenylmethane was added to the distilled tetrahydrofuran under argon and cooled to −78 °C and then treated with *n*-butyllithium until a faint pink color was obtained. Workup as usual consisted of extraction with CH_2Cl_2, drying the organic layer with $CaSO_4$, and concentration in vacuo.

μL, 0.55 mmol) of *n*-BuLi in hexane was added. This solution was stirred for 5 min at −78 °C, and a solution of the benzocyclobutenedione monoketals **13a,b** (0.80 g, 0.42 mmol) in dry THF (5 mL) was added. The resulting bright orange solution was stirred for 30 min at −78 °C. The solution was heated to reflux for 3 h and allowed to return to room temperature; then the reaction was quenched with CH_3OH (3 mL). Solvent was removed to yield an orange solid, which was dissolved in CH_2Cl_2 (10 mL) and washed with water (3 × 15 mL) and brine (15 mL). After drying through Na_2SO_4 and removing the solvent, an orange oil remained which was placed on a Florisil column (2 × 15 cm) and eluted with 50% Et_2O/PE. Elution proceeded as follows: 0–100 mL, nil; 100–250 mL, 84 mg (61% based on **13a,b**) of a yellow oil. This oil could be recrystallized from Et_2O/PE to yield a diastereomeric mixture: mp 106–108 °C; IR (KBr) 1665 (s), 1585 (m), 1475 (s), 1455 (m), 1435 (m), 1310 (s), 1280 (sh), 1265 (s), 1250 (s), 1080 (m), 1050 (s), 980 (s), 760 (m); exact mass calcd for $C_{19}H_{18}O_5$ *m/e* 326.1154, obsd 326.1151.

Separation of 14a and 14b. The oil obtained by chromatography of the crude reaction mixture was separated into its component diastereomers by HPLC on a Varian 5000 instrument using a silica gel column (25 cm) and 80% $CHCl_3$/PE as eluant. The relative amounts of **14a** and **14b** were determined by triangulation or by cutting and weighing the peaks. It was not determined which diastereomer actually corresponded to the major product.

1,4-Dimethoxy-9,10-anthraquinone. A solution of the annelation products **14a** and **14b** (168 mg, 0.54 mmol) in a 5% aqueous HCl solution (25 mL) was stirred for 16 h, then cooled to 0 °C, and neutralized with a 5% aqueous sodium hydroxide solution. The product was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic layers were washed with 20-mL portions of water and brine. After drying through anhydrous $CaSO_4$ and removing the solvent, a bright yellow solid remained. This solid was recrystallized from CH_2Cl_2/Et_2O to yield 120 mg (88%) of fluffy yellow crystals, mp 191–192 °C, identical with a known sample of 1,4-dimethoxy-9,10-anthraquinone.[3b]

