δ 20.6, 22.0, 30.8, 43.9, 47.5, 70.0, 70.9, 83.1, 85.0, 102.1, 113.6, 114.2, 115.2, 126.5, 127.5, 127.7, 127.8, 128.1, 128.3, 128.4, 128.7, 129.0, 133.5, 137.2, 138.5, 149.1, 152.6, 171.1, 200.6; mass spectrum, m/z (relative intensity) 579.2635 (M^+, calcd for $C_{36}H_{37}NO_6$ 579.2621), 382 (1), 331 (5), 309 (1), 255 (1), 218 (1), 190 (1), 148 (2), 128 (3), 91 (100).

Vinylidene Carbonate Cycloadducts 40 and 41. Freshly distilled vinylene carbonate (2.71 g, 2.00 mL, 0.03 mmol) was transferred to a sealed tube apparatus containing nitrone 8β (692 mg, 1.36 mmol) in 10 mL of anhydrous xylenes. The mixture was heated at 120 °C for 72 h and then concentrated in vacuo. Flash chromatography of the residue (2:1 hexane/ethyl acetate) provided a 2:1 mixture of low R_f isomer 41 to high R_f isomer 40 for a combined yield of 55%. The diastereomers were separated by flash chromatography to afford 160 mg (18%) of high R_f isomer 40 and 325 mg (37%) of lower R_f isomer 41.

High-Pressure Cycloaddition of Nitrone 8β with Vinylene Carbonate. Freshly distilled vinylene carbonate (0.50 mL, 0.678 g, 7.87 mmol) was added to a solution of nitrone 8β in 3 mL of anhydrous THF. The solution was placed into a syringe and then into a high-pressure reactor. The vessel was pressurized to 12 kbar and allowed to react for 72 h. The syringe was removed and washed with EtOAc, and the solvent was removed in vacuo. Flash chromatography of the residue (2:1 hexanes/EtOAc) afforded an 80:20 mixture of diastereomers in 60% yield that were separated as above.

Cycloadduct 40. Crystallization of 40 in hexane/methylene chloride (9:1) afforded single crystals suitable for X-ray analysis: mp 200-201 °C; IR ($CHCl_3$) 1819 (vs), 1497 (m), 991 (m); ^1H NMR ($CDCl_3$) δ 1.73 (s, 3 H), 2.64 (s, 3 H), 3.56 (d, J = 2.5 Hz, 1 H), 4.41 (d, J = 2.5 Hz, 3 H), 4.87 (AB q, J = 11.7 Hz, 2 H), 5.01 (AB q, J = 9.8 Hz, 2 H), 5.23 (d, J = 5.3 Hz, 1 H), 5.92 (d, J = 5.3 Hz, 1 H), 6.21 (s, 1 H), 6.87 (dd, J = 8.8, 3.0 Hz, 1 H), 6.97 (d, J = 8.8 Hz, 1 H), 7.29 (d, J = 3.0 Hz, 1 H), 7.36 (m, 15 H); ^{13}C NMR (50 MHz) δ 22.6, 47.4, 70.4, 71.0, 71.3, 77.2, 84.7, 90.1, 103.3, 105.2, 112.3, 112.8, 114.4, 127.1, 127.5, 127.9, 128.4, 128.5, 129.1, 129.2, 129.3, 129.5, 135.7, 136.3, 137.2, 148.4, 152.3, 153.0; mass spectrum, m/z (relative intensity) 595.2209 (calcd for $C_{35}H_{33}NO_8$ 595.2206), 580 (12), 504 (8), 254 (15), 234 (24), 160 (79), 144 (32), 105 (100). **Cycloadduct 41.** Crystallization of 41 in hexane/methylene chloride (9:1) afforded single crystals suitable for X-ray analysis: mp 137-138 °C; IR ($CHCl_3$) 1817 (vs), 1491 (vs), 1378 (m); ^1H NMR ($CDCl_3$) δ 1.76 (s, 3 H), 2.65 (s, 3 H), 4.00 (d, J = 4.4 Hz, 1 H), 4.50 (d, A of AB q, J = 11.5 Hz, 1 H), 4.61 (d, J = 4.4 Hz, 1 H), 4.71 (d, B of AB q, J = 11.5 Hz, 1 H), 5.03 (AB q, J = 9.6 Hz, 2 H), 5.63 (d, J = 5.3 Hz, 1 H), 6.10 (d, J = 5.3 Hz, 1 H), 6.76 (dd, J = 8.9, 3.0 Hz, 1 H), 6.85 (d, J = 8.9 Hz, 1 H), 7.03 (d, J = 3.0 Hz, 1 H), 7.33 (m, 15 H); ^{13}C NMR (50 MHz) δ 21.9, 68.8, 70.2, 71.2, 80.8, 84.8, 87.2, 102.8, 103.9, 113.1, 113.6, 115.1, 126.5, 127.1, 127.5, 127.8, 128.0, 128.4, 128.5, 128.6, 128.9, 129.2, 133.9, 136.1, 137.1, 138.2, 148.6, 152.7, 152.9; mass spectrum, m/z 595.2195 (calcd for $C_{35}H_{33}NO_8$ 595.2206), 505 (29), 504 (89), 296 (19), 254 (18), 234 (32), 168 (20), 163 (27), 144 (59), 105 (100). Anal. Calcd for $C_{35}H_{33}NO_8$: C, 70.58; H, 5.58. Found: C, 70.17; H, 5.57.

