was found to be about 0.1 M. Solutions of 0.15 M **5** were made, irradiated, and analyzed (HPLC) as described above. The quantum yields of **9**, **11**, and **12**, after correction for absorption of light by photoproducts, are presented in Table IX. A linear regression analysis, by least squares, of the plot of ϕ_0/ϕ_q for **12** vs. the concentration of acetone gave a slope of 0.36 M^{-1} an intercept of 0.90, and a ρ of 0.96. The sum of the quantum yields of **9** and **11** were corrected with eq 20 as described above. A value of 0.7 was used for $\phi_{P_2}{}^s$. A plot of the reciprocal of the corrected sum vs. the reciprocal of the acetone concentration was made. A line having an intercept of 1.4 was drawn by inspection. The slope of this line was 2.6 M ($k_q\tau$ = 0.54). Solutions of **5** in acetonitrile/acetone were made, irradiated (2.91×10^{-5} Einstein), and analyzed as described above with colume E. The quantum yields of **12** and of **9** + **11** are presented in Table III. The quantum yields were corrected with respect to light absorption by photoproducts (see Table X for corrected quantum yields). A Stern-Volmer plot of **12** was made. Linear regression analysis gave an intercept of 1.02, a slope of 0.24 M^{-1}, and a ρ of 0.98. Also a double reciprocal plot of **9** + **11** was made. Linear regression gave an intercept of 1.5, a slope of 3.3 M ($k_q\tau$ = 0.45), and a ρ of 1.0.

Acknowledgments. The authors are indebted to the National Science Foundation (Grants CHE-77-20854 and CHE-80-11933), under whose sponsorship this work was initiated, and to the Office of Basic Energy Sciences, U.S. Department of Energy (Contract DE-AC02-79ER 10366), under whose sponsorship the work was completed. S.J.C. wishes to thank the John Simon Guggenheim Memorial Foundation and the University of Colorado Council on Research and Creative Work for fellowship support. The authors also wish to thank Dr. G. O. Mayo and Dr. E. J. Siebert for preliminary work and Danuta Szalecki for technical assistance. Finally, we wish to thank Professor R. L. Sievers for generously allowing us to use his GC equipped with a capillary column and Eric J. Williams for his technical assistance.

Registry No. **1**, 2734-13-6; **2**, 2199-28-2; **3**, 262-89-5; **4**, 58426-49-6; **5**, 82201-51-2; **9**, 85029-18-1; **10**, 85029-19-2; **11**, 85029-20-5; **12**, 85029-21-6; **17**, 19978-14-4; **18**, 85029-22-7; **19**, 85029-23-8; 7-bromo-8-methyl-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene, 85029-24-9.

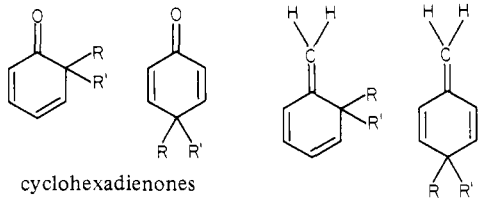
9a-Hydro-9a-methyl-9-anthracenone—A Molecule with Fused Blocked Aromatic Rings

Bernard Miller* and Ajit K. Bhattacharya

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003. *Received August 20, 1982*

Abstract: The title compound (**1**), which contains fused semibenzene and cyclohexadienone rings, was prepared from the adduct of butadiene and 1,4-naphthoquinone in five steps. It is stable to base and undergoes dimerization, rather than rearrangement, in acid. Thermolysis leads to dimerization and to aromatization via a semibenzene rearrangement, yielding 10-methyl-9-anthrone. Photoisomerization results in a series of electrocyclic "aromaticity-switching" steps leading to quantitative formation of 4-methyl-9-anthrone.

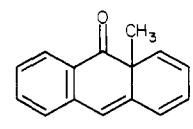
We define a "blocked aromatic molecule" as a molecule in which a nonaromatic ring may be converted to an aromatic ring by a change in the location of a single substituent or hydrogen atom. Blocked aromatic molecules commonly contain cyclohexadienone or methylenecyclohexadiene ("semibenzene") rings.



cyclohexadienones semibenzenes

Rearrangements of cyclohexadienones under thermal, acid-catalyzed, and base-catalyzed conditions have been extensively investigated.[1] Not surprisingly, these processes almost always result in conversion of the cyclohexadienones to aromatic isomers (phenols or aryl ethers). They are often unusually rapid reactions and may involve mechanistic pathways which are not commonly observed in ketones which cannot be directly isomerized to aromatic molecules.[1b] Semibenzenes similarly undergo thermal rearrangments to aromatic isomers.[2] These rearrangements are often so rapid that the intermediate formation of semibenzenes can only be inferred, rather than detected.[2f] Several semibenzene rearrangements have been demonstrated to proceed by free radical chain mechanisms,[2d-g] although concerted paths appear to be followed when the structures of the semibenzenes allow immediate aromization by such routes.[2g]

In molecules with fused blocked aromatic rings, the presence of a single blocking substituent might prevent simultaneous aromatization of two or more nonaromatic rings. Until our preliminary report of part of this work,[3] no examples of such molecules had been described. In this paper we report the synthesis and a study of some of the properties of 9a-hydro-9a-methyl-9-anthracenone (**1**), which contains fused semibenzene and cyclohexadienone rings.



1

(1) Ground-state rearrangement of cyclohexadienones have been reviewed: (a) Miller, B. "Mechanisms of Molecular Migrations"; Thyagarajan, B. S., Ed.; Interscience: New York, 1968; Vol. 1 pp 247-311. (b) Miller, B. *Acc. Chem. Res.* **1975**, *3*, 245. See also: (c) Rhoads, S. J. In "Molecular Rearrangements", Part 1; de Mayo P., Ed.; Interscience: New York, 1963; pp, 600-696. (d) Waring, A. J. In "Advances in Alicyclic Chemistry"; Hart, H.; Karabatsos, G. J., Eds.; Academic Press: New York, 1966; Vol. 1, pp 131-152.

(2) (a) von Auwers, K.; Keil, G. *Chem. Ber.* **1903**, *36*, 1861. (b) von Auwers, K. *Justus Liebigs Ann. Chem.* **1907**, **352**, 216. (c) von Auwers, K.; Jühlicher, W. *Chem. Ber.* **1922**, *55*, 2167. (d) Newman, M. S.; Layton, R. M. *J. Org. Chem.* **1968**, *33*, 2338. (e) Hart, H.; DeVrieze, J. D. *Tetrahedron Lett.* **1968**, 4259. (f) Miller, B.; Lai, K.-H. *J. Am. Chem. Soc.* **1972**, *94*, 3472. (g) Miller, B.; Saidi, M. R. *Ibid.*, **1976**, *98*, 2544.

(3) Miller, B.; Bhattacharya, A. K. *Tetrahedron Lett.* **1981**, *3757*.

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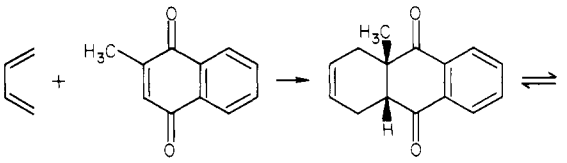
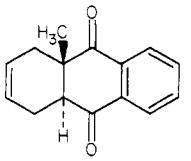
Synthesis of 1

We initially proposed to start our synthesis of ketone **1** by preparing diketone **2**, which contains the carbon skeleton of **1** substituted with functional groups which we thought could be easily modified to yield **1**.

Diels–Alder condensation of butadiene with 2-methylnaphthoquinone proceeded smoothly to yield the expected adduct, **2**, in 56% yield. Attempted purification of **2** by column chromatography on alumina, or reaction of **2** with potassium *tert*-butoxide in *tert*-butyl alcohol solution, converted it to a roughly equimolar mixture of the cis–trans isomers **2** and **3**.



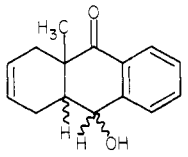
2



3

We anticipated little difficulty in achieving a highly regioselective reduction of **2**, since the carbonyl at C-9, adjacent to the quaternary carbon, was expected to react slowly in comparison to the carbonyl at C-10. However, reaction of diketone **2** with sodium borohydride in ethanol at room temperature or at 0 °C, employing 0.25 mol (1 equiv) of the borohydride per mole of **2**, yielded a complex mixture of products with several methyl peaks in its NMR spectrum. Reduction of **3** under the same conditions gave a similar product mixture, suggesting that epimerization of **2** under the reduction conditions proceeded relatively rapidly compared to reduction of a carbonyl. It was hoped that reduction with lithium tri-*sec*-butylborohydride [L-Selectride (Aldrich)] might give a more stereoselective and therefore cleaner reaction, but the product mixture appeared to be similar to that obtained from reduction with sodium borohydride. Chromatography of the reduction products resulted in separation of some unreacted **2** and **3**, but did not yield any pure ketols.

The formation of what was believed to be a mixture of stereoisomers in the reduction of **2** was not expected to seriously interfere with our overall synthesis, since dehydration of all four stereoisomeric ketols (**4**) was expected to yield the single product



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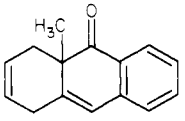
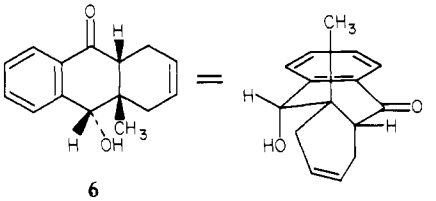


5

5. However, attempted dehydration of the reduction product mixture with either thionyl chloride or phosphorus oxychloride in pyridine solution gave products which still showed strong hydroxy peaks in their IR spectra. The NMR spectra of the products were quite complex and did not suggest that appreciable conversion to **5** had occurred.