8-(1,4-Dithiaspiro[4.5]dec-6-en-7-yl)spiro[bicyclo[4.2.0]-octa-1,3,5-triene-7,2′-[1,3]dioxolan]-8-ol (21c). A solution of 3-bromocyclohexenone 1,2-ethanediyl dithioketal[15] (186 mg, 0.74 mmol) in THF (13 mL) was prepared under an argon atmosphere and cooled to −78 °C; then a 1.6 M solution (515 μL, 0.8 mmol) of *n*-BuLi in hexane was added over 15 min. This was stirred for 15 min at −78 °C, and the benzocyclobutenedione monoketal **2** (100 mg) was added, causing the solution to become red. After stirring for 15 min at −78 °C, an aqueous saturated $NaHCO_3$ solution (10 mL) was added (solution becomes light yellow), and the mixture was allowed to return to room temperature. After separation of layers, the aqueous layer was washed with CH_2Cl_2 (5 mL). The organic layers were washed with water (5 mL) and brine (5 mL), and the solvent was removed to yield a yellow oil from which the product was crystallized with Et_2O/PE to yield 162 mg (82% based on **2**) of **21c** as light yellow crystals. Recrystallization from Et_2O/PE yielded 126 mg (64%) of white crystals, mp 137–138 °C [IR (KBr) 3440 (s), 2925 (s), 1340 (s), 1275 (m), 1260 (s), 1220 (m), 1145 (s), 1120 (m), 1075 (s), 1029 (s), 992 (m), 970 (m), 940 (m), 930 (m), 750 (s); ^1H NMR ($CDCl_3$, 200 MHz) δ 7.44–7.37 (m, 4 H), 5.99 (s, 1 H), 4.28–4.05 (m, 4 H), 3.75 (s, disappears on D_2O wash, 1 H), 3.34–3.23 (m, 4 H), 2.21–2.09 (m, 2 H), 1.83–1.72 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 148.3, 143.3, 136.8, 131.7, 130.1, 128.9, 123.2, 122.8, 113.1, 90.4, 65.9, 65.6, 64.9, 41.3, 39.9 (may be two overlapping carbon resonances), 25.7, 22.8; exact mass calcd for $C_{18}H_{20}O_3S_2$ *m/e* 348.0853, obsd 348.0847].

3′,4′,4′a,9′a-Tetrahydrodispiro[1,3-dioxolane-2,9′(2′*H*)-anthracene-1′(10′*H*),2″-[1,3]dithiolan]-10′-one (22c). A solution of 3-bromocyclohexenone 1,2-ethanediyl dithioketal (930 mg, 3.7 mmol) in dry THF (50 mL) was prepared under argon and cooled to −78 °C and then treated with a 1.6 M solution (2.8 mL, 4.5 mmol) of *n*-BuLi in hexane over 15 min. This solution was stirred for 20 min at −78 °C; then **2** (0.5 g, 2.84 mmol) was added. After being stirred for 20 min, the reaction mixture was allowed to warm to 0 °C and was stirred for 4.5 h. An aqueous saturated $NaHCO_3$ solution was added, causing the reaction mixture to fade to yellow, and the mixture was allowed to return to room temperature. After separation of the layers, the aqueous phase was washed with CH_2Cl_2 (10 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (25 mL) and brine (25 mL) and dried through Na_2SO_4. Removal of solvent yielded a yellow solid, which was recrystallized from CH_2Cl_2/Et_2O to yield 598 mg (60% based on **2**) of white crystals: mp 187–188.5 °C [IR (KBr) 2915 (m), 1678 (s), 1595 (w), 1285 (m), 1228 (s), 1138 (m, br), 1090 (m), 1063 (s), 1020 (m), 945 (m), 780 (m), 760 (m); ^1H NMR ($CDCl_3$, 200 MHz) δ 8.0 (unsymm d, *J* = 8 Hz, 1 H), 7.56–7.38 (m, 3 H), 4.38–4.02 (m, 4 H), 3.35–3.00 (m, 6 H), 2.41–2.29 (m, 2 H), 2.00–1.56 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 198.0, 142.8, 133.4, 132.0, 129.0, 126.6, 124.8, 108.5, 69.7, 65.0, 64.8, 53.8, 48.5, 42.6, 39.0, 38.2, 25.2, 23.7; exact mass calcd for $C_{18}H_{20}O_3S_2$ *m/e* 348.0855, obse 348.0841]. Anal. Calcd for $C_{18}H_{20}O_3S_2$: C, 62.04; H, 5.78. Found: C, 61.47; H, 5.82. In smaller runs of this reaction (50–150 mg of **2**), yields were 70–75% based on **2**.

