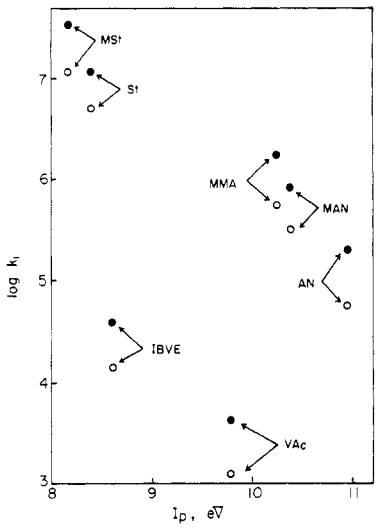

Figure 4. Plots of log k_1 vs. the ionization potentials of vinyl monomers (I_p); ○ and ● denote the 1- and 2-naphthalenylthio radicals, respectively.

established during the xenon flash duration (ca. 10 μs).

Figure 3 shows the plot of log k_1 vs. log Kk_2; a linear free-energy relationship is established. This suggests that the reactivities of each naphthalenylthio radical toward various vinyl monomers are mainly determined by the thermodynamic stabilities of the adduct carbon-centered radicals. On the other hand, it can be presumed that the dependence of the k_1 values upon the ionization potentials of vinyl monomers is a measure of the polar transition state.[18] In Figure 4, the upper group contains conjugated vinyl monomers, and the lower group contains nonconjugated ones; each group shows a negative dependence, which can be interpreted by the contribution of a polar resonance structures such as [NaphS$^-$, CH_2=CHY^+·]. Thus, the both factors from the linear free-energy relationship and the polar transition state are affecting the reactivities.

For each vinyl monomer, the k_1 value for the 2-naphthalenylthio radical is greater than that for the 1-naphthalenylthio radical by a factor of 2.5–3.8; such a difference is sufficiently greater than the estimation error in our experiments. Although the addition of the 1-naphthalenylthio radical is considered to be entropically less favorable, it is found that such a steric factor may not influence the reactivity since the points for both the naphthalenylthio radicals in Figure 3 fit to one line. The polar nature of both the thio radicals is also same since the similar tendency is seen in Figure 4. As seen in Figure 3, the greater exothermicity of the 2-naphthalenylthio radical compared with that of the 1-naphthalenylthio radical corresponds to the higher reactivity toward each vinyl monomer; thus the 2-naphthalenylthio radical is thermodynamically less stable than the 1-naphthalenylthio radical.

The phenylthio radical is more reactive than the naphthalenylthio radicals (PhS·/2-NaphS·/1-NaphS· ratio of 6:3:1),[11] which also reflect the less stable phenylthio radical. The resonance energies calculated for the benzyl radical and the 1- and 2-naphthylmethyl radicals are (in β units) 0.022, 0.024, and 0.026, respectively. This order is in good agreement with our observation about the stabilities of the thio radicals. It is notable that the reactions producing the naphthalene-substituted radicals as mentioned in the introduction[1-4] can also be interpreted by the linear free-energy relationship; the reactivities are proportional to the stabilities of the radicals in the products.

Experimental Section

Naphthyl disulfides were prepared from the commercially available naphthalenethiols by the action of iodine. Vinyl monomers were used after distillation under reduced pressure. Cyclohexane and *n*-heptane used as solvents were of spectrophotometric grade.

The flash experiments were made at room temperature which was controlled at 23 ± 1 °C. The flash apparatus was of standard design; the half-duration and flash energy of the xenon flash lamp (Xenon Corp., N-851C) were ca. 10 μs and 150 J, respectively. The flash light in the range of 350–400 nm was selected by the use of appropriate light filter to prevent the excitation of the vinyl monomers. Kinetic observations were made with a continuous monitor light source and photomultiplier detection. The oxygen concentrations in solution were calculated from the Henry law by dissolving oxygen under partial pressure after degassing the solution.[19]

Registry No. 1-Naphthalenylthio radical, 85736-23-8; 2-naphthalenylthio radical, 85736-24-9; styrene, 100-42-5; methyl methacrylate, 80-62-6; methyacrylonitrile, 126-98-7; acrylonitrile, 107-13-1; isobutyl vinyl ether, 109-53-5; vinyl acetate, 108-05-4; α-methylstyrene, 98-83-9.

(18) (a) Kobayashi, T.; Arai, T.; Sakuragi, H.; Tokumura, K.; Utsunomiya, C. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1658. (b) Houk, K. H.; Munchausen, L. *J. Am. Chem. Soc.* **1976**, *98*, 937. (c) Sustmann, R.; Trill, H. *Tetrahedron Lett.* **1972**, 4271.

(19) Murov, S. I. "Handbook of Photochemistry"; Mercel Dekker: New York, 1973; p 89.

Formation and Rearrangements of Blocked Aromatic Molecules Substituted with O$^-$ Groups

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Reaction of diketone **7** with strong bases results in migration of the angular methyl group to form 10-hydroxy-10-methyl-9-anthrone (**9a**). Surprisingly, no similar reaction occurs on treatment of diketone **11**, the 1-methyl analogue of **7**, with base. Reaction of **7** with base is therefore considered to result in stereospecific abstraction of the pseudoaxial β proton to yield the blocked aromatic anion **3**. Rearrangement of diketone **15**, the 6-methyl analogues of **7**, yields 2,10-dimethyl-10-hydroxy-9-anthrone (**16**), indicating that rearrangements of **3** and **15** proceed by [1,2] migrations of the angular methyl groups.

Molecules containing "blocked aromatic"—cyclohexadienone or methylenecyclohexadiene (semibenzene)—rings undergo an exceptional variety of rearrangement processes to yield products in which the blocked aromatic

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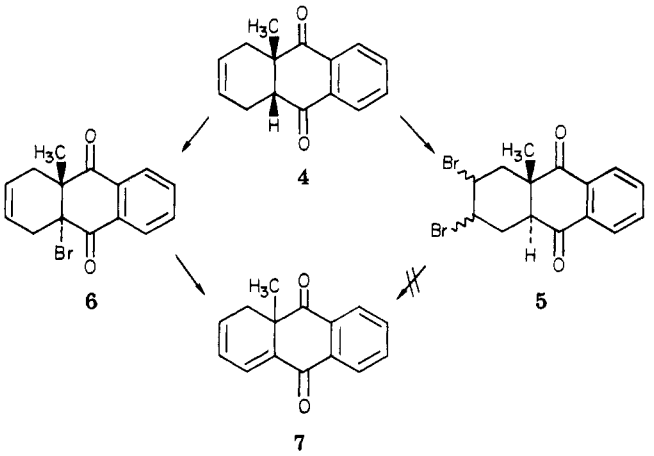
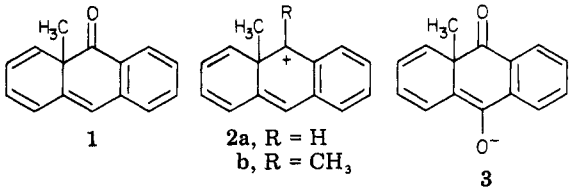
Scheme I



rings are transformed to aromatic isomers.[1,2] We recently reported the synthesis and properties of ketone **1**, the first