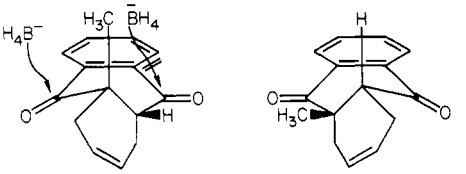
We therefore returned to the reduction step. In an attempt to increase the relative rate of carbonyl reduction compared to epimerization, we added a solution of diketone **2** to *2* equiv of sodium borohydride in ethanol at 0 °C. The reaction was initially carried out for short reaction times to minimize overreduction, but this precaution proved to be unnecessary. Only one carbonyl of **2** was reduced even after long reaction times. The reduction proved to be quite regio- and stereoselective, and a single ketol was produced in nearly quantitative yield. Its NMR spectrum showed a sharp, one-hydrogen singlet at δ 4.85 ppm, which was assigned to the carbinol hydrogen.

The fact that the carbinol proton signal of the reduction product showed no spin–spin coupling indicated that the C-9 carbonyl, adjacent to a quaternary center, had been reduced to yield ketol **6**, thus accounting for the difficulties we experienced in attempting



6

to dehydrate the reduction products to form **5**. Careful oxidation of **6** resulted in re-formation of diketone **2**, thus demonstrating that the cis geometry is retained at the ring juncture. The geometry at the carbinol center has not been conclusively established, but we believe it has the hydroxy group trans to the angular methyl. Diketone **2** can exist in two conformations (**2′** and **2″**)



2′ **2″**

in which both nonaromatic rings have semichair structures. In both conformations the tricyclic ring system forms a deep "cage" in which approach of a reducing agent from the side cis to the cyclohexene ring would be quite hindered, so that we favor addition of a hydride ion trans to that ring. This geometrical assignment is supported by the evidence for similar stereochemistry in the reduction of **7** (see below).

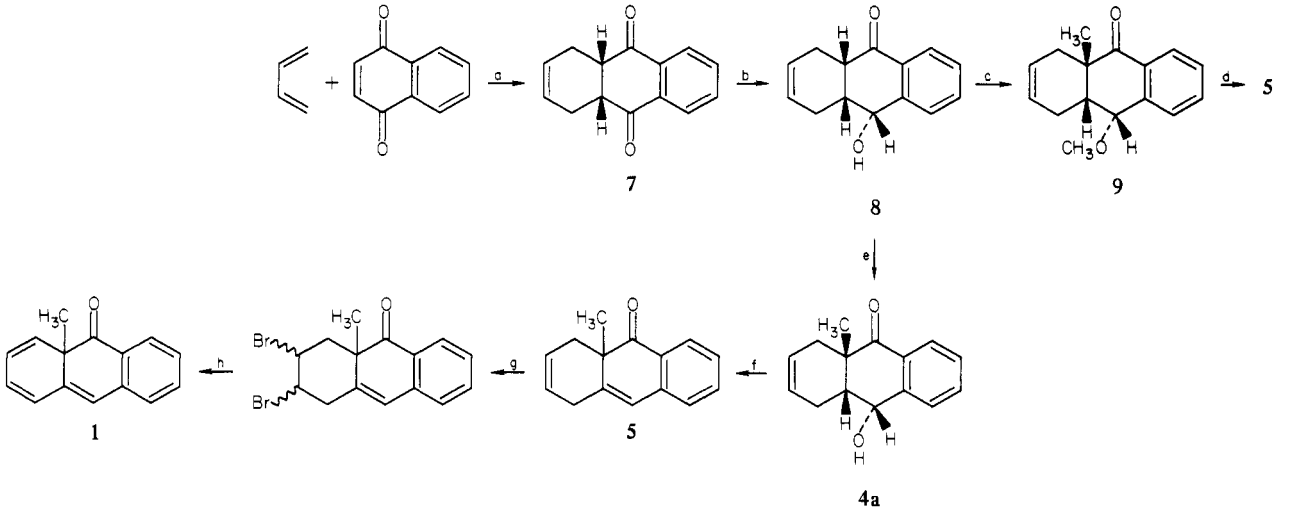
We are not aware of any instance, other than reduction of **2**, in which the more hindered carbonyl group of a cyclic 1,4-diketone is preferentially reduced by hydride donors. It is, however, well known that hydride donors preferentially reduce the more hindered carboxyl groups of cyclic anhydrides, and this phenomenon has been ascribed, in part, to 1,3-repulsions in nonperpendicular attack at the π systems of the carbonyls.[4a] Perhaps we should have been perceptive enough to foresee that similar effects would determine the products from reduction of **2**. In view of the partial flattening of the cyclohexane-1,4-dione chair by the fused aromatic ring of **2** however, the high degree of regiospecificity exhibited in the reaction still surprises us.

Since reduction of **2** does not proceed in the manner desired for synthesis of **1**, we decided to see whether the desired ketol, **4**, could be prepared by introduction of a methyl group α to the carbonyl group of ketol **8**. To prepare **8**, diketone **7** was obtained by Diels–Alder reaction of butadiene and 1,4-naphthoquinone (Scheme I). The yields of **7** were poor (ca. 18%) when carried out at 100 °C as described by Diels and Alder,[4b] but satisfactory yields were obtained by carrying out the condensation at 40–45 °C.

We initially attempted to reduce **7** employing 0.25 mol (1 equiv) of sodium borohydride or 1 mol of L-Selectride. In each case a mixture of epimers was obtained, which was not separated. Although this mixture could be employed with some success in succeeding steps leading to formation of **1**, a much cleaner reaction was obtained by adding **7** to 2 equiv of sodium borohydride. As was observed in the reduction of **2** under these conditions, only one of the two carbonyl groups was reduced, and a single ketol, assigned structure **8**, was obtained. It was assumed that the cis ring juncture is maintained in the product, as it was in reduction of **2** under similar conditions. A cis relationship for the carbinol hydrogen and the adjacent hydrogen at the ring juncture would

(4) (a) for discussion and references, see: Kayser, M. M.; Morand, P. *Can J. Chem.* **1978**, *56*, 1524. (b) Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1928**, *460*, 98.

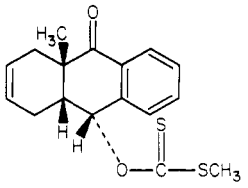
Scheme I. Synthesis of Ketone 1



(a) 45 °C; (b) $NaBH_4$, 2 equiv; (c) NaH, CH_3I; (d) C_6H_6, pTsOH, Δ; (e) $(i\text{-Pr})_2NLi$; CH_3I; (f) pTsCl, C_5H_5N; (g) Br_2, C_6H_6; (h) DBU, C_6H_6

be expected to result from addition of a hydride ion from the outside of the tricyclic cage. This configurational assignment is supported by the thermal stability of dithiocarbonate **10** (see below) and by the moderate (4.5 Hz) coupling constant shown by the carbinol hydrogen, since ketol **8** should exist predominantly in a conformation similar to **2'** (though lacking the angular methyl group), in which the carbinol and angular hydrogens are both in an axial–equatorial relationship.

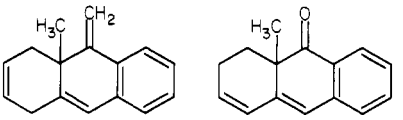
Reaction of ketol **8** with 2 mol of sodium hydride followed by 2 mol of methyl iodide yielded the ether (**9**) of the desired α-methyl ketone, which lost methanol on reaction with *p*-toluenesulfonic acid to form the unsaturated ketone **5**. However, yields in this reaction sequence were modest, and monomethylation of the dianion of **8** (formed by reaction of **8** was 2 mol of lithium diisopropylamide) proved to be more satisfactory. When pure **8** was employed in this reaction, a single product, assigned structure **4a**, was obtained in quantitative yield. When a mixture of stereoisomers of **8** (obtained from reduction of **7** with 1 equiv of sodium borohydride) was employed in the methylation step, a mixture of methylation products was obtained. Reaction of this mixture with sodium hydride, carbon disulfide, and then methyl iodide and fractional crystallization of the product yielded a single pure xanthate (**10**) which was converted to ketol **4a** on basic hydrolysis.



10

Oxidation of **4a** with *p*-toluenesulfonyl chloride and pyridine in Me_2SO solution converted it quantitatively to diketone **2**. Thus, methylation of the enolate anion of **8** occurs from the outside of the tricyclic cage, yielding **4a** with a cis-fused ring juncture. The trans relationship of the hydroxy groups and the vicinal hydrogens at the ring junctures in **4a** and **10** was demonstrated by the fact that xanthate **10** was recovered unchanged from attempted pyrolysis in refluxing *N,N*-dimethylformamide, under conditions in which a cis elimination, if it were geometrically possible, should have readily occurred.[5]

Dehydration of ketol **4a** with *p*-toluenesulfonyl chloride in pyridine solution proceeded smoothly to yield ketone **5**. We attempted to convert **5** to **11** (which should be a useful intermediate for the synthesis of a hydrocarbon with fused semibenzene rings) by reaction with methylenetriphenylphosphorane in Me_2SO.



11 12

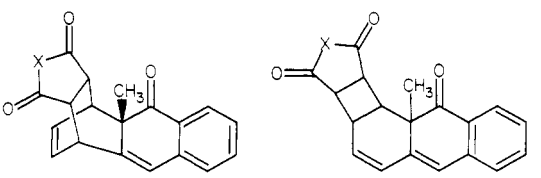
However, no Wittig reaction was observed. Instead, **5** was isomerized to the conjugated diene **12**, most likely by reaction with excess dimsylsodium.