8-(1,4-Dithiaspiro[4.5]dec-6-en-7-yl)-4′-methylspiro[bicyclo[4.2.0]octa-1,3,5-triene-7,2′-[1,3]dioxolan]-8-ols (21a,b). This mixture of the four diastereomers was prepared essentially as described for **21c** by reacting **17** with a ca. 40:60 mixture of **13a** and **13b**. The ^1H NMR spectrum (200 MHz, C_6D_6) shows methyl doublets (*J* = 6 Hz) of comparable intensity at δ 1.10, 1.06, 0.94, 0.93. When **17** was reacted with **13b** and the **21** fraction separated by Florisil chromatography, the ratio of the two high-field methyl doublets was 1:1. There was less than 5% of the diastereomers having methyl doublets at δ 1.10 and 1.06; exact mass calcd for $C_{19}H_{22}O_3S_2$ *m/e* 362.1010, obsd 362.1001.

3′,4′,4′a,9′a-Tetrahydro-4-methyldispiro[1,3-dioxolane-2,9′(2′*H*)-anthracene-1′(10′*H*),2″-[1,3]dithiolan]-10′-ones (22a,b). This same mixture of diastereomers was obtained from either **13a** or **13b** via a procedure similar to that described for **22c**. The distinctive feature of the ^1H NMR (200 MHz, C_6D_6) was the methyl doublets (*J* = 6 Hz) at δ 1.05 and 1.01; exact mass calcd for $C_{19}H_{22}O_3S_2$ *m/e* 362.1010, obsd 362.1063.

Compound **22b** has also been prepared by treatment of **21b** (10 mg, 0.03 mmol) in dry THF (2 mL) under argon with a 1.6 M solution (24 μL, 0.04 mmol) of *n*-BuLi in hexane at −78 °C. After being stirred for 15 min, the mixture was warmed to 0 °C, stirred for 3 h, and worked up to afford **22b** (30%), whose spectra agreed with those above.

3′,4′,4′a,9′a-Tetrahydrodispiro[1,3-dioxolane-2,1′(10′*H*)-anthracene-10′,2″-[1,3]dioxolan]-9′(2′*H*)-one (24). A solution of 2-bromocyclohex-2-enone ethylene glycol ketal (300 mg, 1.4 mmol) in dry THF (10 mL) under argon was prepared, cooled to −78 °C, and slowly treated with a 1.6 M solution (1.05 mL, 1.7 mmol) of *n*-BuLi in hexane. After stirring for 20 min, **2** (175 mg, 1.0 mmol) was added, causing the solution to become orange. The solution was stirred for 20 min at −78 °C and then heated to reflux for 2 h. After being cooled to room temperature, the reaction was quenched by addition of a 5% aqueous $NaHCO_3$ solution (5 mL). The layers were separated, and the organic layer was washed with 5% aqueous $NaHCO_3$ (5 mL) and brine (5 mL) and dried through Na_2SO_4. Removal of solvent yielded an orange oil, which was placed on a Florisil column (1 × 12 cm) and eluted with 25% Et_2O/PE: 0–50 mL, nil; 50–200 mL, 129 mg (45% based on **2**) of **24** as a white solid, which was recrystallized from Et_2O to yield fluffy white crystals, mp 111.5–112 °C [IR (neat) 2950 (s), 2890 (d), 1695 (s), 1305 (s), 1250 (s), 1230 (s), 1202 (s), 1180 (s), 1150 (s), 1120 (s), 1055 (vs), 1025 (s), 972 (s), 947 (s), 765 (s); ^1H NMR ($CDCl_3$, 200 MHz) δ 7.96 (structured d, *J* = 7 Hz, 1 H), 7.51–7.39 (m, 3 H), 4.40–4.32 (m, 2 H), 4.11–3.87 (m, 6 H), 3.10 (d, *J* = 12.7 Hz, 1 H, the signal collapsed to a singlet upon irradiation of the multiplet at 2.7), 2.74–2.62 (symm six-line m, 2 H), 2.09–1.97 (m, 2 H), 1.82–1.76 (m, 2 H); exact mass calcd for $C_{18}H_{20}O_5$ *m/e* 316.1311, obsd 316.1346]. Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.12; H, 6.55.