Acknowledgment. We thank the National Institutes of General Medical Sciences (GM 37014) for generous financial support of this program. Dr. Michael Dicken, Thuy Le, Dr. Steve Lander, Jr., and Dr. Grady Lamb are acknowledged for helpful discussions during the course of this investigation. Finally, we acknowledge the support of Dr. Masood Parvez (X-ray, Pennsylvania State University), Dr. Yiu-Fai Lam (NMR), and Caroline Preyer (MS) in obtaining spectral data.

Supplementary Material Available: ^1H NMR spectra of compounds 8α, 8β, 11, 17, 18, 24-30, 33, 34, 38, and 39; ORTEP diagrams and X-ray data of compounds 8β, 28, 40, and 41; and tables of fractional coordinates and temperature factors, bond distances in angstroms, and bond angles in degrees (44 pages). Ordering information is given on any current masthead page.

Anthracenediols as Reactive Dienes in Base-Catalyzed Cycloadditions: Reduction-Cycloaddition Reactions of Anthraquinones[1]

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Anthraquinone is readily reduced to the hydroquinone (9,10-anthracenediol), which under basic conditions serves as a reactive diene for cyloaddition purposes. Catalytic hydrogenation in pyridine solvent provides convenient access to this species, and efficient reactions occur with dienophiles in situ, provided that they are sufficiently reactive. Thus *N*-methylmaleimide (NMM) gives the bicyclic bridgehead diol in near quantitative yield when the H_2/Pd reduction of anthraquinone is carried out in pyridine containing 1 equiv of NMM. Fumaronitrile and maleonitrile similarly give high yields in stereospecific reactions, with the dienophile geometry retained in the cycloadduct. Less reactive dienophiles suffer competitive reduction. Dimethyl fumarate in situ gives cycloadduct (stereospecifically) in only 35-60% yield, with the remainder of the dienophile reduced to dimethyl succinate. Stepwise reduction followed by addition of dienophile leads to a higher yield in this and related reactions. The benzologues 5,12-naphthacenedione and 6,13-pentacenedione undergo analogous reactions with NMM, leading to novel bridgehead diols. The monimine of anthraquinone exhibits NMR features attributed to syn/anti isomerism. Under neutral or mildly basic conditions, the aromatic protons on the ring proximal to the NH are clearly distinguished (500 MHz) from those on the distal ring. The addition of acid causes rapid syn/anti NH exchange leading to time averaged symmetry. This imine behaves similarly to anthraquinone in the reduction/cycloaddition sequence. For example, with NMM in situ an essentially quantitative yield of the novel bridgehead amino alcohol adduct is obtained. Related benzologue reactions and attempts to extend the sequence to the oxime and methylene analogues of anthraquinone are described. Base-catalyzed ring opening of the cycloadduct of NMM/anthracenediol leads to a novel retro-bis-aldol reaction, resulting in the formation of anthraquinone and *N*-methylsuccinimide.