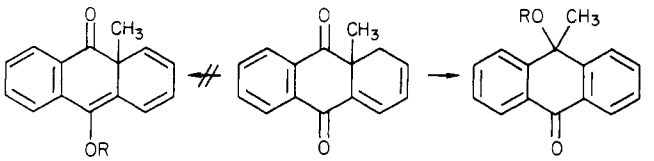
example of a molecule containing fused semibenzene and cyclohexadienone rings.[3] We also reported the syntheses and reactions of carbenium ions **2a** and **2b**, the first examples of blocked aromatic carbenium ions of a type which might result from alkylation of fused aromatic rings at a ring juncture. Not unexpectedly, these ions were found to undergo unusual aromatization processes.[4]

In this paper we report the preparation and reactions of anion **3** and its analogues, in which the fused blocked aromatic system of ketone **1** is modified by an oxyanion substituent at C-10.[5]

Preparation and Rearrangement of Anion 3. Ketone **4**, the starting material for preparation of **3**, is readily available from Diels–Alder condensation of 2-methylnaphthoquinone with butadiene.[3] We expected to be able to convert **4** to **7**, a conjugate acid of **3**, by addition of bromine to the isolated double bond of **4**, followed by bis dehydrobromination (Scheme I). However, addition of bromine to **4** was unexpectedly slow and was accompanied by evolution of HBr. In the initial run, nonetheless, dibromide **5** (shown by the coupling constants of the hydrogen at the ring juncture, C-4a, to have the trans-fused ring system) was obtained in 50% yield. In a second run under (apparently) the same conditions, the principal product isolated was the α-bromo ketone **6**, together with smaller amounts of **5**. Inspection of the NMR spectrum of the reaction product from the initial bromination run showed that **6** was also formed in ca. 25% yield in that reaction. Bromo ketone **6** could best be prepared by adding hydrochloric acid to **4** before addition of bromine. Under these conditions little, if any, **5** is produced.

Attempts to form diketone **7** by reaction of **5** with potassium *tert*-butoxide in *tert*-butyl alcohol or Me_2SO gave only intractable tars. However, **7** could be obtained in 46% yield by dehydrobromination of bromo ketone **6** with lithium bromide and lithium carbonate in refluxing DMF.

Deprotonation of **7** with potassium *tert*-butoxide in HMPT to form anion **3** followed by reaction of the anion with methyl trifluoromethanesulfonate was expected to yield the enol ether **8a**. However, no evidence could be detected for formation of this product. Instead, 10-hydroxy-10-methyl-9-anthrone (**9a**) and its ether **9b** were

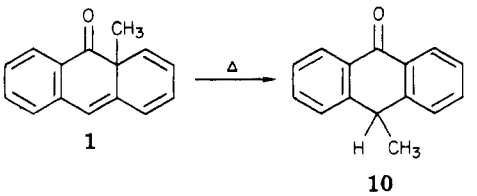


8a, R = CH_3
b, R = $C(O)CH_3$ **7** **9a**, R = H
b, R = CH_3

isolated and identified by comparison with authentic samples. When **7** was reacted with potassium *tert*-butoxide in HMPT or THF solution, **9a** was isolated in high yield and could be converted to **9b** on methylation with methyl iodide.

Mechanism of Base-Catalyzed Rearrangement of 7

Rearrangement of diketone **7** in base to form **9a** adds a new type of rearrangement to the many known reactions of blocked aromatic molecules, since the first step in the rearrangement process is almost certainly formation of the blocked aromatic anion **3**. Anthrone **9a** could then have been formed from **3** either by a [1,2] migration of the angular methyl group to the adjacent carbonyl carbon (C-9) or by a [1,3] migration to C-10. The latter "semibenzene rearrangement" would closely resemble the thermal rearrangement of **1** to form 10-methyl-9-anthrone (**10**).[3]



1 **10**

Semibenzene rearrangements requiring migrations of methyl groups (unlike those involving migrations of allyl, benzyl, or polyhalomethyl groups[2]) normally proceed only at high temperatures. However, the CH_3–C bond energy in anion **3** should be appreciably lower than the comparable bond energy in **1**, so that the possibility of a low-temperature semibenzene rearrangement in **3** cannot automatically be ruled out.

Due to the high degree of symmetry in **9a** and **9b**, identical products would be obtained from [1,2] and [1,3] migrations in anion **3**. To distinguish between the two possible modes of migration, it was necessary to examine the rearrangement of an analogue of diketone **7** with a symmetry-breaking "label". For this purpose, diketone **11** was prepared as shown in Scheme II. Reaction of 2-methylnaphthoquinone with *trans*-piperylene gave a mixture which appeared to contain two major and two minor Diels–Alder adducts (NMR analysis). When the

(1) Ground-state rearrangements of cyclohexadienones: (a) Miller, B. In "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"; de Mayo, P., Ed.; Interscience: New York, 1963; part 1, pp 600–696. (d) Waring, A. J. In "Advances in Alicyclic Chemistry"; Hart, H., Karabatsos, G. J., Eds.; Academic Press: New York, 1966, Part 1, pp 131–152.

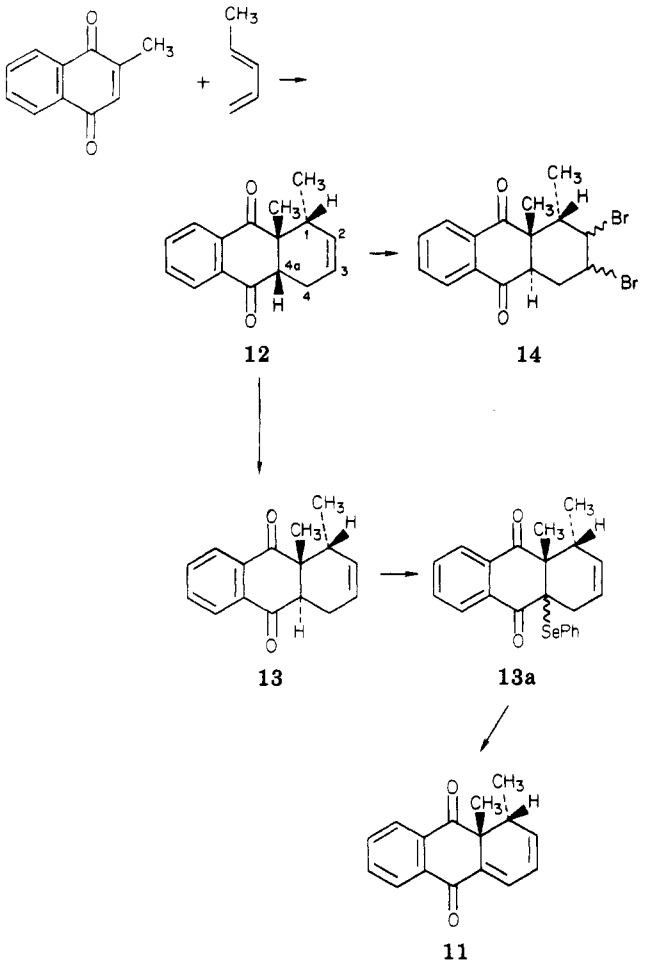
(2) Rearrangements of semibenzenes: (a) von Auwers, K.; Keil, G. *Chem. Ber.* **1903**, *36*, 1861. (b) von Auwers, K. *Justus Liebigs Ann. Chem.* **1907**, *352*, 216. (c) von Auwers, K.; Jühlicher, W. *Chem. Ber.* **1922**, *55*, 2167. (d) Newman, M. S.; Layton, R. M. *J. Org. Chem.* **1968**, *33*, 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. *J. Am. Chem. Soc.* **1983**, *105*, 3234.