2-(7-Hydroxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)-*p*-benzoquinone, Bis(dimethyl acetal) and 2-*o*-Toluyl-*p*-benzoquinone, Bis(dimethyl acetal) (26 and 27). A solution of 3,3,6,6-tetramethoxy-1-bromo-1,5-cyclohexadiene (850 mg, 3.0 mmol) in dry THF (10 mL) was prepared and cooled to −78 °C and then treated with a 1.6 M solution (2.13 mL, 3.4 mmol) of *n*-BuLi in hexane. This solution was stirred for 30 min at −78 °C and then treated with a solution of freshly distilled benzocyclobutenone (300 mg, 2.5 mmol) in THF (3 mL), causing the solution to become dark red. After 30 min at −78 °C, CH_3OH (3 mL) was added, quenching the reaction and causing the color of the solution to return to light yellow. After returning to room

temperature, the solvent was removed, and the product was partitioned between CH_2Cl_2 and an aqueous solution of saturated $NaHCO_3$. The layers were separated, and the aqueous layer was washed with CH_2Cl_2 (5 mL). All organic layers were washed with brine and dried through Na_2SO_4. The product was placed on a Florisil column (2 × 10 cm) and eluted with 30% Et_2O/PE: 0–50 mL, nil; 50–250 mL, 395 mg (49% yield based on benzocyclobutenone) of **27** as a white solid, which was recrystallized from PE, mp 83.5–84.5 °C [IR (KBr) 2950 (m), 1680 (s), 1250 (s), 1235 (m) 1155 (m), 1128 (s), 1080 (s), 1049 (m), 985 (m), 917 (m), 750 (m); ^1H NMR ($CDCl_3$, 200 MHz) δ 7.54 (str d, J = 7 H, 1 H), 7.37–7.16 (m, 3 H), 6.04 (d, J = 1.5 Hz, 1 H), 5.08 (d, J = 6.1 Hz, 1 H), 3.96 (d of d, J = 1.6, 6.1 Hz, 1 H), 3.49 (s, 3 H), 3.38 (s, 3 H), 3.37 (s, 3 H), 3.30 (s, 3 H), 2.50 (s, 3 H); exact mass calcd for $C_{18}H_{22}O_5$ m/e 318.1461, obsd 318.1504]. Anal. Calcd for $C_{18}H_{22}O_5$ C, 67.91; H, 6.97. Found: C, 67.51; H, 7.00.

Elution was continued as follows: 250–750 mL, 218 mg (27% yield based on benzocyclobutenone) of **26** as a yellow solid, which was recrystallized from Et_2O/PE, mp 110–112.5 °C [IR (KBr) 3450 (s, br), 2940 (m), 1610 (m), 1560 (s), 1420 (m), 1296 (m), 1275 (m), 1243 (s), 1140 (s), 1095 (s), 915 (m), 748 (m); ^1H NMR (C_6D_6, 200 MHz) 7.49–7.45 (m, 1 H), 7.04–7.00 (m, 3 H), 6.07 (d of d, J = 10.3, 1.8 Hz, 1 H), 5.63 (d, J = 10.3 Hz, 1 H), 4.94 (d, J = 1.8 Hz, 1 H), 3.50 (s, 3 H), 3.28 (s, 3 H), 3.06 (s, 3 H). 2.71 (s, 3 H), 2.46 (s, 2 H); exact mass calcd for $C_{18}H_{22}O_5$, m/e 318.1461, obsd 318.1483].