Introduction

Novel base-catalyzed Diels-Alder reactions of 9-anthrone have recently been described.[1,2] The oxyanion or an amine hydrogen-bonded variant is believed to be the intermediate responsible for the very rapid cycloadditions which are observed in the presence of base. The possibility that hydroquinones and other substituted anthrone analogues

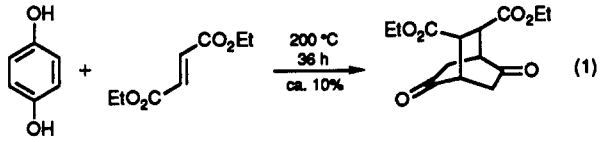
(1) A preliminary communication has appeared: Koerner, M.; Rickborn, B. *J. Org. Chem.* **1989**, *54*, 6.

(2) Koerner, M.; Rickborn, B. *J. Org. Chem.* **1990**, *55*, 2662.

0022-3263/91/1956-1373$02.50/0

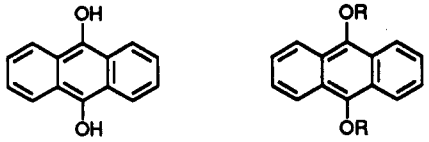
might exhibit similar behavior led to the present study.

Hydroquinone itself has been used in (uncatalyzed) Diels–Alder reactions by Nakazaki et al.[3] and by Jefford et al.[4] to give products such as that shown in eq 1, in which cycloaddition takes place across the 2,5-positions of the aromatic ring. This regiochemistry may be the result of thermodynamic control, since cycloaddition across the 1,4-positions would likely be readily reversible for simple hydroquinones.



(1)

Apparently no other arene 1,4-diols have been used as cycloaddition partners, although Krohn and Meihe[5a] have described reactions of substituted anthracenediols which in principle could have given Diels–Alder adducts although none were found (see later discussion). The parent 9,10-anthracenediol (1) appears to have escaped examination as a prospective diene, although this material has been known for many years.[6]

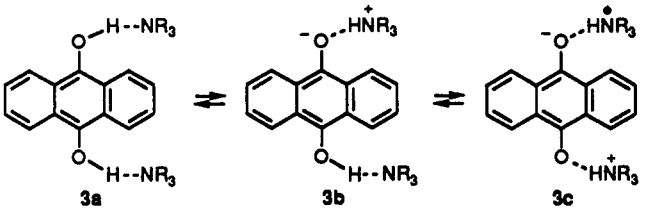


1 2a, R = Me 2b, R = SiMe3

The dimethyl ether derivative **2a** has been studied by Sauer and Wiest,[7] who found it to be somewhat *less* reactive than the parent hydrocarbon in cycloaddition with maleic anhydride. More recently Czarnick et al.[8] prepared the cycloadduct of ethyl acrylate with the bis(trimethylsiloxy)anthracene **2b**. These authors did not comment on any unusual reactivity features. The bis(trimethoxysiloxy) cycloadduct was subsequently converted to the corresponding bridgehead diol, thereby providing an alternative synthetic route to diols similar to those described below.

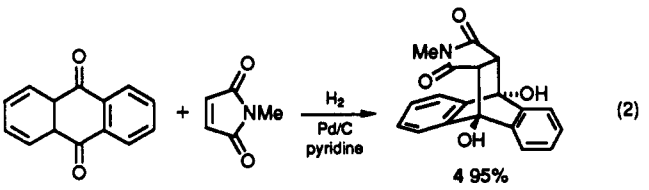
Results and Discussion

Catalytic reduction of anthraquinone in pyridine solvent gives a very dark solution. It is assumed, in analogy with base-catalyzed reactions of anthrone, that hydrogen bonded species such as **3a–c** (R_3N = pyridine) are formed.[9] An "oxyanion" complex of this kind is believed to be the reactive intermediate responsible for the reactions described below.



3a 3b 3c

Addition of *N*-methylmaleimide (NMM) to the dark solutions leads to the formation of the cycloadduct **4**. Interestingly, *catalytic reduction of a mixture of anthraquinone and NMM in pyridine also gives this product, in excellent yield* (eq 2).