(4) Bhattacharya, A, K.; Miller, B. *J. Am. Chem. Soc.* **1983**, *105*, 3242.

(5) A preliminary report of this work has been published: Miller, B.; Bhattacharya, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 2450.

Scheme II. Synthesis of Diketone 11



mixture was allowed to stand, one of the components (12) precipitated in nearly pure form (27% yield). The fact that the NMR signal for the angular hydrogen at C-4a was split by two adjacent hydrogens with almost equal coupling constants indicated that 12 possessed a cis ring juncture. (Compare the spectrum of 12 with the spectra of its epimer, 13, and those of adduct 4 and its trans isomer.[3]) The splitting of the signal for the angular proton similarly indicated that, as expected, the secondary methyl group in 12 was located at C-1 rather than C-4. The geometry at C-1 could not be established from the spectra of 12, but chemical evidence (see below) suggests that the C-1 methyl group is trans to the angular methyl. The trans geometry of the two methyl groups is the geometry which would arise from the expected "endo" addition of the quinone to the butadiene system.

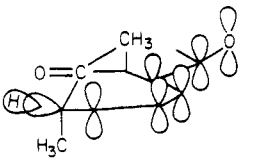
Epimerization with lithium diisopropylamide resulted in 90% conversion of 12 to a stereoisomer, 13, which could not be obtained in crystalline form. The NMR spectrum of the mixture of products from the Diels–Alder condensation of 2-methylnaphthoquinone with *trans*-piperylene indicated that it contained approximately equal quantities of 12 and 13. Together, these two stereoisomers comprised ca. 72% of the Diels–Alder products. The two minor products could not be isolated or identified.

Reaction of diketone 12 with bromine in the presence of hydrochloric acid gave the addition product 14 in high yield, in contrast to bromination of the desmethyl analogue 4 under the same conditions which resulted almost entirely in formation of the α-bromo ketone. At present, we can offer no satisfactory explanation for the differences in the nature of the products obtained from reaction of 4 and 12 with bromine.

Attempts to dehydrohalogenate 14, like similar reactions with dibromide 5, resulted solely in formation of tarry products. No evidence for formation of 11 could be observed. However, 11 was obtained in 65% yield by introduction of a phenylseleno group at C-4a of 12, followed by oxidative elimination to introduce the second double bond in the cyclohexadiene ring.

In contrast to 7, diketone 11 could not be caused to rearrange to a hydroxyanthrone. Reaction of 11 with base under the conditions employed for rearrangement of 7 (potassium *tert*-butoxide in THF or HMPT solutions) resulted in recovery of unchanged 11, as did prolonged heating in the presence of tertiary amines. When reaction of 11 with potassium *tert*-butoxide in THF was carried out in the presence of deuterium oxide, no incorporation of deuterium could be detected, demonstrating that formation of the anion of 11 could not be achieved under these conditions. When much stronger bases (e.g., lithium diisopropylamide) were employed, only tarry, uncharacterized products were obtained.

We suggest that the surprising difference in ease of formation of the anions of 7 and 11 is due to the rigidity of the cyclohexadiene ring in each of these compounds. One substituent at C-1 of both 7 and 11 is fixed in a quasi-equatorial postion, almost orthogonal to the π orbitals of the dienone unit, while the other substituent occupies a quasi-axial position in which its bond to the ring is essentially coplanar with the π system. Since both substituents in 7 are hydrogen atoms, reaction of 7 with bases readily results in abstraction of the axial proton to form anion 3. In contrast, if diketone 11 has the postulated

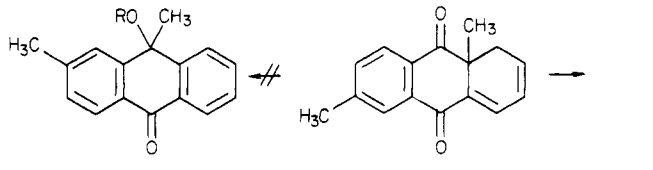


11

trans-dimethyl structure, the C-1 proton would occupy a pseudoequatorial position. The transition state for abstraction of that proton should be far less stabilized by interaction with the adjacent π system than the transition state for reaction of the pseudoaxial proton of 7.

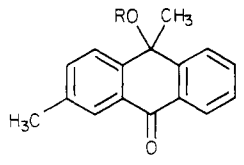
Since 11 thus proved unexpectedly worthless for determining the mechanism of rearrangement of 7 to 9, we decided to prepare another "nonsymmetrical" analogue of 7 which would be more likely than 11 to undergo rearrangement. Diketone 15 was synthesized in good yield in the same manner as 11 by starting with the Diels–Alder reaction of butadiene with 2,6-dimethylnaphthoquinone. On reaction with potassium *tert*-butoxide in HMPT, 15 was converted to a compound which was clearly a 10-hydroxy-10-methyl-9-anthrone. The two possible products were 16 (derived from a [1,2] methyl migration) or 17 (from a [1,3] migration). Initial evidence that the actual structure was 16 was obtained by methylation of the hydroxy group of the rearrangement product to form a 10-methoxy-10-methyl-9-antrone, mp 68–69 °C. Since the 10-methoxyantrone 19 has been reported to have a melting point of 111 °C,[6] it was concluded that the ether obtained by methylation of the rearrangement product was 18. Independent synthesis of anthrone 16 as shown below yielded a product identical with that obtained by rearrangement of 15.

(6) Mancilla, J. M.; Nonbel, D. C.; Russell, J. A. *Tetrahedron*. 1975, *31*, 3097.

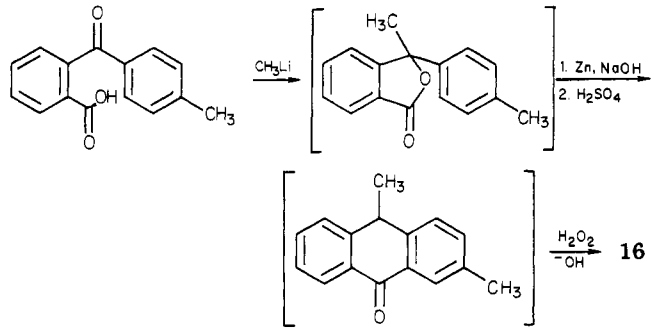


17, R = H
19, R = CH_3

15

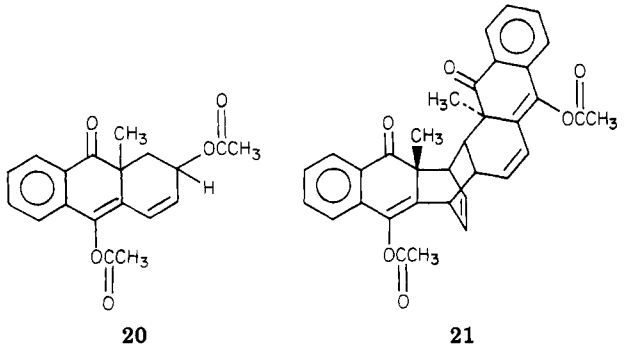


16, R = H
18, R = CH_3



Thus, the base-catalyzed rearrangements of **7** and **15** must have proceeded by [1,2] methyl shifts rather than [1,3] shifts.