1,4-Dimethoxyspiro[anthracene-9(10*H*),2′-[1,3]dithiolan]-10-one (29). A solution of 3,3,6,6-tetramethoxy-1-bromo-1,4-cyclohexadiene (279 mg, 1.0 mmol) in dry THF (6 mL), maintained under argon atmosphere, was treated with a 1.54 M solution (0.65 mL, 1.0 mmol) of *n*-BuLi in hexane at −65 °C. After 4 min, this mixture was treated with a solution of **28** (229 mg, 1.1 mmol) in dry THF (1.0 mL) at a rate to maintain the reaction temperature below −60 °C. After being stirred for 30 min at −65 °C, the red reaction mixture was warmed to room temperature and heated to reflux for 3 h. The cooled reaction mixture was quenched with CH_3OH (2 mL) and concentrated in vacuo. The residue was partitioned between water (10 mL) and CH_2Cl_2 (4 × 10 mL). The combined organic layers were dried through anhydrous $CaSO_4$ and concentrated in vacuo to yield 409 mg of a light orange foam as a mixture of **29** and 1,4-dimethoxy-9,10-anthraquinone. Pure **29** was obtained via preparative TLC with Et_2O as eluant, followed by recrystallization from Et_2O/PE to yield light orange crystals: mp 144–146 °C: IR (KBr) 3020 (m), 1670 (s), 1590 (m), 1495 (m), 1330 (m), 1260 (s), 1060 (m), 970 (m), 735 (m); ^1H NMR ($CDCl_3$, 60 MHz) δ 8.20–7.95 (m, 2 H), 7.70–7.20 (m, 2 H), 7.0 (center of AB, $\Delta\nu$ = 15.6 Hz, J = 10 Hz, 2 H), 3.94 and 3.90 (overlapping s, 10 H); exact mass calcd for $C_{18}H_{16}O_3S_2$, m/e 344.0541, obsd 344.0549.

The yield of the annelation process was determined by hydrolysis of **29** to the 1,4-dimethoxy-9,10-anthraquinone. The remainder of the crude orange foam and the pure **29** was dissolved in acetone/water (25 mL:5 mL) and treated with 543 mg of mercuric chloride. After being refluxed for 3 h, the mixture was cooled and filtered. The filtrate was concentrated in vacuo, and the residue was partitioned between water (10 mL) and CH_2Cl_2 (4 × 5 mL). The combined organic layers were washed with 1 M potassium iodide (2 × 50 mL) and dried through anhydrous $CaSO_4$. Concentration in vacuo yielded an orange oil, which was chromatographed on a preparative TLC plate with Et_2O as the eluant. The products from this and the previous plate were combined and crystallized to yield 122 mg (46%) of pure 1,4-dimethoxy-9,10-anthraquinone which was identical with a known sample.[3a]

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Supplementary Material Available: ^1H NMR data for **13a**, **13b**, **14a**, and **14b**; lanthanide shift studies for **13a**; graphs of chemical shifts vs. concentration of lanthanide shift reagents; and a discussion of lanthanide shift studies (11 pages). Ordering information is given on any current masthead page.

Kinetic and Thermodynamic Study of the Reaction of 2,4,6-Triphenylthiopyrylium Ion with Butylamine and Cyclohexylamine in Dimethyl Sulfoxide

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A kinetic and thermodynamic study of the reaction of the 2,4,6-triphenylthiopyrylium ion (1) with butylamine and cyclohexylamine has been performed in Me_2SO at 25 °C. The reaction involves the initial formation of both the corresponding 2*H*- and 4*H*-thiopyrans, which equilibrate to form only the more stable 2*H* adduct. The kinetic data are consistent with a two-step process wherein the formation of the protonated 2*H*- and 4*H*-thiopyran intermediates is the rate-controlling step. A comparison with the addition reaction of 1 with CH_3O^- shows that the relative stabilities of the 2*H* and 4*H* isomers are strongly affected by the charge of the thiopyran derivative. Equilibrium data indicate that the acidity of the ammonium ion is strongly enhanced by the presence of the thiopyranyl moiety.

In recent years the heteroaromatic pyrylium and thiopyrylium cations have found valuable biological, industrial, and synthetic applications.[1] These ions are also of interest because, in contrast to benzenoid systems, they are in-

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