(2)
4 95%

Successful application of this in situ dienophile procedure requires that both reduction of anthraquinone and cycloaddition be faster than hydrogenation of the dienophile. Reduction of the dienophile can certainly occur under these conditions, as shown by the formation of *N*-methylsuccinimide from any excess NMM employed. NMM is a very reactive dienophile, as shown in the base-catalyzed cycloaddition to anthrone reported earlier.[2] In that reaction the intermediate oxyanion is trapped so rapidly by NMM that proton transfer from anthrone to Et_3N becomes rate determining. For the reaction shown in eq 2, reduction of anthraquinone is probably the rate-limiting step. The fact that anthraquinone is reduced more rapidly than NMM can be attributed to preferential catalyst interaction and/or lower reduction potential.

The particular advantage of the in situ dienophile procedure stems from the very facile air oxidation of anthracenediol **1** under basic conditions, which tends to interfere with the stepwise method. However, the latter is preferred or needed for less reactive dienophiles, as outlined in some examples discussed below.

Fumaronitrile and maleonitrile are also very reactive dienophiles and work well in the in situ mode with anthraquinone. These reactions are stereospecific, leading exclusively and essentially quantitatively to cycloadducts **5** and **6**, respectively, with no indication of the alternative stereoisomer being formed in either reaction (by NMR, it is estimated that any amount over 1% would have been detected). These results parallel those reported earlier for the base-catalyzed reactions with anthrone and are likewise thought to be the result of concerted cycloaddition.

Dimethyl fumarate is estimated to be ca. 10^{-2} as reactive as NMM. This difference is sufficient to introduce difficulties into the in situ dienophile approach. Under the same conditions (slight excess of dienophile) that led to quantitative yields of cycloadducts with the more reactive dienophiles, dimethyl fumarate gave yields of only 35–60% of **7** in different runs. The remainder of the dienophile was reduced to dimethyl succinate, presumably by competitive catalytic hydrogenation (see later discussion).

(3) Nakazaki, M.; Naemura, K.; Yoshihara, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3278.

(4) Jefford, C. W.; Wallace, T. W.; Acar, M. *J. Org. Chem.* **1977**, *42*, 1654.

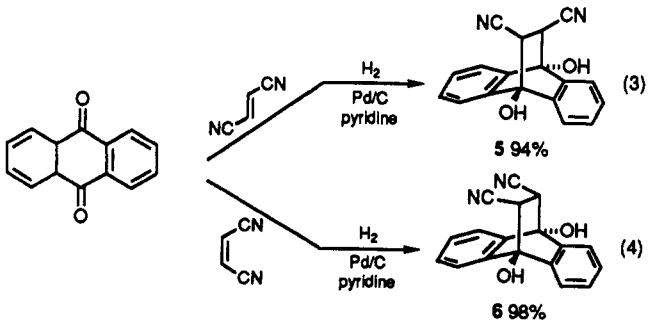
(5) (a) Krohn, K.; Miehe, F. *Liebigs Ann. Chem.* **1985**, 1329. (b) The reaction of the parent anthracenediol (anion) with MVK was described somewhat earlier: Dimmel, D. R.; Shepard, D. *J. Org. Chem.* **1982**, *47*, 22.

(6) Anthracene-9,10-diol was first generated as the red dianion by Zn/NaOH reduction of the quinone in 1870 (Boettger, R. *J. Prakt. Chem.* **1870**, *2*, 133). Subsequently, several reducing agents including most commonly $Na_2S_2O_4$ in NaOH solution (Grandmougin, E. *Chem. Ber.* **1906**, *39*, 3563) and H_2/Pt (Manchot, W.; Gall, H. *Chem. Ber.* **1925**, *58*, 486) have been employed. The diol is rapidly air oxidized to the quinone, especially under basic conditions. For more recent applications of preformed 9,10-anthracenediol, see ref 5b and Landucci, L. L.; Ralph, J. *J. Org. Chem.* **1982**, *47*, 3486. The latter papers describe reactions with *p*-quinone methides, which have been suggested as models for the catalytic effect of anthraquinone on delignification of wood under reductive conditions. Cycloaddition–cleavage pathways similar to those described in the present work are conceivable mechanistic alternatives to the Michael additions depicted in these papers, and indeed this possibility has previously been suggested by Ralph (J. Ralph, 1989, *Proceedings of the Intl. Symposium on Wood & Pulping Chemistry*, N.C. State University, Raleigh, NC, May 22–25, 1986, Session 4–2, p 61). We thank Dr. Ralph for calling this work to our attention.