Acetylation of 7. The [1,2] migration of a methyl group to C-9 of diketone **7** seemed likely to proceed in the presence of acid as well as of basic catalysts. However, diketone **7** was recovered unchanged after standing in acetic acid containing sulfuric acid or from ether containing boron trifluoride. When **7** was allowed to stand in a solution of acetic anhydride containing sulfuric acid, a mixture was obtained from which two crystalline products were isolated by column chromatography. The major product (mp 178–179 °C) appeared to be formed by addition of the elements of acetic anhydride to **7**. Its spectra corresponded to that expected of the 1,4-addition product **20**, a structure suggested by a referee for this paper.



20 21

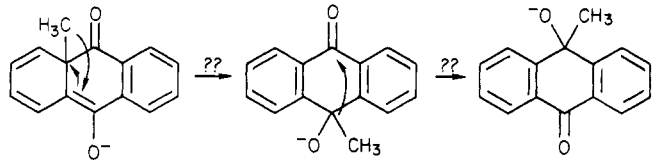
TLC and spectroscopic evidence indicated that the minor product was a single, pure compound, although, despite repeated recrystallization and column chromatography, its melting point remained broad (153–158 °C). Its elemental analysis corresponded to that of a monoacetylation product of **7**, and acetylation with acetic anhydride in pyridine at 100 °C gave the same product. The NMR spectrum of the product (see Experimental Section) suggested it to be a dimer resulting from Diels–Alder condensation of the two molecules of the blocked aromatic enol acetate **8b**. (Both the UV and NMR spectra are quite similar to those of the dimer obtained from ketone **1** on heating or reaction with acids.[3]) We tentatively propose structure **21** for this product, on the assumption that dimerization of **8b** proceeds by a "head to head" process.

Formation of **20** and **8b** rather than products of methyl migration in the acid-catalyzed acylation of **7** can be attributed to preferential acylation of the less hindered carbonyl at C-10. It is of interest that dimerization of **8b** (presumably catalyzed by acid) appears to be more rapid than migration of a methyl group, even though the migration would result in aromatization of the semiaromatic ring.

Discussion

When diketones **7** and **15** are reacted with strong bases, the angular methyl groups migrate to the carbonyl carbons at C-9 to form 10-hydroxy-10-methyl-9-anthrones. Blocked aromatic anions (**3** and its 6-methyl derivative) are almost certainly intermediates in these rearrangements.

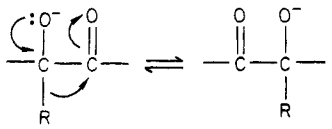
It has been suggested (by a referee for our preliminary paper[5]) that the apparent [1,2] methyl shifts in these arrangements might proceed by [1,3] shifts to C-10, followed by [1,4] migrations to C-9 (as shown below). However,



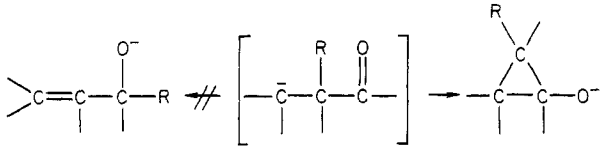
it has been observed that even benzyl groups (which, unlike methyl groups, will indeed undergo [1,4] migrations in 9-anthracenyl cations[7,8]) do not undergo such shifts in 10-hydroxy-9-anthrones.[8] Furthermore, an equilibrium mixture of anthrones **16** and **17** should have been produced from rearrangement of diketone **15**, if it indeed proceeded by the [1,3] shift mechanism. Since no evidence was observed for formation of **17** in that reaction, we can be confident that rearrangements of **7** and **15** proceed by direct [1,2] methyl shifts.

Base-catalyzed migrations of alkyl or aryl groups to electron-deficient centers are well-known, but in all such reactions—benzilic acid rearrangements,[9] acyloin rearrangements of α-ketols,[10] *quasi*-Favorskii rearrangements of halo ketones,[11] and semipinacolic rearrangements of β-halo alcohols[12]—the migration origins are substituted with oxygen atoms, so that rearrangement results in formation of a new bond of a carbonyl or carboxylate group:

(7) Beckwith, A. L. J.; Renfrow, W. B.; Renfrow, A.; Teubner, J. K. *Tetrahedron. Lett.* **1968**, 3463.
(8) Creedon, V. C. Ph.D. Dissertation, University of Massachusetts, 1979.
(9) For a brief review of the benzilic acid rearrangement, see: Collins, C. J.; Eastham, J. F. In "The Chemistry of the Carbonyl Group"; Patai, S., Ed.; Interscience: New York, 1966, pp 778–787.
(10) (a) Mazur, Y.; Nussim, M. *Tetrahedron Lett.* **1961**, 817. (b) Wendler, N. L. In "Molecular Rearrangements"; de Mayo, P., Ed.; Interscience: New York, 1963, Vol. 2, pp 1114–1121. (c) Nickon, A.; Nishida, T.; Lin, Y.-I. *J. Am. Chem. Soc.* **1969**, *91*, 6861. (d) Urry, W. H.; Duggan, J. C.; Pai, M.-S. H. *Ibid.* **1970**, *92*, 5785. (e) Paukstelis, J. V.; Stephens, D. N. *Tetrahedron Lett.* **1971**, 3549. (f) Nickon, A.; Nishida, T.; Frank, J.; Muneyuki, R. *J. Org. Chem.* **1971**, *36*, 1075.
(11) E.g.: (a) Mousseron, M.; Phvou Du, N. *Hebd. Seances Acad. Sci.* **1944**, *218*, 281. (b) Tchoubar, B. *Bull. Soc. Chim. Fr.* **1955**, 1363. (c) Baudry, D.; Bégué, J. P.; Charpentier-Morize, M. *Ibid.* **1971**, 1416. (d) Conia, J. M.; Salaun, J. R. *Acc. Chem. Res.* **1972**, *5*, 33. (e) Kende, A. *Org. React. (N.Y.)* **1963**, *11*, 261.
(12) E.g.: (a) Wendler, N. L. *Chem. Ind. (London)* **1958**, 1663. (b) Mousseron, M.; Winternitz, F.; Crastes de Paulet, A. *C. R. Hebd. Seances Acad. Sci.* **1958**, *246*, 2200. (c) Winteritz, F.; Crastes de Paulet, A. *Bull. Soc. Chim. Fr.* **1960**, 1460. (d) Puterbaugh, W. H.; Hauser, C. R. *J. Am. Chem. Soc.* **1964**, *86*, 1105.