Addition of 1 mol of bromine to ketone **5** proceeded slowly and yielded a mixture of dibromides from which no single isomer could be isolated. No reaction occurred when we attempted to dehydrobrominate the mixture by reaction with pyridine, but reaction with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) proceeded smoothly to form the desired trienone **1** as a bright yellow oil in 72% overall yield from **5**. Addition of bromine to **12** similarly gave a mixture of dibromides which, on reaction with DBU, was converted to **1** in 53% yield. Characteristic features of the spectra of **1** are tabulated in Table I.

Properties of 1

Diels–Alder Reactions. As expected of a cyclohexadiene derivative, ketone **1** reacted with maleic anhydride and *N*-phenylmaleimide in refluxing toluene to yield 1:1 adducts, whose IR and NMR spectra were in accord with those expected of the Diels–Alder adducts of **1**. However, the UV spectra of the adducts, which were expected to resemble that of **5**, instead had absorption maxima at ca. 373 nm, which is very similar to the long wavelength absorption of ketone **12**. The extinction coefficients, however, were only about one-third as large as that of **12**.

On the assumption that reaction occurs by endo addition of the dienophile to the less hindered side of the diene ring, we assign structures **13a** and **13b** to these products. Despite the surprisingly



13a, X = O
13b, X = N-CH_3

14

long wavelength UV absorptions for the adducts, we believe these products do indeed have typical Diels–Alder structures such as **13**. We specifically reject the 1,2-addition structure **14**, since the

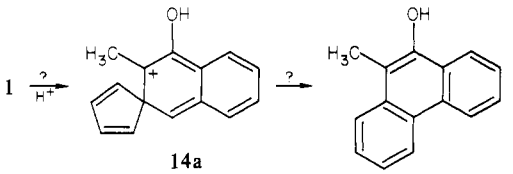
(5) De Puy, C. H.; King, R. W. *Chem. Rev.* **1960**, *5*, 431.

NMR spectra of the products are inconsistent with structures of this type, as are their low UV extinction coefficients. We believe the long wavelength absorption is due to homoconjugation between the isolated double bonds and the conjugated systems.

Homoconjugation in cyclic ketones has frequently been observed to result in spectra whose $\pi-\pi^*$ absorption wavelengths approach those of fully conjugated systems, but whose extinction coefficients (presumably due to lack of planarity of the homoconjugated molecules) are much smaller than those of the conjugated analogues.[6] The $\pi-\pi^*$ absorption wavelengths in bicyclo[2.2.1]-heptenones and bicyclo[2.2.2]octenones appear within 10–20 nm of the wavelength for 2-cyclohexenone, and at much longer wavelengths than the corresponding absorptions for bicyclo-[2.2.1]heptanones and octanones. The extinction coefficients of the homoconjugated molecules, however, are only about one-third as large as that of 2-cyclohexenone.[6a-c] In a molecule which more closely approaches the structures of **13a** and **13b**, it has been observed that 2-acetylbicyclo[2.2.1]heptadiene has an appreciably longer UV absorption wavelength than does 1-acetylcyclohexene.[6d] However, the extinction coefficient of this molecule is, again, only about one-third that of 1-acetylcyclohexene.[6d] The observed spectra of **13a** and **13b** thus correspond to those which would be expected to result from homoconjugation in these adducts.

An inspection of molecular models indicates that homoconjugation in **13a** and **13b** is sterically feasible only when the vinyl bridges are anti to the angular methyl groups, thus providing support for the geometries assigned to the Diels–Alder adducts.

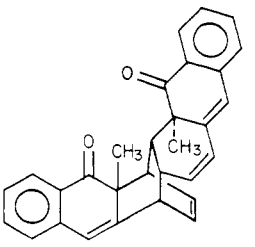
Acid-Catalyzed Reactions. The aromatic and carbonyl-bearing rings of **1** constitute an α-naphthalenone structure, and we therefore expected **1** to undergo dienone–phenol rearrangements in strong acid solutions. Analogy with the reactions of other α-naphthalenones[7] suggests that the methyl group would migrate to the carbonyl carbon, to avoid disrupting the aromaticity of ring C. On the other hand, the high migratory aptitude of the vinyl group might favor formation of the spirocyclic carbonium ion **14a**



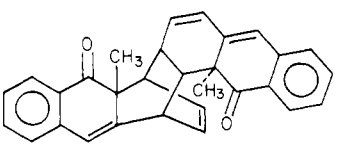
14a

(although products of such quinonoid structures have not been observed in other rearrangements of α-naphthalenones),[7] followed by formation of a phenanthrene ring system.

After reaction of **1** with a 1% solution of sulfuric acid in acetic anhydride for 20 h, ca. 7% of the starting material was recovered unchanged. The remainder appeared to have been converted to a mixture of isomeric dimers, from which one isomer could be isolated in 47% yield by column chromatography and fractional crystallization. The NMR spectrum of this dimer (see Experimental Section) was consistent with that expected of a product of Diels–Alder dimerization of **1**. The terminal double bond of the triene system of **1** appears to act as the dienophilic site, since the UV spectrum of the dimer exhibits a maximum at 373 nm (with a shoulder at 383 nm), indicating the presence of a chromophoric system similar to that of **12**. However, the extinction coefficient of the dimer is greater than that of **12**, and, in fact, is equal to the sum of the extinctions of **12** and **13**. We therefore suggest that the dimer has either structure **15a** or **15b**, since these dimers contain the chromophoric systems of both **12** and **13**. The geometry proposed for these dimers is based (a) on the belief that the approach to **1** from the side cis to the angular methyl group is less hindered than from the underside of the tricyclic "cage"; (b) on the necessity for the vinyl bridges in **15a** and **15b** to be



15a

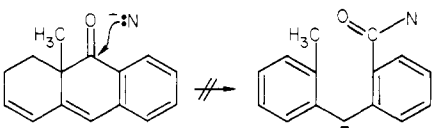


15b

trans to the adjacent methyl groups for significant homoconjugation to occur; and (c) on the upfield shift of the NMR signal for one methyl group in the dimer, compared to the positions of the methyl signals for every other compound in this series. This shift suggests that the methyl may be in the deshielding region of a double bond, as in **15a** or **15b**.

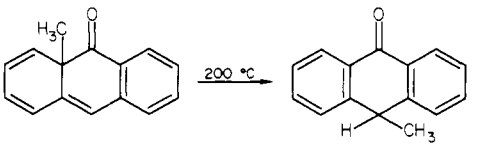
Catalysis of the dimerization of **1** by sulfuric acid is rather suprising, since appreciable accelerations of the rates of Diels–Alder reactions have usually required strong Lewis acid catalysis.[8] More surprising, perhaps, is the absence of any detectable products of rearrangement of **1** under these conditions. This cannot be attributed solely to the rapid rate of the competing dimerization process, since some **1** remains unreacted after 20 h, while 2,2-dimethyl-1-naphthalenone is completely converted to 3,4-dimethyl-1-naphthyl acetate after 5 h under the same conditions.[7a] For comparison with **1**, we attempted to examine the reaction of ketone **5** in strong acid. In addition to undergoing rearrangement by migration of a methyl group, **5** might react by migration or fragmentation of the allyl moiety. However, **5** was recovered unchanged even after solution for 4 days in a 5% solution of sulfuric acid in acetic anhydride, as compared to the complete rearrangement of 2,2-dimethyl-1-naphthalenone after 5 h in 1% sulfuric acid solution.[7a] We are unable to offer any satisfactory explanation for the lack of rearrangement of **1** and **5** under these conditions.

We originally thought that **1** might be sensitive to base as well as acid, since a reasonable fragmentation–aromatization process seemed to be available. However, **1** was recovered unchanged



after reaction with a variety of strong bases, including sodium ethoxide in ethanol, potassium *tert*-butoxide in Me_2SO, and lithium diisopropylamide in ether solution.

Thermolysis of 1. When ketone **1** was heated in decalin solution or in the absence of solvent at 195–200 °C for 15 min, it decomposed to the extent of 40–50% to yield a product containing two major components in roughly equimolar yields (NMR). Heating for longer reaction times gave more complex mixtures, which were not further examined. The two major components were isolated by column chromatography and identified as 10-methylanthrone and the Diels–Alder dimer (**15a** or **15b**) obtained



from reaction of **1** with acid. No evidence for formation of the "double aromatization product", 9-methoxyanthracene, could be detected, although 9-methoxyanthracene was shown to be stable under the thermolysis conditions. 4-Methylanthrone, which might be formed by a [1,5] methyl migration in **1**, was similarly not detected.

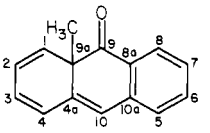
Analogy with other semibenzene rearrangements[2] suggests that 10-methylanthrone was formed via a radical-chain process in-

(6) (a) Bays, D. E.; Cookson, R. C.; Mackenzie, S. *J. Chem. Soc. B* **1967**, 215. See also: (b) Grob, C. A.; Weiss, A. *Helv. Chim. Acta* **1960**, *43*, 1390. (c) Wilcox, C. F.; Winstein, S.; McMillan, W. G. *J. Am. Chem. Soc.* **1960**, *82*, 5450. (d) Jones, E. R. H.; Mansfield, G. H.; Whiting, M. C. *J. Chem. Soc.* **1956**, 4073.