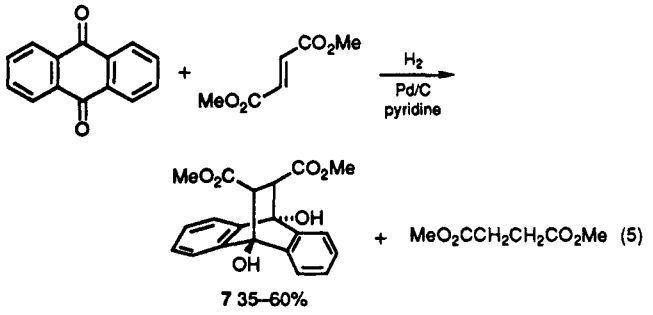
(7) Sauer, J.; Wiest, H. *Angew. Chem., Int. Ed. Engl.* **1961**, *1*, 269.

(8) Chung, Y.; Duerr, B. F.; McKelvey, T. A.; Nanjappan, P.; Czarnik, A. W. *J. Org. Chem.* **1989**, *54*, 1018.

(9) Similar hydrogen-bonded complexes have been postulated by Baba and Takemura for hydrocarbon solutions of anthrone to which Et_3N has been added: Baba, H.; Takemura, T. *Tetrahedron* **1968**, 4779.



Although the yield of cycloadduct **7** is modest the trans stereochemistry of the fumarate is retained in the product.



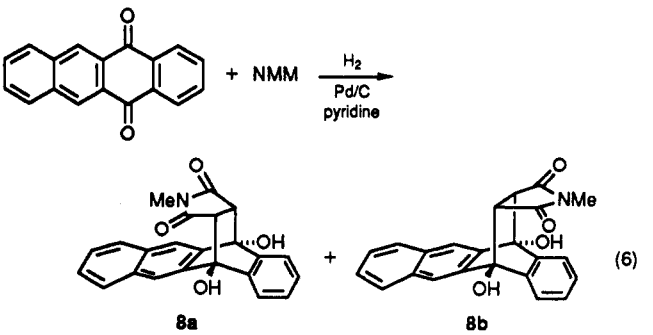
Competitive reduction of the dienophile can easily be avoided by separating the reduction and cycloaddition steps. Application of this sequential approach to the reaction of anthraquinone and dimethyl fumarate (1 equiv) caused the yield of **7** to rise to 80%. The procedure was the same as for the in situ dienophile reaction, except that the quinone was stirred under H_2 for 0.5 h, after which the atmosphere was replaced by Ar, and then the dienophile was introduced.

Direct evidence for base catalysis was obtained by examining the NMR spectra of a mixture of preformed **1** and dimethyl fumarate in acetone-d_6 solvent under various conditions. Neither the neutral mixture nor one treated with acid gave any indication of reaction after 2 h. However, an aliquot treated with Et_3N (ca. 5 equiv) gave 30% of cycloadduct in this same time period. This result also has significance for the related reactions of anthrones, reinforcing the conclusion[2] that the phenol tautomer itself is not the highly reactive species for cycloaddition.

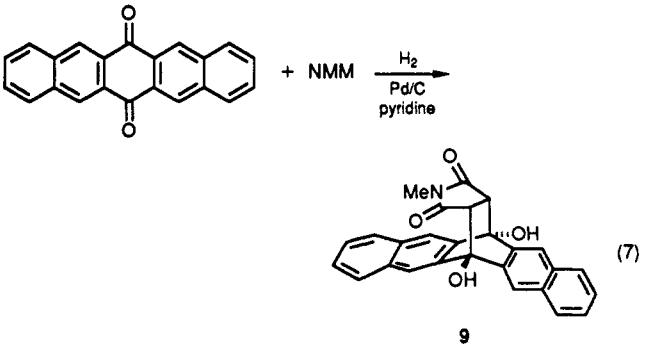
Linear benzannulation is known to enhance the reactivity of aromatic hydrocarbons toward dienophiles. Thus, the reactivity order pentacene > naphthacene > anthracene is observed for cycloaddition with maleic anhydride.[10] However, 5-naphthacenone proved to be less reactive than anthrone with NMM under base-catalyzed cycloaddition conditions.[2] We attributed this inversion of normal reactivity to diminished concentration of the reactive oxyanion intermediate. It was not clear from this experience what to expect for benzannulated anthraquinones, but the experiments described below indicate that high reactivity toward NMM is retained.