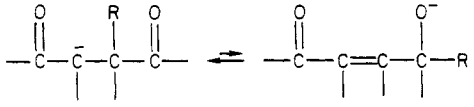
In principle, migration of an alkyl group from a non-hetero-substituted carbon atom to a carbonyl carbon might similarly occur in a β-keto anion such as **22**. However,



22

no such rearrangements have been reported. Instead, simple β-keto (homoenolate) anions have always been observed to rearrange via cyclopropanol formation and reopening, rather than by [1,2] alkyl migrations.[13]

We have been unable to find in the literature any examples of rearrangement of "stabilized" homoenolate anions comparable to **3**. Such rearrangements appear highly improbable in systems lacking semiaromatic rings, since the keto–hydroxy enol transformations would be thermodynamically unfavorable:



As so often happens, the thermodynamic drive accompanying transformation of a semiaromatic ring in **3** to an aromatic ring allows occurrence of a previously unknown type of anionic rearrangement.

Experimental Section

General Methods. 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 with Me_4Si as an internal standard. UV spectra were taken on a Carey Model 14 spectrometer. 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. Microanalyses were carried out by the University of Massachusetts Microanalytical Laboratory, Amherst, MA. Melting and boiling points are uncorrected.

1,2,3,4,4aβ,9a-Hexahydro-2,3-dibromo-9aα-methyl-9,10-anthracenedione (5). A solution of bromine (1.90 g, 0.0106 mol) in 20 mL of cold carbon tetrachloride was added rapidly to a stirred solution of 1,4,4aα,9a-tetrahydro-9aα-methyl-9,10-anthracenedione (**4**; 2.26 g, 10 mmol) in 25 mL of carbon tetrachloride at −8 °C. After 5 min the cooling bath was removed. The deep red bromine color began to lighten after an additional 5 min and had turned to a pale yellow after 5 min more. Some HBr vapor was produced during the reaction. The solution was filtered free of a small amount of white solid, washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated to give 3.1 g of a pale yellow solid. Three recrystallizations from methylene chloride–hexane yielded **5** (1.93 g, 50%) as a white solid: mp 205–208 °C. (An analytical sample was recrystallized from ethanol, mp 207–209 °C); ^{1}H NMR δ 1.22 (s, 3 H), 2.0–3.15 (m, 4 H), 3.15 (dd, J = 4, 12 Hz, 1 H at C-4a), 3.75–4.65 (m, 2 H), 7.70–8.25 (m, 4 H); IR 1685, 1700 cm^{-1}. Anal. Calcd for $C_{15}H_{14}Br_2O_2$: C, 46.63; H, 3.63. Found: C, 46.39; H, 3.60.

4aβ-Bromo-1,4,4a,9a-Tetrahydro-9aα-methyl-9,10-anthracenedione (6). A solution of bromine (10.0 g, 62.5 mmol) in 125 mL of cold methylene chloride was added dropwise to a stirred solution of **4** (13.56 g, 60.0 mmol) containing 0.1 mL of hydrochloric acid in 100 mL of methylene chloride at 0 °C. Stirring was continued for 5 min to give a pale yellow solution, which was washed with ice water and dried over sodium sulfate. The solution was filtered and the solvent evaporated to give 21 g of a pink solid, which was stirred and heated in 125 mL of a mixture of ethanol and benzene (4:1). The mixture was cooled and filtered, and the filtrate evaporated to ca. one-fourth its original volume to yield 15.30 g (80%) of an apparent 3:1 mixture of **6** and its 4α-bromo isomer (based on the appearance of two methyl singlets at δ 1.23 and 1.65), mp 78–80 °C. An analytical sample of **6** (mp 99–100 °C) was prepared by two further recrystallizations from ethanol: ^{1}H NMR δ 1.23 (s, 3 H), 2.20–3.30 (m, 4 H), 5.75–5.95 (m, 2 H), 7.10–8.45 (m, 4 H). Anal. Calcd for $C_{15}H_{13}BrO_2$: C, 59.03; H, 4.29; Br, 26.19. Found: C, 59.02; H, 4.25; Br, 25.98.

1,9a-Dihydro-9a-methyl-9,10-anthracenedione (7). A mixture of **6** and its 4a epimer (12.2 g, 0.040 mol) was added in portions to a suspension of lithium bromide (8.0 g, 0.092 mol) and lithium carbonate (10.0 g, 0.135 mol) in 120 mL of anhydrous *N,N*-dimethylformamide. The mixture was stirred under nitrogen at room temperature for 10 min and then at 125 °C for 2 h. Part of the solvent (80 mL) was distilled off at 0.05 torr, and the remaining solution was cooled in ice and diluted with ice water. The resulting suspension was carefully acidified with 1 M hydrochloric acid and extracted with ether. The ether extracts were washed with water and dried over sodium sulfate, and the solvent was removed under vaccum to leave 8.5 g of orange oil. The oil was chromatographed on 300 g of silica gel (100–200 mesh), by elution with 15% ethyl acetate in hexane, to yield pure **7**: 4.1 g (46%), pale yellow needles; mp 71–72 °C (from ether); ^{1}H NMR δ 1.25 (s, 3 H), 2.78 (d, J = 2.5 Hz, 2 H), 6.25–6.45 (m, 2 H), 7.28–7.47 (m, 1 H at C-4), 7.60–7.97 (m, 2 H), 8.00–8.40 (2 H); IR 1685, 1695 cm^{-1}. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.36. Found: C, 80.14; H, 5.56.

Reaction of 7 with Potassium *tert*-Butoxide and Methyl Trifluoromethanesulfonate. Potassium *tert*-butoxide (896 mg, 8.0 mmol) was added to a stirred solution of **7** (448 mg, 2.0 mmol) in 10 mL of hexamethylphosphoric triamide (HMPT) under nitrogen at −8 °C. The resulting black suspension was stirred for 10 min, and methyl trifluoromethanesulfonate (0.45 mL, 5.6 mmol) was then added dropwise while the temperature was maintained below −3 °C. The reaction mixture was stirred for 10 min, diluted with ice–water, acidified with 1 M hydrochloric acid, and extracted with ether. The ether extracts were washed with water, dried over sodium sulfate, and filtered, and the solvent was evaporated to give 525 mg of a light brown oil. The crude product was chromatographed on silica gel, eluting with 20% ethyl acetate in hexane, to give 10-methoxy-10-methyl-9-anthrone (**9b**, 130 mg, 27%) as white needles, mp 111–112 °C (lit. mp 111–112 °C,[6] 115–116 °C[15]). Its ^{1}H NMR and IR spectra were identical with those previously reported.[15] Further elution gave 10-hydroxy-10-methyl-9-anthrone (**9a**): 55 mg (12%); pale yellow crystals; mp 148–150 °C (lit.[16] double mp 146–148 °C, 153.2–155 °C); ^{1}H NMR δ 1.59 (s, 3 H), 3.3 (br s, 1 H), 7.16–8.30 (m, 8 H); IR 1640, 3440 cm^{-1}.

The NMR spectrum of the product before chromatography showed it to consist of **9b** and **9a** in the ratio 3.5:1.