(7) (a) Marvell, E. M.; Geiszler, A. O. *J. Am. Chem. Soc.* **1952**, *74*, 1259. (b) Marvell, E. N.; Magoon, E. *Ibid.* **1954**, *76*, 5118.

(8) Yages, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436.

Table I. Spectroscopic Characteristics of 1



^{1}H NMR peaks (270 MHz)								
chem shifts (ppm)	1.22	6.10–6.19	6.22–6.39	6.56	6.83–6.89	7.14–7.22 7.26–7.34	7.46–7.58	8.00–8.03
splitting, rel areas	s, 3 H	m, 1 H	m, 1 H	s, 1 H	m, 2 H	m, 2 H	m, 1 H	m, 1 H
suggested assignments	CH_3	H-1	H-2	H-10	H-3, H-4	H-7, H-5	H-6	H-8
^{13}C NMR Peaks								
chem shifts (ppm)	31.13	51.71	121.89, 123.12, 125.17, 125.78			127.32, 127.46, 127.71, 132.69, 134.28		
rel areas	217	35	224, 196, 243, 195			260, 286, 294, 189, 236		
suggested assignments	CH_3	C-9a	C-1–C-4			C-5–C-8, C-10		
	147.30		200.87					
	33		14					
	C-4a		C-9 (C=O)					

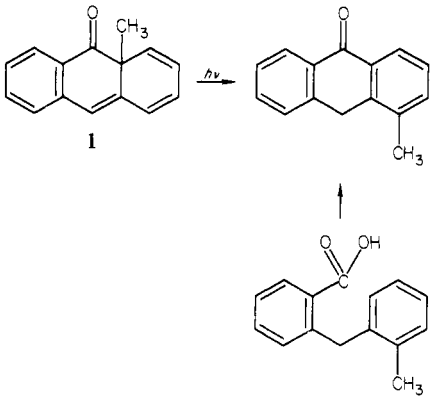
UV, λ_{max} (ϵ)
222 nm (30 200), 254 (15 600), 260 (14 575), 275 (11 040), 285 (9215), 315 (sh, 5470), 329 (7250), 342 (7295), 407 (4155), and 428 (sh, 3035)

IR (cm^{-1})
1680, 1606, 1594

mass spec (peak heights)
208 (M^+, 95), 193 (90), 178 (42), 165 (100)

volving free methyl radicals as chain carriers. When 0.04 equiv of 1,4-benzoquinone as added to a refluxing solution of **1** in decalin, the ratio of 10-methylanthrone to dimer was reduced by ca. 50%, offering some support for the radical-chain mechanism.

Photorearrangement and Photoreactions of 1.[9] Irradiation of solutions of **1** in benzene, ether, or chloroform by a 275-W UV lamp for times ranging from 20 min to 2.5 h quantitatively converted **1** to 4-methylanthrone.[10] The product was identified



1

by its spectra and by comparison with an authentic sample prepared by Friedel–Crafts cyclization of 2-(2-methylbenzyl)benzoic acid. Formation of 4-methylanthrone by photorearrangement of **1** is an exceptionally clean reaction, and no evidence for formation of other products could be detected.

Formation of 4-methylanthrone might have proceeded either by a 1,5 methyl shift or by electrocyclic opening of the central ring to form the *o*-xylylene ketene **16**, followed (after rotation around a single bond) by reclosure of the ring to form **17** (Scheme II). (The mechanism shown in Scheme II constitutes an interesting set of "aromaticity-switching" steps, unique to molecules with fused blocked aromatic rings, in which the left- and right-hand rings go from nonaromatic to aromatic and back to nonaromatic states, or vice versa.)

To distinguish between the two mechanisms for formation of 4-methylanthrone, we attempted to trap the intermediate ketene **16** by reaction with nucleophiles. Photoirradiation of **1** in methanol solution, however, again resulted in quantitative formation of 4-methylanthrone, with no indication of formation of a methyl ester. Addition of 1 equiv of diethylamine to the solution similary yielded only 4-methylanthrone. However, when photoirradiation was carried out employing diethylamine as the solvent, *N*,*N*-diethyl-2-(2-methylbenzyl)benzamide (**18**) was isolated in 79% yield. The amide was identified by comparison with a sample prepared independently from 2-(2-methylbenzyl)benzoic acid. When **1** was kept in diethylamine solution in the dark no reaction occurred.

Photoirradiation of **1** in the presence of **4** molar equiv of maleic anhydride gave, in addition to 4-methylanthrone, a 1:1 adduct of **1** and maleic anhydride. The spectra and properties of the adduct (see Experimental Section) agreed with those expected of enol **19**.

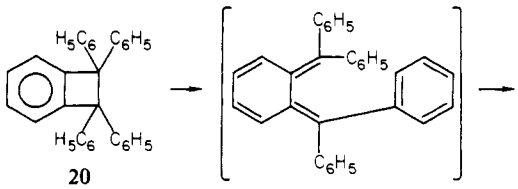
Although the possibility of direct photoreaction of **1** with diethylamine and maleic anhydride to form **18** and **19** cannot be unequivocally ruled out, formation of these products can be most reasonably be explained by intermediate formation of ketene **16**.

To determine whether the [1,3] hydrogen shift in conversion of ketone **17** to 4-methylanthrone proceeds by an intramolecular photochemical process or by an intermolecular step, **1** was irradiated for 30 min in methanol-*O*-*d* solution. The NMR spectrum of the product showed a one-proton absorption for the methylene (C-10) group, demonstrating that one-half the protons had come from the solvent. Irradiation for an additional 30 min did not change the intensity of the methylene adsorption.

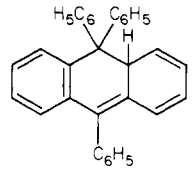
One question left unanswered in regard to the photorearrangement of **1** is whether cyclization of **16** to form **17** proceeds by a thermal or photochemical process. We have no evidence that bears on this question, but the demonstration that benzocyclobutene **20** cyclizes thermally (below 0 °C) to form semibenzene **21**[11] (a reaction which most probably proceeds via an *o*-xylylene intermediate) suggests that the **16** → **17** conversion similarly proceeds by a nonphotochemical path.

Most cyclohexa-2,4-diene-ones readily undergo photochemical ring opening to form ketenes.[12] However, no evidence could be obtained for formation of a similar ketene intermediate in the

(9) A preliminary report of this work has been published: Miller, B.; Bhattacharya, A. K. *Tetrahedron Lett.* **1981**, 3760.
(10) Bergmann, E. D.; Loewenthal, E. *Bull. Soc. Chim. Fr.* **1952**, 66.
(11) Quinkert, G.; Wiersdorff, W. W.; Finke, M.; Opitz, K. *Tetrahedron Lett.* **1966**, 2193.
(12) E.g.: Barton, D. H. R.; Quinkert, G. *J. Chem. Soc.* **1960**, 1. Quinkert, G. *Angew. chem., Int. Ed. Engl.* **1965**, *4*, 211. Collins, P. M.; Hart, H. *Chem. Commun.* **1967**, 1197. Griffiths, J.; Hart, H. *J. Am. Chem. Soc.* **1968**, *90*, 3297. Baldwin, J. E.; McDaniels, M. C. *Ibid.* **1968**, *90*, 6118.

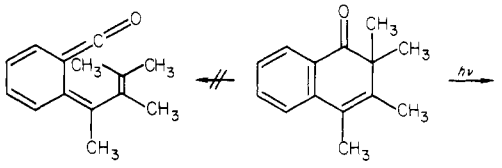


20



21

photoarrangement of naphthalenone **22**, which instead followed an oxa di-π-methane path to form **23**.[13] Clearly, opening of the



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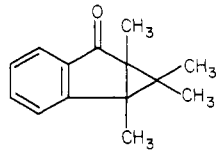


23

napthalenone ring system to form an *o*-xylylene ketene is difficult because disruption of an aromatic ring is necessary. The unique structure of **1**, in which conversion of a blocked aromatic ring to an aromatic one can compensate for disruption of the existing aromatic ring, allows formation of the *o*-xylylene ketene.[14]

Experimental Section

General. All reagents and solvents were Reagent Grade or were purified by standard methods before use. Unless otherwise specified, all ^{1}H NMR spectra were taken at 60 MHz on a Perkin-Elmer Model R12A spectrometer in deuteriochloroform solution, using Me_4Si as an internal standard. The 270-MHz spectra were taken on a Varian HX 270 spectrometer at the Northeast Regional NSF-NMR Facility at Yale University, New Haven, CT, in deuteriochloroform solution. C^{13} NMR spectra were taken on a Varian FT-80A spectrometer in deuteriochloroform solution. UV spectra were taken on a Cary Model 14 spectrometer in 95% ethanol solution. IR spectra were recorded on Perkin-Elmer Model 237B or 727 spectrometers. Spectra of solids were taken in mineral oil mulls, and spectra of oils were taken without solvent. Mass spectra were taken on a Perkin-Elmer Model RMUL6 single-focusing spectrometer. Microanalyses were carried out by the University of Massachusetts Microanalytical Laboratory. Melting points and boiling points are uncorrected.