Catalytic reduction of a mixture of 5,12-naphthacenedione and NMM in pyridine gave two products identified as exo and endo cycloadducts **8a** and **8b**. These two very similar materials are formed in a ratio of 1.5/1; it is not known which is the major isomer.

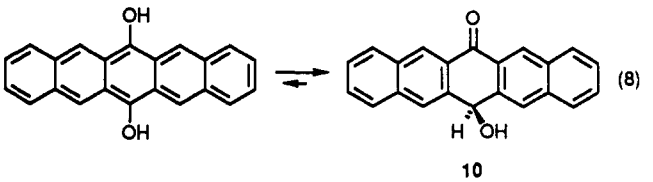
The reaction with 5,13-pentacenedione is even more striking because this material has only slight solubility in pyridine. In spite of this handicap, dissolution, reduction, and cycloaddition all occur in competition with reduction



of NMM, as shown by the isolation of cycloadduct **9** in 42% yield.

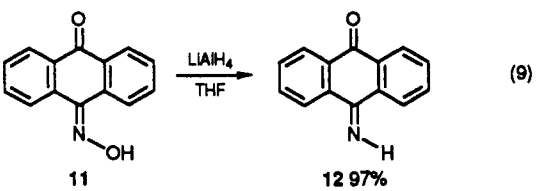


By analogy with the corresponding hydrocarbons, one might expect the pentacenediol intermediate to be more reactive (unstable) than anthracenediol. However, this reduction state proved to be readily isolable, apparently because of strong preference for the keto tautomer structure **10**, a conclusion supported by the NMR spectrum of this material.



Isolated compound **10** serves nicely as a "diene" under basic conditions, leading to **9** in excellent yield. The encouraging results with NMM in this stepwise procedure suggest that polycyclic quinones may also be employed with less reactive dienophiles, although this point was not examined in the present study.

Anthraquinone Monimine: NMR and Reactions. The monimine (**12**) appears to be the only analogue of anthraquinone with the same oxidation state and general structure that has been reported. It has been prepared[11] by $LiAlH_4$ reduction of the oxime **11** as shown in eq 9.



We employed both this method and an alternative catalytic reduction procedure described below to obtain **12**. Very different NMR spectra were exhibited by products from these methods, although other evidence suggested that the materials were the same. These initially puzzling observations are attributed to the large chemical

(10) Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3163.

(11) Costa, A.; Riego, J. M.; Garcia-Raso, A.; Sinisterra, J. V. *Liebigs Ann. Chem.* **1981**, 2085.