Base-Catalyzed Rearrangement of 7. Solid potassium *tert*-butoxide (224 mg, 2.0 mmol) was added to a stirred solution of **7** (100 mg, 0.446 mmol) in 3 mL of HMPT at −10 °C under

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(14) The formation of diketone **7** in 5.4% yield (VPC analysis) by condensation of crotonaldehyde with 2-methylnaphthoquinone was reported by: Casiraghi, G.; Casnati, G.; Salerno, G. *Chem. Commun.* **1972**, 955. No physical constants or experimental details were reported.

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nitrogen. The resulting black solution was stirred at −10 °C for 25 min and at room temperature for an additional 20 min. A mixture of ice and water was added to the reaction mixture, which was then acidified with 1 M hydrochloric acid and twice extracted with ether. The ether extracts were washed with water, dried over sodium sulfate, and filtered, and the solvent was evaporated to yield **9a** (85 mg, 85%) as a yellow solid.

1α,4,4aα,9a-Tetrahydro-1β,9aα-dimethyl-9,10-anthracenedione (12). A solution of 2-methyl-1,4-naphthoquinone (24.0 g, 0.14 mol), *trans*-piperylene (10.0 g, 0.147 mol), and hydroquinone (0.5 g, 4.5 mmol) in 150 mL of absolute ethanol was stirred and heated in a pressure reactor at 150 °C for 7 h. Evaporation of the solvent left a viscous oil, which was extracted with hexane, and the insoluble black residue was discarded. Evaporation of the solvent left 25.6 g of a yellow oil, which was redissolved in a small amount of hot hexane. On cooling, **12** (9.1 g, 27%) was obtained as white crystals, mp 102–105 °C. An analytical sample had the following properties: mp 108–108.2 °C (from ethanol); ^{1}H NMR δ 1.06 (d, J = 6.0 Hz, 3 H), 1.17 (s, 3 H), 2.35–2.90 (m, 3 H), 3.33 (t or dd, J = 8.0 Hz, 1 H), 5.62–5.85 (m, 2 H), 7.60–8.35 (m, 4 H). Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.67. Found: C, 80.17; H, 6.79.

Epimerization of 12. A solution of **12** (240 mg, 1.0 mmol) in 5 mL of anhydrous tetrahydrofuran was added dropwise to a stirred solution of lithium diisopropylamide in 5 mL of tetrahydrofuran at −73 °C. The reaction mixture was stirred at −73 °C for 12 min. It was then warmed to room temperature, and stirring was continued for an additional 8 min. The resulting red solution was cooled to −65 °C, diluted with 2 mL of water, acidified with 1 M hydrochloric acid, and extracted with ether. The ether extracts were washed with dilute hydrochloric acid and with brine, dried over sodium sulfate, filtered, and evaporated under vacuum to give 248 mg of a yellow oil, shown by NMR analysis to consist of 10% of **12** and 90% of 1α, 4,4aβ,9a-tetrahydro-1β,9aα-dimethyl-9,10-anthracenedione (**13**): ^{1}H NMR δ 0.73 (d, J = 7.0 Hz, 3 H), 1.48 (s, 3 H), 1.90–2.90 (m, 3 H), 2.95–3.25 (m, 1 H), 5.60–5.85 (m, 2 H), 7.60–8.35 (m, 4 H).

1α,2,3,4,4aβ,9a-Hexahydro-2,3-dibromo-1β,9aα-dimethyl-9,10-anthracenedione (14). A solution of bromine (0.90 g, 5.6 mmol) in 10 mL of methylene chloride was added dropwise over a 15-min period to a stirred solution of **12** (1.20 g, 5.0 mmol) and 0.1 mL of concentrated hydrochloric acid in 25 mL of methylene chloride at 0–3 °C. Stirring was continued at room temperature for 5 min to give a light red solution to which was added just enough dilute sodium sulfite solution to reduce the residual red color to a pale yellow. The reaction mixture was washed with water, the methylene chloride layer was dried over sodium sulfate and filtered, and the solvent was evaporated under vacuum to give 1.185 g of a pale yellow solid. Two recrystallizations from absolute ethanol yielded **14**: 1.40 g (70%); white needles: mp 155.5–157 °C; ^{1}H NMR δ 1.51 (d, J = 7.5 Hz, 3 H), 1.58 (s, 3 H), 2.55–3.25 (m, 3 H), 3.86 (dd, J = 9.0, 5.0 Hz, 1 H at C-4a), 4.75–4.90 (m, 1 H), 4.85–5.12 (m, 1 H), 7.65–8.35 (m, 4 H); IR 1685, 1703 cm^{-1}. Anal. Calcd for $C_{16}H_{16}Br_2O_2$: C, 48.03; H, 4.03; Br, 39.94. Found: C, 48.14; H, 4.12; Br, 40.29.

1α,4,4a,9a-Tetrahydro-1β,9aα-dimethyl-4a-(phenylseleno)-9,10-anthracenedione (13a). A solution of **12** (1.92 g, 8.0 mmol) in 15 mL of anhydrous tetrahydrofuran was added dropwise over a 10-min period to a stirred solution of lithium diisopropylamide (9.0 mmol) in 20 mL of anhydrous tetrahydrofuran under nitrogen at −68 °C. The temperature was then allowed to rise to −25 °C, maintained at that temperature for 25 min, and again lowered to −70 °C. A solution of phenylselenium bromide (2.09 g, 8.8 mmol) in 15 mL of anhydrous tetrahydrofuran was aded dropwise to the solution over an 8-min period. The mixture was then warmed to 25 °C, stirred at that temperature for 3.5 h, and poured into ice-cold 1 M hydrochloric acid solution. It was then extracted with ether, and the ether layer washed with dilute hydrochloric acid and with water and dried over magnesium sulfate. It was filtered and the solvent evaporated under vacuum to give 3.41 g of a red oil, which was chromatographed on silica gel by eluting with 12% ethyl acetate in hexane. The title compound (2.47 g, 78%) was obtained as a yellow solid: mp 104–105 °C (from methanol); ^{1}H NMR δ 0.54 (d, J = 7.0 Hz, 3 H), 1.76 (s, 3 H), 2.15–3.45 (m, 3 H), 5.54–5.75 (m, 2 H), 7.10–7.45 (m, 5 H), 7.50–7.90 (m, 3 H), 7.90–8.30 (m, 1 H); IR 1685, 1695 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_2Se$: C, 66.84; H, 5.06. Found: C, 66.71; H, 5.31.

1α,9a-Dihydro-1β,9aα-dimethyl-9,10-anthracenedione (11). A solution of sodium periodate (10.0 g, 0.0467 mol) in 90 mL of water was added over a 10-min period to a stirred solution of **13a** (1.77 g, 4.5 mmol) in 90 mL of methanol at 10 °C. The reaction mixture was stirred at room temperature for 6.5 h and then diluted with 300 mL of water. The mixture was extracted with ether, the ether layer washed with water, dried over magnesium sulfate, and filtered, and the solvent was evaporated under vacuum to give 1.14 g of orange-yellow oil. The oil was chromatographed on silica gel, eluting with 15% ethyl acetate in hexane to yield **11**: 0.90 g (84%); yellow solid; mp 75–77 °C (from ether); ^{1}H NMR δ 0.92 (d, J = 7.0 Hz, 3 H), 1.40 (s, 3 H), 2.75–3.30 (m, 1 H), 6.20–6.50 (m, 2 H), 7.28–7.45 (m, 1 H), 7.62–8.00 (m, 2 H), 8.05–8.49 (m, 2 H); IR 1660, 1682, 1692 cm^{-1}; UV (MeOH) λ_{max} 231 nm (ε 9700), 247 (23 200), 325 (sh, 6960), 338 (7770). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.37; H, 5.91.