1,4,4a,9aα-Tetrahydro-4aα-methyl-9,10-anthracenedione (2). To a solution of 2-methyl-1,4-naphthoquinone (35.0 g, 0.204 mol) in 300 mL of benzene were added 1,3-butadiene (20 mL, ca. 0.32 mol), which had been liquefied in a dry ice–acetone bath, and hydroquinone (1.0 g, 0.0091 mol). The mixture was stirred and heated in a pressure reactor at 150 °C for 4 h. Volatile materials were then removed under vacuum. NMR analysis showed the residue to consist of a 2:3 mixture of the desired adduct and 2-methyl-1,4-naphthoquinone. The residue was dissolved in 400 mL of toluene and cooled in dry ice. Additional 2-methyl-1,4-naphthoquinone (30.0 g, 0.174 mol) and hydroquinone (1.5 g, 0.0136 mol) were added. The mixture (heterogeneous) was cooled in dry ice, and butadiene (45 mL, ca. 0.70 mol) was added. The mixture was stirred and heated at 150 °C for 6 h. Volatile materials were removed under vacuum and the residue was recrystallized three times from hexane to yield **2** (50.5 g, 59%) as pale yellow crystals, mp 80.5–81.5 °C: ^{1}H NMR δ 1.37 (s, 3 H), 1.60–2.90 (m, 4 H, allylic H's), 3.05 (dd, J = 5.6 Hz, H at 9a), 5.65–5.80 (narrow m, 2 H), 7.6–7.9 (m, 2 H, β-Ar H's), and 7.95–8.25 (m, 2 H, α-Ar H's); IR 1680 and 1690 cm^{-1}. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.65; H, 6.20. Found: C, 79.93; H, 6.42.

1,4,4a,9aβ-Tetrahydro-4aα-methyl-9,10-anthracenedione (3). A mixture of diketone **2** (ca. 80%) and 2-methyl-1,4-napthoquinone (20%) (65.0 g total) obtained from a Diels–Alder reaction as described above was chromatographed on 500 g of alumina, eluting with petroleum ether–methylene chloride (4:1). Two fractions (containing a total of 45 g of solid free of quinone) were obtained. Each fraction showed two methyl peaks at δ 1.35 and 1.12 in its ^{1}H NMR spectra in approximately 1:1 area ratios. The combined product fractions were dissolved in hot hexane, cooled slowly, and then allowed to stand overnight at room temperature. Crystals were obtained which were recrystallized twice more from hexane to yield 6.7 g of **3** as white needles, mp 84–85 °C: ^{1}H NMR δ 1.13 (s, 3 H), 2.25–2.65 (m, 4 H, allylic H's), 3.20 (dd, J = 10,5 Hz, 1 H at C-9a), 5.70–5.90 (narrow m, 2 H), 7.60–7.90 (m, 2 H, β-Ar H's), 7.95–8.25 (m, 2 H, α-Ar H's); IR 1690 and 1700 cm^{-1}. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.65; H, 6.20. Found: C, 79.63; H, 6.39.

Epimerization of 2. Ketone **2** (0.50 g) was dissolved in 20 mL of methanol, and a solution of 0.2 g of potassium hydroxide in 1 mL of water was added. The deep purple solution was allowed to stand at room temperature for 4 h, then poured into dilute HCl solution. The mixture was extracted with methylene chloride; the organic layer was washed with water, dried over magnesium sulfate, and filtered, and the solvent was evaporated. The ^{1}H NMR spectrum of the residue was identical with that expected of a mixture of **2** and **3**. Peaks at δ 1.12 and 1.34 were present in the area ratio 8:9.

1,4,4aα,9aα-Tetrahydro-9,10-anthracenedione (7). A solution of crude 1,4-naphthoquinone (184 g, 1.1634 mol, obtained from Aldrich Chemical Co.) and hydroquinone (5.5 g, 0.050 mol) in 950 mL of 95% ethanol was cooled in a dry ice–acetone bath, and 1,3-butadiene (150 mL, ca. 2.5 mol) was added. The mixture was stirred and heated at 45 °C in a pressure reactor for 20 h, and allowed to stand at ambient temperature for an additional 45 h. Filtration afforded brown crystals. Evaporation of the mother liquors gave a black residue which was extracted with hot hexane, leaving a tarry black insoluble residue (95 g) which was discarded. On cooling, the hexane extracts deposited gray needles which were combined with the brown needles obtained above. Two recrystallizations from acetone yielded **7** (114 g, 0.54 mol, 46%) as light gray needles, mp 99–100 °C (lit.[4] mp 102–103 °C): ^{1}H NMR δ 1.90–2.90 (m, 4 H), 3.20–3.60 (m, 2 H), 5.70–5.90 (m, 2 H), 7.65–7.95 (m, 2 H), and 8.00–8.30 (m, 2 H); IR 1690 cm^{-1}.

1,4,4aα,9aα,10aα-Pentahydro-10β-hydroxy-9-anthracenone (8). A solution of dione **7** (31.8 g, 0.15 mol) in 320 mL of ethyl acetate was added dropwise to a stirred solution of sodium borohydride (3.1 g, 0.0816 mol) in 420 mL of absolute ethanol. The mixture was maintained at 0 °C under an atmosphere of nitrogen. Addition was complete after 75 min; the mixture was maintained at 0 °C and stirring was continued for an additional 40 min. The pale brown reaction mixture was carefully poured into 500 mL of 0.5 M HCl at 0 °C. The white precipitate obtained was filtered off, and the mother liquor extracted twice with ether. The ether extracts were washed with water, dried over sodium sulfate, and filtered, and the solvent was evaporated. The residue was combined with the precipitate obtained above and recrystallized from ether–ethyl acetate to yield **8** (28.6 g, 0.134 mol, 89%) as white needles, mp 137–138 °C, apparently pure by ^{1}H NMR. An analytical sample (mp 140–141 °C) was obtained by recrystallization from absolute ethanol: ^{1}H NMR δ 1.60–3.30 (m, 7 H), 5.32 (d, J = 4.0 Hz, 1 H, carbinol H), 5.50–5.95 (m, 2 H), 7.20–7.95 (m, 3 H), and 7.95–8.15 (m, 1 H); IR 3280–3480 and 1685 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.49; H, 6.58. Found: C, 78.29; H, 6.47.

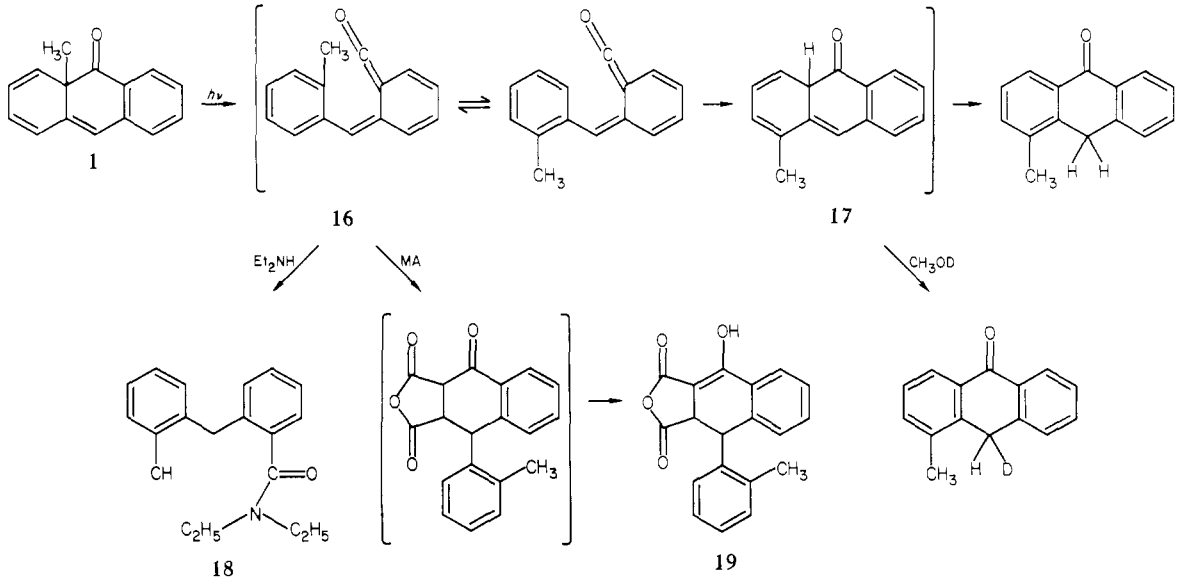
1,4,9aα,10aα-Pentahydro-4aα-methyl-10β-hydroxy-9-anthracene (6). A solution of sodium borohydride (100 mg, 2.63 mmol) in 10 mL of absolute ethanol was stirred under a nitrogen atmosphere at −8 °C, and a solution of diketone **2** (1.13 g, 5.00 mmol) in 10 mL of ethyl acetate was added dropwise over a 14-min period. The solution was stirred at 0 °C for an additional 40 min and then carefully poured into ice-cold 0.5 M hydrochloric acid. The mixture was extracted with ether and the organic layer washed with water, dried over sodium sulfate, and filtered; the solvent was evaporated to leave 1.12 g of a white solid. Recrystallization from absolute ethanol yielded **6** (0.95 g, 4.16 mmol, 83%) as white crystals, mp 123–124 °C: ^{1}H NMR δ 1.35 (s, 3 H), 1.70–3.35 (m, 6 H), 4.87 (s, 1 H, carbinol H), 5.46–5.85 (m, 2 H), 7.20–8.0 (m, 3 H), and 8.05–8.22 (m, 1 H); IR 3550 and 1660 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.73; H, 7.11.

1,4,4aα,9a,10aα-Pentahydro-9aα-methyl-10β-hydroxy-9-anthracenone (4a). A solution of 1.3 M methyllithium in ether (323 mL, 0.42 mol)

(13) Hart, H.; Murray, R. K., Jr. *J. Org. Chem.* **1970**, *35*, 1535.

(14) An *o*-xylylene ketene is probably formed as an intermediate in the pyrolysis of 3,3-diphenyl-1,2-indanedione: Rigaudy, J.; Paillous, N. *Bull. Soc. Chim. Fr.* **1971**, 576.