1,4,4aα,9a-Tetrahydro-6,9aα-dimethyl-9,10-anthracenedione (23). 2,6-Dimethyl-1,4-naphthoquinone[17] (46.0 g, 0.2473 mol) and hydroquinone (2.0 g, 0.0182 mol) were suspended in 400 mL of absolute ethanol, and the mixture cooled to −50 °C. 1,3-Butadiene (50 mL, ca. 0.8 mol), liquefied in a dry ice bath, was added and the mixture was then stirred and heated at 95 °C in a pressure reactor for 5 h. The cooled mixture was filtered to yield 31.5 g (68%) of recovered 2,6-dimethyl-1,4-naphthoquinone. The solvent was evaporated under vacuum to leave a brown residue which was recrystallized twice from hexane and once from 5% ethyl acetate in hexane to yield **23** (11.3 g, 19%) as pale yellow needles, mp 66–68 °C. An analytical sample was obtained as colorless needles: mp 70.0–71.5 °C (absolute ethanol); ^{1}H NMR (CCl_4) δ 1.29 (s, 3 H), 1.50–2.80 (m, 4 H), 2.45 (s, 3 H), 2.93 (t or dd, J = 6.0 Hz, 1 H at C-4a), 5.50–5.73 (br s, 2 H), 7.49 (dd, J = 8.0 Hz, 1 Hz, 1 H at C-7), 7.71 (br s, 1 H at C-5), 7.87 (d, J = 8.0 Hz, 1 H); IR 1680, 1692 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.96; H, 6.72. Found: C, 79.86; H, 6.97.

1,9a-Dihydro-6,9a-dimethyl-9,10-anthracenedione (15). A solution of **23** (6.40 g, 0.0267 mol) in 40 mL of anhydrous tetrahydrofuran was added dropwise over a 20-min period to a stirred solution of lithium diisopropylamide (0.030 mol) in 50 mL of tetrahydrofuran under nitrogen at −70 °C. The reaction mixture was allowed to warm to −30 °C over a 30-min period and then again cooled to −70 °C. A solution of phenylselenium bromide (6.7 g, 0.0282 mol) in 40 mL of tetrahydrofuran was added dropwise over a 20-min period, while the reaction temperature was maintained below −62 °C. The mixture was warmed to 25 °C, stirred at that temperature for 2.5 h, and poured into cold 1 M hydrochloric acid solution. The acid mixture was extracted with hexane, and the hexane layer was washed with dilute hydrochloric acid and with water and dried over sodium sulfate. Evaporation of the solvent under vacuum left 10.9 g of an orange oil, which was dissolved in 250 mL of 95% ethanol. To this solution was added, with stirring, a solution of sodium periodate (35.0 g, 0.1636 mol) in 250 mL of water. The resulting suspension was stirred at room temperature for 3 h. Water (1 L) was added and the mixture extracted twice with ether. The combined ether extracts were washed with water, dried over sodium sulfate, and filtered, and the solvent was evaporated under vacuum to give 7.2 g of a yellow solid. Recrystallization from 25% ethyl acetate in hexane yielded **15**: 2.93 g (46%); yellow solid; mp 114.5–115.5 °C; ^{1}H NMR δ 1.25 (s, 3 H), 2.51 (s, 3 H), 2.70–2.90 (m, 2 H), 6.26–6.45 (m, 2 H), 7.33 (dd, J = 4, 2.5 Hz, 1 H at C-4), 7.58 (dd, J = 7, 1.5 Hz), 8.0 (d, J = 7 Hz, 1 H at C-8), 8.09 (s, 1 H at C-5). UV (MeOH) λ_{max} 233 nm (ε 9875), 249 (23 790), 325 (sh, 7005), 340 (7892). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80,74; H, 5.80.

2,10-Dimethyl-9-anthrone. A suspension of 2-*p*-toluoylbenzoic acid[18] (24.0 g, 0.10 mol) in 260 mL of anhydrous ether was stirred and cooled in a dry ice–acetone bath. A solution of methyllithium in ether (2.0 M, 0.23 mmol) was added dropwise over a 1-h period. The cooling bath was then removed and the reaction mixture stirred for an aditional 1.5 h. The mixture was poured into a

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solution of dilute hydrochloric acid containing ice to give a white precipitate, which was filtered and air-dried to give 36 g of white powder. Part of the powder (24 g) was added to a mixture of zinc (40 mesh, 13 g) and sodium hydroxide (15 g) in 150 mL of water, and the mixture heated at reflux for 10 h. Additonal zinc (20 g) and a solution of sodium hydroxide (20 g) in 150 mL of water were added to the reaction, and refluxing was continued for 20 h. A final portion of zinc (5 g) was added and refluxing continued for 20 h. The reaction mixture was cooled and poured into ice-cold hydrochloric acid solution, and the mixture was extracted with methylene chloride. The methylene chloride layer was washed with water, dried over anhydrous magnesium sulfate, and filtered, and the solvent was evaporated under vacuum to give 8.4 g of a white solid, which was suspended in 70 mL of concentrated sulfuric acid. The mixture was warmed on a steam bath for 5 min to form a green solution which was allowed to stand at room temperature for 4 h and was then poured into ice, and the mixture was extracted with methylene chloride. The methylene chloride layer was washed with water, dried over magnesium sulfate, and filtered, and the solvent was evaporated to give 7.8 g of 2,10-dimethylanthrone: mp 65–67 °C (from ethanol) (lit.[19] mp 63–64 °C); ^{1}H NMR δ 1.44 (d, J = 7.5 Hz, 3 H), 2.35 (s, 3 H), 4.10 (q, J = 7.5 Hz, 1 H), 7.2–7.5 (m, 5 H), 8.03 (br s, 1 H), 8.15–8.35 (m, 1 H).

Base-Catalyzed Rearrangement of 15. Potassium *tert*-butoxide (2.0 g, 0.0179 mol) was added in small portions via a connecting tube to a solution of **15** (1.60 g, 6.7 mmol) in 25 mL of HMPT under nitrogen at 20 °C. The resulting black suspension was stirred for 1.25 h, and 100 mL of water was then added. The mixture was acidified with 100 mL of 1 M hydrochloric acid and immediately extracted several times with ether. The combined ether extracts were washed with water, dried over sodium sulfate, and filtered, and the solvent was evaporated under vacuum to give 1.70 g of a yellow-orange solid. Recrystallization from absolute ethanol yielded 2,10-dimethyl-10-hydroxy-9-anthrone (**16**) as a yellow solid which had a melting point, a mixture melting point, and spectra identical with those of a sample prepared by oxidation of 2,10-dimethyl-9-anthrone.