Scheme II. Photoreactions of 1



was added to a solution of diisopropylamine (42.9 g, 0.425 mol) in 450 mL of anhydrous tetrahydrofuran at −75 °C. (In later runs, the reaction was carried out at −10 °C.) The mixture was stirred under nitrogen for 1 h, and a solution of ketol **8** (30.0 g, 0.1415 mol) in 180 mL of anhydrous tetrahydrofuran was added dropwise over a 40-min period. The reaction mixture was stirred for an additional 25 min, and methyl iodide (45.6 g, 0.321 mol) was then added over a 5-min period. Stirring was continued at −75 °C for 3 h. Workup of an aliquot showed that only about 20% of the ketol had been methylated (NMR). Methyl iodide (75.3 g, 0.5303 mol) was again added at −75 °C, and the reaction mixture was allowed to warm to room temperature. Stirring was continued for 4 h at room temperature, and the solution was then poured into 1 L of 2.5 N sulfuric acid. The organic phase was separated and the aqueous phase extracted with ether. The combined organic extracts were washed with dilute sulfuric acid and with brine, dried over sodium sulfate, and filtered. Evaporation of the solvent under vacuum left 32.4 g (0.142 mol, 100%) of **4a** as a viscous brown oil: ^{1}H NMR δ 1.23 (s, 3 H), 1.50–3.15 (m, 5 H), 3.23 (s, hydroxy H), 5.47 (d, J = 4 Hz, 1 H), 5.55–5.75 (m, 2 H), 7.20–7.93 (m, 3 H), and 7.93–8.20 (m, 1 H); IR 3500 and 1685 cm^{-1}.

***S*-Methyl Xanthate of 4a.** A solution of **4a** (5.0 g, 0.0219 mol) in 25 mL of anhydrous tetrahydrofuran was added dropwise to a stirred suspension of sodium hydride (1.0 g, 0.042 mol) in 25 mL of anhydrous THF under nitrogen. After completion of the addition, stirring was continued for 15 min, and the solution was cooled in ice. A solution of carbon disulfide (12.7 g, 0.17 mol) in 20 mL of tetrahydrofuran was added drop by drop over a 15-min period. The ice bath was removed and the mixture stirred for an additional 1.5 h. Methyl iodide (12 g, 0.085 mol) was added and the mixture heated under reflux for 16 h. Tetrahydrofuran (ca. 50 mL) was partially evaporated under vacuum and the remaining material poured into 1 M hydrochloric acid solution. The mixture was extracted with ether, and the ether extracts were washed with water, dried over sodium sulfate, and filtered; the solvent was evaporated to leave 9.6 g of a brown, viscous oil. The product was chromatographed on silica gel, eluting with 5% ethyl acetate in hexane, to yield 5.0 g (15.7 mmol, 72%) of xanthate **10**, mp 89–91 °C (from ethanol). An analytical sample, recrystallized twice more from ethanol, had mp 92.5–94.0 °C: ^{1}H NMR δ 1.34 (s, 3 H), 1.60–2.20 (m, 3 H), 2.62 (s, 3 H), 2.65–3.20 (m, 2 H), 5.50–5.75 (m, 2 H), 7.27–7.80 (m, 4 H), and 8.00–8.25 (m, 1 H); IR 1687, 1212, and 1068 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_2S_2$: C, 64.12; H, 5.70; S, 20.14. Found: C, 64.18; H, 5.92; S, 20.03.

Hydrolysis of the *S*-Methyl Xanthate of 4a. A solution of 1.5 g of potassium hydroxide in 25 mL of water was added to a solution of the *S*-methyl xanthate of **4a** (mp 89–91 °C) (4.9 g, 0.154 mol) in 75 mL of ethanol. The mixture was stirred and heated at reflux under nitrogen for 2 h. It was then poured into a mixture of ice and water, acidified with dilute hydrochloric acid, and extracted with ether. The ether phase was washed with water, dried over sodium sulfate, and filtered; the solvent was evaporated to leave 3.25 g (93%) of **4a**.

1,4,9a-Trihydro-9a-methyl-9-anthracenone (5). Freshly recrystallized *p*-toluenesulfonyl chloride (28.0 g, 0.147 mol) was added to an ice-cooled solution of **4a** (32.4 g, 0.142 mol) in 160 mL of pyridine. The ice bath was removed and the solution allowed to stand at room temperature for 24 h. Workup of an aliquot showed that dehydration was not complete, and 20 mL of pyridine and *p*-toluenesulfonyl chloride (3.0 g, 0.0157 mol) were added. The solution was allowed to stand for an additional 43 h. It was then poured into ice water and extracted with hexane. The hexane solution was washed with saturated sodium bicarbonate solution, then with dilute sulfuric acid and brine. The solution was dried over sodium sulfate and filtered; the solvent was evaporated to yield 32.0 g of yellow oil, which was chromatographed on silica gel, eluting with hexane, to yield 23.7 g (0.113 mol, 79%) of **5** as a pale yellow oil: ^{1}H NMR δ 1.35 (s, 3 H), 2.20–2.55 (m, 2 H), 2.90–3.20 (m, 2 H), 5.65–5.85 (m, 2 H), 6.35–7.80 (m, 4 H), and 7.95–8.20 (m, 1 H); IR 1675, 1650, and 1600 cm^{-1}; UV λ_{max} 237 nm (ε 31 440), 260 (sh, 6920), 272 (sh, 4630), 282 (sh, 2960), and 333 nm (2520). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.41; H, 6.82.

1,2,9a-Trihydro-9a-methyl-9-anthracenone (12). A suspension of sodium hydride (76 mg, 3.1 mmol) and triphenylmethane (10 mg, 0.041 mmol) in 6 mL of anhydrous dimethyl sulfoxide was heated at 75 °C under nitrogen for 1 h. The resulting red solution was cooled to 23 °C and methyltriphenylphosphonium bromide (560 mg, 1.57 mmol) was added. A solution of **5** (157 mg, 0.75 mmol) in 2 mL of anhydrous dimethyl sulfoxide was added and the reaction mixture stirred for 17 h. It was then poured into a mixture of ice and water, which was acidified with dilute hydrochloric acid and extracted with hexane. The organic layer was washed with water, dried over sodium sulfate, filtered, and evaporated. The residue was chromatographed on silica gel using 5% ethyl acetate in hexane as the eluent to yield **12** (86 mg, 0.41 mmol, 55%) as a yellow oil: ^{1}H NMR δ 1.24 (s, 3 H), 1.45–1.95 (m, 1 H), 2.00–2.60 (m, 3 H), 5.70–6.40 (m, 3 H), 7.10–7.75 (m, 3 H), and 7.90–8.15 (m, 1 H); IR 1680 and 1590 cm^{-1}; UV λ_{max} 252 nm (37 770), 260 (39 010), 290 (11 880), 297 (12 400), 307 (sh, 9840), 363 (sh, 3380), 373 (3720), and 383 (sh, 3150). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.52; H, 6.95.

Reduction of 7 with Lithium Tri-*sec*-butylborohydride. A solution of **7** (70.0 g, 0.33 mol) in 1400 mL of anhydrous tetrahydrofuran was cooled in a dry ice–acetone bath and the solution stirred under 1 atm of nitrogen. A 1 M solution of lithium tri-*sec*-butylborohydride (335 mL, 0.335 mol) was added drop by drop over a 2-h period. The cooling bath was removed, and stirring was continued for an addition 4 h. The temperature rose to 2 °C, and the mixture was then cooled in an ice bath. A solution containing 120 g of potassium hydroxide and 170 mL of 30% hydrogen peroxide solution in 600 mL of water was added drop by drop to the green reaction mixture over a period of 1 h. (A strong exotherm developed during the initial addition period.) The resulting black suspension was stirred for an additional hour and the temperature allowed to rise to 20 °C. The mixture was again cooled in an ice bath and a 15% sulfuric acid solution was added dropwise over a 1-h period until the pH of the solution was lowered to 6.0. A solution of 30 g of potassium iodide in 200 mL of water was added, and the iodine formed was reduced by addition of 1 M sodium thiosulfate solution. The two layers were separated, and the organic layer filtered free of suspended solid. The aqueous layer was extracted with ether, and the combined organic layers were cooled and again filtered, washed with water, dried over sodium sulfate,

and filtered; the solvent was evaporated to yield 40 g of crude **8** as a dark, viscous oil. Its ^{1}H NMR spectrum suggested it to be ca. 60% **8**, and ca. 40% isomers with carbinol hydrogen absorptions at δ 3.6 and 3.8. Reduction with 0.25 mol of sodium borohydride yielded a similar mixture.

Preparation of 5 by Dialkylation and Demethanolation of 8. A solution of crude **8** (16.0 g, 0.075 mol), prepared by reduction of **7** with lithium tri-*sec*-butylborohydride, in 90 mL of tetrahydrofuran was added dropwise over a 1.25-h period to a suspension of sodium hydride (6.5 g, 2.71 mol) in 100 mL of tetrahydrofuran. The mixture was stirred under nitrogen for an additional 1.5 h, and a solution of methyl iodide (18.7 mL, 0.3 mol) in 20 mL of tetrahydrofuran was added dropwise (40 min). An appreciable exotherm resulted during the initial 20 min of addition. The mixture was heated at reflux for 15 h, and the solvent removed under vacuum. The residue was added to ice water; the mixture was acidified with dilute sulfuric acid and extracted with ether. The ether layer was washed with water, dried over magnesium sulfate, and filtered; the solvent was removed under vacuum to leave 13.3 g of a partially solid brown oil. The oil was triturated with 5:1 hexane–ether and filtered. The solid was discarded. The solvent was evaporated to give 12.0 g of brown oil which showed singlets at δ 1.24 and 3.52 in its NMR spectrum.