2,10-Dimethyl-10-hydroxy-9-anthrone (16). A solution of potassium hydroxide (4.0 g, 0.0714 mol) in 20 mL of water was added to a solution of 2,10-dimethyl-9-anthrone (1.60 g, 7.2 mmol) in 40 mL of hot methanol. The resulting reddish brown solution was stirred, and 10 mL of 30% hydrogen peroxide solution was added. The mixture was heated on a steam bath for 20 min, until the color had turned a pale yellow. Ice–water was added, and the resulting precipitate was filtered off and recrystallized twice from ethanol and once from 30% ethyl acetate in hexane to yield **16**: 0.71 g (41%); white crystals; mp 143.0–144.5 °C; ^{1}H NMR δ 1.54 (s, 3 H), 2.33 (s, 3 H), 3.40 (br s, OH), 7.12–8.17 (m, 7 H); IR 1653, 3490 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.63; H, 5.93. Found: C, 80.41; H, 5.98.

2,10-Dimethyl-10-methoxy-9-anthrone (18). A solution of **16** (1.20 g, 5.0 mmol) in 15 mL of dimethyl sulfoxide was added dropwise over a 15-min period to a stirred suspension of sodium hydride (1.0 g, 0.042 mol) in 10 mL of dimethyl sulfoxide under an atmosphere of nitrogen. The mixture was stirred for an additional 10 min, and methyl iodide (6 mL, 0.096 mol) was added dropwise over a 15-min period. The deep violet color of the mixture faded to give a yellow suspension. The mixture was stirred for an additional 2 h, poured into ice–water, and extracted with ether. The ether extracts were washed with water, dried over sodium sulfate, and filtered, and the solvent was evaporated under vacuum to give 1.36 g of a yellow oil, which was chromatographed on silica gel by elution with 7% ethyl acetate in hexane, to yield **18**: 1.08 g (85%); white needles; mp 68–69 °C (from hexane); ^{1}H NMR δ 1.66 (s, 3 H), 2.42 (s, 3 H); 2.86 (s, 3 H); 7.25–7.95 (m, 5 H), 8.15 (br s, 1 H at C-1), 8.32 (dd, J = 7.5, 1.5 Hz, 1 H at C-8); IR 1670 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.91; H, 6.40. Found: C, 80.76; H, 6.65.

Reaction of 7 with Acetic Anhydride and Sulfuric Acid. Concentrated sulfuric acid (0.1 mL) was added to a solution of **7** (2.5 g, 105 mmol) in 100 mL of acetic anhydride under a nitrogen atmosphere, and the solution was stirred at room temperature for 20 h. Most of the solvent was then removed under vacuum at a temperature of ca. 50 °C, and the residue was shaken with water and extracted with ether. The ether layer was washed with water and with sodium bicarbonate solution, dried over sodium sulfate, and filtered, and the solvent was evaporated to give 3.1 g of yellow oil. TLC showed the presence of three major components. Chromatography (twice) on silica gel, by elution with 20% ethyl acetate in hexane, gave two crystalline fractions, A (0.41 g) and B (1.38 g). Fraction B was rechromatographed and then recrystallized twice from absolute ethanol and once from ethyl acetate to yield 0.64 g of a white solid (**20**): mp 178–179 °C; ^{1}H NMR δ 1.45 (s, 3 H), 2.05 (s, 3 H), 2.38 (s, 3 H), 5.60 (m, 1 H), 6.10 (dd, J = 12, 6 Hz, 1 H), 6.58 (d, J = 12 Hz, 1 H), 7.15–7.85 (m, 3 H), 8.07 (dd, J = 8, 2 Hz, 1 H) (the three methyl singlets were superimposed on a multiplet whose area could not be determined); IR 1683, 1727, 1760 cm^{-1}; UV (MeOH) λ_{max} 252 (ϵ 62 009), 262 (sh, 24 690), 273 (19 204), 328 (6035). Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.94; H, 5.55. Found: C, 69.68; H, 5.41.

Fraction A was recrystallized four times from absolute methanol to yield 47 mg of a white solid (**21**): mp 153–158 °C; ^{1}H NMR δ 1.04 (s, 3 H), 1.24 (s, 3 H), 2.35 (s, 3 H), 2.38 (s, 3 H), 2.60–3.25 (m, 2 H), 3.42–3.80 (m, 2 H), 5.60–6.44 (m, 4 H), 7.05–7.70 (m, 6 H), 8.06 (dd, J = 7, 1.5 Hz, 1 H), 8.38 (dd, J = 8, 1.5 Hz, 1 H); IR 1652, 1674, 1733, 1745 cm^{-1}; UV (MeOH) λ_{max} 244 nm (ϵ 47 020), 259 (53 301), 297 (18 123), 369 (6048), 379 (sh, 4110). Anal. Calcd for $C_{34}H_{28}O_6$: C, 76.67; H, 5.30. Found: C, 76.91; H, 5.34.

Acetylation of 7. A solution of **7** (210 mg, 0.90 mmol) in 4 mL of a 1:1 mixture of acetic anhydride and pyrdine was heated on a steam bath for 4.5 h. The solvents were evaporated under vacuum, and the residue was shaken with water for 10 min and then extracted with ether. The ether extracts were washed with water, dried over sodium sulfate, and filtered, and the solvent was evaporated to leave 225 mg of brown oil. The oil was chromatographed on silica gel, by eluting with 30% ethyl acetate in hexane, to give 124 mg of a crystalline product. This was recrystallized three times from ethanol to yield 17 mg of a pale yellow solid (mp 153–157 °C) identical with product A from reaction of **7** with acetic anhydride and sulfuric acid.

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Registry No. **3**, 85762-92-1; **4**, 84945-28-8; **5**, 85762-93-2; 4aα-**6**, 85762-94-3; 4aβ-**6**, 85762-95-4; **7**, 38251-14-8; **9a**, 17104-31-3; **9b**, 53190-24-2; **11**, 85781-11-9; **12**, 78931-96-1; **13**, 85762-96-5; **13a**, 85762-97-6; **14**, 85762-98-7; **15**, 74047-85-1; **16**, 85762-99-8; **18**, 85763-00-4; **20**, 85763-01-5; **21**, 85763-02-6; 2-methyl-1,4-naphthoquinone, 58-27-5; *trans*-piperylene, 2004-70-8; phenylselenium bromide, 34837-55-3; 2,6-dimethyl-1,4-naphthoquinone, 6290-94-4; 1,3-butadiene, 106-99-0; 1,4,4aα,9a-tetrahydro-6,9aα-dimethyl-9,10-anthracenedione, 85763-03-7; 1,4,4a,9a-tetrahydro-6,9aα-dimethyl-4aα-(phenylseleno)-9,10-anthracenedione, 85781-12-0; 2,10-dimethyl-9-anthrone, 85763-04-8; 2-*p*-toluoylbenzoic acid, 85-55-2; methyllithium, 917-54-4; 3-methyl-3-*p*-tolylisobenzofuranone, 85763-05-9; *o*-[1-(*p*-tolyl)ethyl]benzoic acid, 85763-06-0.

(19) Shemyakin, M. M.; Kolosov, M. N.; Hsieh, Y.-Y.: Karapetyan, M. G.; Shen, H.-Y.; Gurevich, A. I. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1964**, 1013; *Chem. Abstr.* **1964**, *61*, 9446.