The oil from the methylation reaction was dissolved in 200 mL of benzene, *p*-toluenesulfonic acid (3.0 g, 0.052 mol) was added, and the mixture was heated at reflux for 19 h. The solution was cooled, washed with sodium bicarbonate solution, dried over magnesium sulfate, and filtered; the solvent was evaporated to give 11.9 g of yellow oil. The oil was twice chromatographed on activity III alumina, eluting with 10% ether in hexane, to yield 4.2 g (0.0196 mol) of essentially pure **5**.

Oxidation of Ketol 4a to Diketone 2. Freshly recrystallized *p*-toluenesulfonyl chloride (150 mg, 0.79 mmol) was added slowly to a cold solution of **4a** (103 mg, 0.45 mmol) in a mixture of 2 mL of dimethyl sulfoxide and 1 mL of pyridine. The solution was allowed to stand at 23 °C for 24 h, and additional *p*-toluenesulfonyl chloride (100 mg, 0.53 mmol) was added. The reaction mixture was allowed to stand for an additional 77 h, and the pale yellow solution poured into ice water. It was extracted with ether; the ether solution was washed with sodium bicarbonate solution and dried over sodium sulfate, and filtered, and the ether was evaporated to yield 101 mg (100%) of **2**.

Attempted Pyrolysis of Xanthate 10. A solution of xanthate **10** (160 mg) in 3 mL of purified *N*,*N*-dimethylformamide was heated at reflux under an atmosphere of nitrogen for 2 h. The solution was allowed to cool to room temperature, poured into water, and extracted with ether. The ether solution was washed three times with water, dried over sodium sulfate, and filtered; the solvent was evaporated to yield 150 mg of unchanged **10**. The recovered material was dissolved in 3 mL of *N*,*N*-dimethylformamide and heated under reflux for an additional 9.5 h. Workup as described above gave 140 mg of unchanged starting material.

9a-Hydro-9a-methyl-9-anthracenone (1). A solution of bromine (4.80 g, 0.030 mol) in 30 mL of benzene was added dropwise over a 20-min period to a stirred solution of ketone **5** (6.30 g, 0.030 mol) in 140 mL of benzene at 10–15 °C. Stirring was continued for 1 h at 23 °C until the deep red color had significantly lightened. A solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (18.0 g, 0.118 mol) in 50 mL of benzene was added dropwise at 10–15 °C, and the resulting yellow suspension was stirred in the dark at 23 °C under nitrogen for 16 h. The reaction mixture was poured into water and acidified with dilute sulfuric acid, and the benzene layer separated. The aqueous layer was extracted with hexane and the combined organic layers were washed with dilute sulfuric acid and then with brine, dried over sodium sulfate, and filtered; the solvent was removed under vacuum. The residue (6.4 g) was chromatographed on silica gel, eluting with 3% ethyl acetate in hexane, to yield **1** (4.3 g, 0.0206 mmol, 69%) as a deep yellow oil. Its spectra are outlined in Table I. Anal. Calcd for $C_{15}H_{12}O$: C, 86.50; H, 5.82. Found: C, 86.40; H, 5.94.

Reaction of *N*-Phenylmaleimide with 1. A solution of **1** (416 mg, 2.0 mmol) and *N*-phenylmaleimide (600 mg, 3.47 mmol) in 20 mL of benzene was kept at 23 °C for 20 h, and then heated at reflux for 3 h. The solvent was removed under vacuum and the residue chromatographed on silica gel to yield 474 mg (2.74 mmol) of recovered *N*-phenylmaleimide. The remaining material from the chromatographic separation was recrystallized from ethyl acetate–hexane to yield **13b**, the *N*-phenylmaleimide adduct of **1** (282 mg, 0.74 mmol, 37%), as pale yellow crystals, mp 221–222 °C: ^{1}H NMR δ 1.20 (s, 3 H), 2.70–3.25 (m, 2 H), 3.70–4.35 (m, 2 H), 6.20–6.75 (m, 3 H), 7.00–8.10 (m, 9 H); IR 1777 (w), 1713, and 1695 cm^{-1}; UV (95% EtOH) λ_{max} 238 nm (ϵ 43 000), 246 (sh, 37 250), 270 (4300), 277 (4400), 288 (sh, 3050), 317 (1640), 327 (sh, 1500), 370 (1400), 384 (sh, 1130). Anal. Calcd for $C_{25}H_{19}NO_3$: C, 78.72; H, 5.02. Found: C, 78.66; H, 4.83.

Reaction of Maleic Anhydride with 1. A solution of **1** (180 mg, 0.865 mmol) and maleic anhydride (200 mg, 2.04 mmol) in 9 mL of toluene was allowed to stand at room temperature for 20 h. UV analysis indicated that little reaction had occurred. A solution of maleic anhydride (200 mg, 2.04 mmol) in 16 mL of toluene was added, and the mixture was heated at reflux in the dark under nitrogen for 23 h. The solvent was removed under vacuum and excess maleic anhydride removed by vacuum sublimation at 100 °C to leave 270 mg of a tan solid. Recrystallization from ethyl acetate yielded **13a**, the maleic anhydride adduct of **1** (210 mg, 0.68 mmol, 79%), as colorless crystals, mp 207–208 °C: ^{1}H NMR δ 1.21 (s, 3 H), 2.95–3.50 (m, 2 H), 3.75–4.20 (m, 2 H), 6.35–6.65 (m, 3 H), 7.10–7.75 (m, 3 H), and 7.75–8.00 (m, 1 H); IR 1863 (m), 1838 (m), 1778, and 1690 cm^{-1}; UV λ_{max} 241 nm (ϵ 42 540), 247 (sh, 38 250), 271 (4460), 278 (4600), 288 (sh, 3120), 318 (1800), 327 (sh, 1660), 370 (1560), and 388 (sh, 1170). Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.29; H, 4.45.

Dimerization of 1 in Acetic Anhydride–Sulfuric Acid. Concentrated sulfuric acid (0.05 mL, 1.6 mmol) was added to a solution of ketone **1** (570 mg, 2.74 mmol) in 8 mL of acetic anhydride. The solution was stirred at room temperature for 20 h and then poured into ice water. The mixture was stirred for 2 h and extracted with chloroform. The chloroform layer was washed with sodium bicarbonate solution and then with water, dried over sodium sulfate, and filtered; the solvent was evaporated under vacuum to give 580 mg of a brown residue, which was chromatographed on silica gel, eluting first with 700 mL of 10% ethyl acetate in hexane and then with 800 mL of 20% ethyl acetate in hexane. The initial eluents yielded 40 mg (0.19 mmol, 7%) of recovered **1**. The main fraction obtained by elution with 20% ethyl acetate was twice recrystallized from ethyl acetate–hexane and then from methylene chloride–hexane to yield 268 mg (0.64 mmol, 47%) of a dimer of **1**, mp 177–179 °C: ^{1}H NMR δ 0.96 (s, 3 H), 1.18 (s, 3 H), 2.45 (d, J = 8 Hz, 1 H), 2.65–3.0 (m, 1 H), 3.03–3.3 (m, 1 H), 3.4–3.7 (m, 1 H), 5.6–6.27 (m, 4 H), 6.38 (s, 1 H), 6.47 (s, 1 H), 7.1–7.8 (m, 6 H), 8.10 (dd, J = 8 Hz, 1 Hz, 1 H), 8.38 (dd, J = 8, 1 Hz, 1 H); UV 237 nm (ϵ 49 724), 254 (62 438), 262 (sh, 55 010), 290 (17 074), 300 (16 878), 310 (sh, 13 277), 370 (5505), and 388 (sh, 3909). Anal. Calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.51; H, 6.01.

Attempted Rearrangement of Ketone 5 in Acetic Anhydride–Sulfuric Acid. Concentrated sulfuric acid (0.1 mL, 3.2 mmol) was added to a solution of ketone **5** (529 mg, 2.51 mmol) in 20 mL of acetic anhydride. The solution was kept under an atmosphere of nitrogen and heated at reflux for 3.25 h. Most of the acetic anhydride was removed under vacuum and the residue poured into water, stirred for 1 h, and extracted with ether. The ether solution was washed with sodium bicarbonate solution, dried over sodium sulfate, and filtered; the solvent was evaporated to leave 620 mg of a brown oil, which was shown by its IR and NMR spectrum to consist of **5** and acetic anhydride. The residue was redissolved in 35 mL of acetic anhydride, and concentrated sulfuric acid (1 mL, 32 mmol) was added dropwise while the solution was stirred. The mixture was stirred at room temperature for 4 days and worked up as described above to give 123 mg of recovered **5**.

Thermolysis of 1. (a) Without Solvent. Ketone **1** (348 mg, 1.67 mmol) was sealed in a Pyrex tube and kept in an oil bath at 200 °C for 15 min. It was then cooled in an ice bath. The methyl region in its NMR spectrum showed the peak at δ 1.25 assigned to **1** (ca. 45% of total), in addition to singlets at δ 0.98 and 1.22 assigned to the dimer of **1** (ca. 25% of total) and a doublet at δ 1.60 (ca, 30–35% of total). The product was chromatographed on silica gel, eluting first with 5% ethyl acetate in hexane to yield 122 mg (0.58 mmol, 35%) of recovered **1**. Elution with 10% ethyl acetate in hexane gave 69 mg of oily solid, which was rechromatographed to yield 10-methylanthrone (22 mg, 0.105 mmol, 6%), mp 63–65 °C (lit.[15] mp 64.5–65.5 °C). Elution of the original column with 20% ethyl acetate in hexane yielded 97 mg of tan solid, which after two crystallizations from ethyl acetate yielded 51 mg (0.12 mmol, 14%) of a dimer of **1**, identical with that obtained by acid-catalyzed dimerization.

(b) In Decalin Solution. A solution of ketone **1** (156 mg, 0.75 mmol) was heated at reflux for 15 min. Most of the solvent was removed by distillation under vacuum, and the residue was then subjected to steam distillation for 10 min. The mixture was cooled and extracted with methylene chloride; the organic layer was dried over magnesium sulfate and filtered, and the solvent was evaporated. The NMR spectrum of the residue (147 mg) was essentially identical with that of the product obtained by method a.

Photorearrangement of 1. A solution of **1** (150 mg, 0.72 mmol) in 10 mL of benzene in a Pyrex flask was cooled in an ice bath and irradiated by a GE 275-W sun lamp at a distance of 6 in. for 2.5 h. Evaporation of the solvent under vacuum left 151 mg of a pale yellow solid: ^{1}H NMR δ 2.27 (s, 3 H), 3.97 (s, 2 H), 7.4 (m, 5 H), and 8.2 (m, 2 H). Recrystallization from ethanol yielded 4-methylanthrone (137 mg, 0.65 mmol, 90%), mp 128–129 °C (lit.[10] 128.5–129.5 °C from ligroin). A

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mixture melting point with an authentic sample showed no melting point depression.

Samples similarly irradiated in chloroform solution for 35 min and in methanol solution for 2.5 h were quantitatively converted to 4-methylanthrone.

A sample was irradiated in deuteriochloroform, and aliquots were removed at 5-min intervals. No peaks not attributable to **1** or 4-methylanthrone could be detected in any spectrum. Conversion was essentially complete after 20 min.

2-(2-Methylbenzyl)benzoic Acid. 2-(2-Methylbenzoyl)benzoic acid[16] (2.75 g, 11.45 mmol) was dissolved in 70 mL of a 10% solution of sodium hydroxide in water. Zinc dust (5.0 g, 0.077 mol) and $CuSO_4 \cdot 5H_2O$ (50 mg) were added, and the mixture was heated under reflux for 64 h. It was cooled and the liquid decanted from the solid residue, which was washed with water and 0.5 M hydrochloric acid. The combined aqueous solutions were acidified with 6 M hydrochloric acid, cooled in ice, and filtered to give a white solid which was recrystallized from ethanol to yield 2-(2-methylbenzyl)benzoic acid (2.52 g, 11.15 mol, 97%) as white prisms, mp 127-128 °C (lit.[17] mp 126-129.5 °C): ^{1}H NMR δ 2.22 (s, 3 H), 4.45 (s, 2 H), 7.2 (m, 8 H), and 8.14 (dd, J = 7, 2 Hz, 1 H).

4-Methylanthrone. 2-(2-Methylbenzyl)benzoic acid (325 mg, 153 mmol) was dissolved in 10 mL of concentrated sulfuric acid. The deep yellow solution was kept at room temperature for 5 h. It was then poured into ice, cold water was added, and the mixture was extracted with ether. The ether layer was extracted with dilute sodium hydroxide solution and with brine, dried over magnesium sulfate, and filtered. Evaporation of the solvent under vacuum left a pale yellow solid which was recrystallized from ethanol to yield 4-methylanthrone (177 mg, 0.85 mol, 56%) as yellow needles, mp 128-129 °C (lit.[10] mp 128.5-129.5 °C from ligroin).

Photoirradiation of 1 in Diethylamine Solution. A solution of ketone **1** (117 mg, 0.56 mmol) in 5 mL of diethylamine was flushed with nitrogen for 20 min. It was then cooled in an ice water bath and irradiated by a GE sun lamp for 30 min. Evaporation of diethylamine under vacuum left 135 mg of a light brown oil, which was chromatographed on 230-400 mesh silica gel, eluting with 12% ethyl acetate in hexane to yield ***N,N*-diethyl-2-(2-methylbenzyl)benzamide** (125 mg, 0.44 mmol, 79%) as a colorless oil: ^{1}H NMR δ 0.98 (t, J = 7 Hz, 3 H), 1.15 (t, J = 7 Hz, 3 H), 2.20 (s, 3 H), 2.99 (q, J = 7 Hz, 2 H), 3.49 (bq, J = 7 Hz, 2 H), 4.00 (s, 2 H), 7.15 (m, 8 H); IR (neat) 1670 cm^{-1}. Anal. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24. Found: C, 79.76; H, 8.58.

***N,N*-Diethyl-2-(2-methylbenzyl)benzamide.** 2-(2-Methylbenzyl)-benzoic acid (196 mg, 0.92 mmol) was dissolved in a solution containing *N,N*-dimethylformamide (1.5 g) in 2.5 mL of thionyl chloride. The solution was allowed to stand under an atmosphere of nitrogen for 20 h and excess thionyl chloride was evaporated under vacuum. The residue was dissolved in 10 mL of methylene chloride and cooled in an ice-water bath. The solution was stirred while diethylamine (5 mL) was added drop by drop. After completion of the addition of diethylamine the mixture was removed from the ice bath and stirred an additional 10 min. It was then poured into ice water and extracted with methylene chloride. The organic layer was washed with 0.5 M hydrochloric acid and then with brine, dried over sodium sulfate, and filtered; the solvent was evaporated to yield *N,N*-diethyl-2-(2-methylbenzyl)benzamide (252 mg, 0.90 mmol, 96%) as a brown oil. Its NMR and IR spectra and behavior on thin layer chromatography were identical with those of the product obtained from the photorearrangement of **1**.

Attempted Reaction of 1 with Diethylamine. A solution of **1** (106 mg) in 4 mL of diethylamine was allowed to stand at room temperature in the dark for 65 h. Evaporation of the diethylamine under vacuum left unchanged **1** (107 mg).

Photocondensation of 1 with Maleic Anhydride. A stream of nitrogen gas was bubbled through a solution of **1** (1.05 g, 5.05 mmol) and maleic anhydride (1.49 g, 15.1 mmol) in 60 mL of methylene chloride for 10 min. The reaction flask was then sealed with a serum cap, cooled in ice, and irradiated with a sun lamp for 2 h. The solvent was evaporated under vacuum to give 2.34 of of a light brown solid, which was stirred with 20 mL of methylene chloride and filtered. The residue was washed with a small amount of methylene chloride and twice recrystallized from ethyl acetate to yield **1,2-dihydro-4-hydroxy-1-(2-methylphenyl)naphthalene-2,3-dicarboxylic anhydride** (716 mg, 2.34 mmol, 46%) as a white powder, mp 219-222 °C: ^{1}H NMR δ 2.45 (s, 3 H), 3.52 (d, J = 3 Hz, 1 H, H at C-2), 4.97 (d, J = 3 Hz, H at C-1), 7.3 (m, 9 H); IR 3507 (vs), 1860 (m), 1860 (m), and 1770 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.69; H, 4.83.

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Registry No. **1**, 80716-28-5; **2**, 84945-28-8; **3**, 84945-29-9; **4a**, 80716-24-1; **5**, 80716-26-3; **5** dibromide derivative, 84945-37-9; **6**, 84945-30-2; **7**, 52103-68-1; **8** α-OH derivative, 80716-23-0; **8** β-OH derivative, 84945-31-3; **8** *cis*-dialcohol derivative, 84945-35-7; **8** *trans*-dialcohol derivative, 84945-36-8; **9** α-OCH_3 derivative, 84945-32-4; **9** β-OCH_3 derivative, 84945-33-5; **10**, 80716-25-2; **12**, 80716-27-4; **12** dibromide derivative, 84945-34-6; **13a**, 85026-70-6; **13b**, 85026-15-9; **18**, 80716-39-8; **19**, 80716-40-1; 1,3-butadiene, 106-99-0; 2-methylnaphthoquinone, 58-27-5; 1,4-naphthoquinone, 130-15-4; 10-methylanthrone, 73653-01-7; 9-methoxyanthracene, 2395-96-2; 4-methylanthrone, 80716-38-7; *N*-phenylmaleimide, 941-69-5; 2-(2-methylbenzyl)benzoic acid, 7111-77-5.

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Rearrangement and Fragmentation Reactions of Blocked Aromatic Alcohols

Ajit K. Bhattacharya and Bernard Miller*

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003. *Received August 20, 1982*

Abstract: Alcohols **3** and **5**, which contain semibenzene ring systems, react unusually slowly in acidic solutions. Reaction of **3** with sulfuric acid in acetic acid gives ketone **9**, resulting from fragmentation of the central ring. Alcohol **5** under the same conditions gives a rearrangement product, 9-methylanthracene, as well as a fragmentation product. In solutions containing acetic anhydride both **3** and **5** give solely products resulting from molecular rearrangements. Factors responsible for determining the reaction products and reactivities of the starting alcohols are discussed.

In the preceding paper we reported the synthesis of ketone **1**, the first reported compound δ containing two rings which are simultaneously prevented from achieving aromaticity by the presence of a single blocking group.[1] We hoped to be able to convert **1** to the fused blocked aromatic hydrocarbon **2** by reaction with methylenetriphenylphosphorane, but our attempts failed. Only recovered **1** was obtained. Similarly, reaction of **1** with lithium trimethylsilylmethide[2] or with magnesium and diiodo-

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