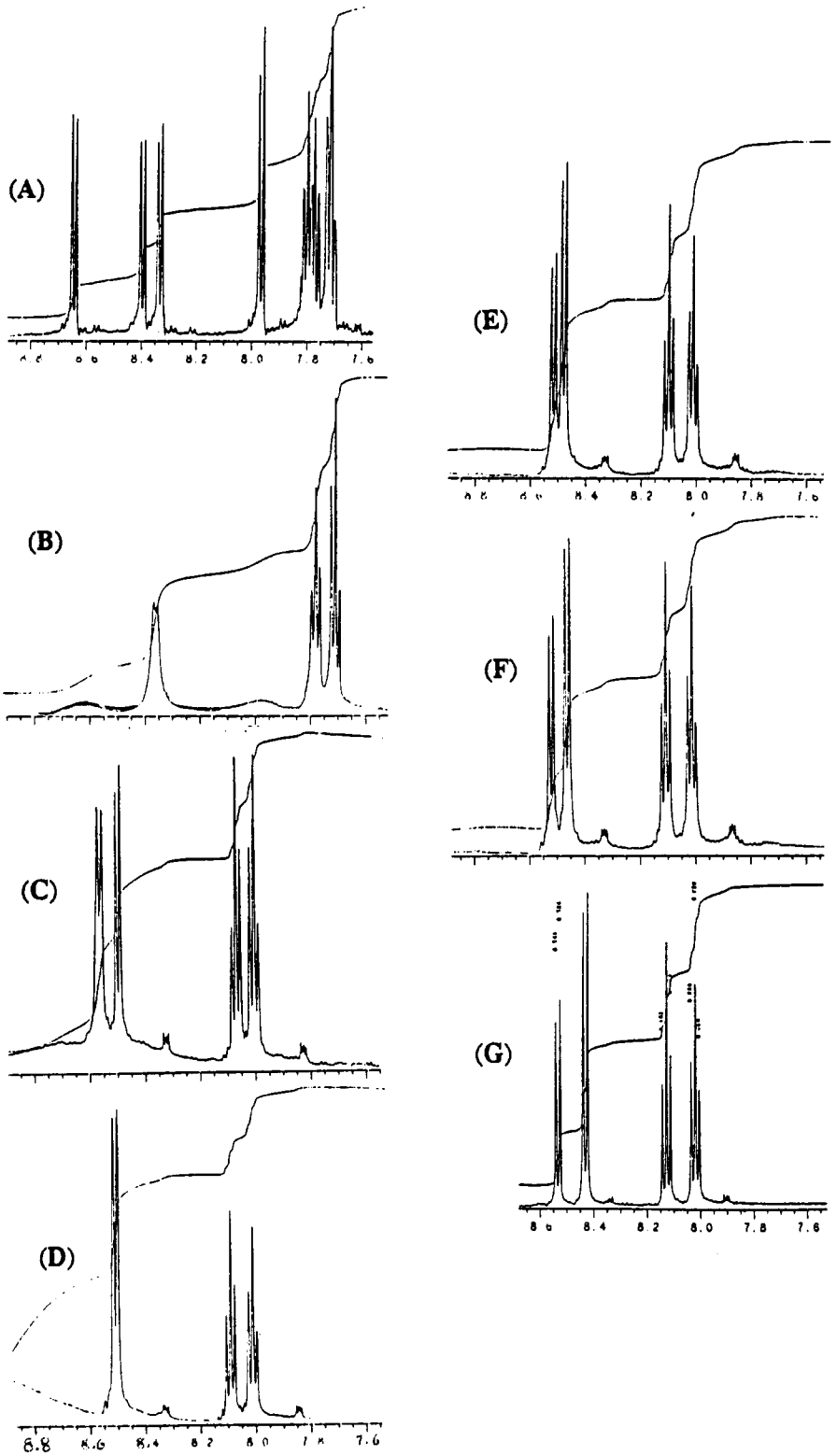
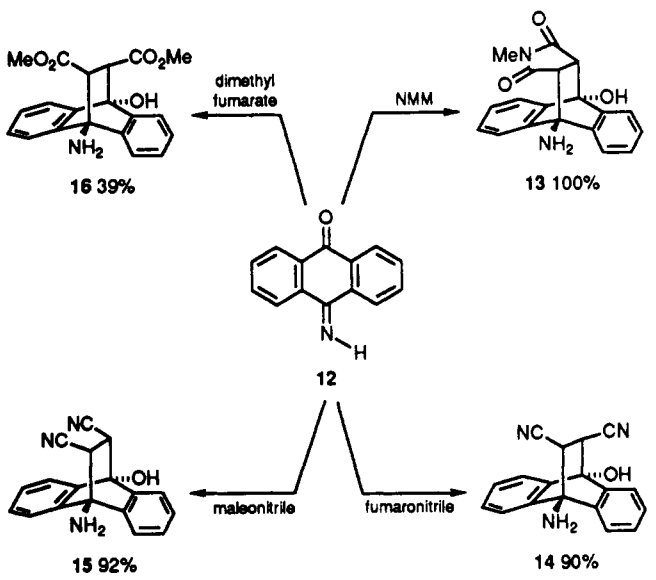


Figure 1. Spectra were obtained at 500 MHz in $CDCl_3$ solvent. A illustrates 12 as isolated from the $LiAlH_4$ reduction of oxime 11. B shows 12 which has been recrystallized from acetone; similar spectra were obtained when 12 was prepared by catalytic reduction of 11. Spectra C through G show the effects of adding increasing amounts of trifluoroacetic acid (TFA) to the NMR sample used to obtain B. The amounts of TFA added were: 4 μL (C), 8 μL (D), 12 μL (E), 20 μL (F), and a large excess, ca. 100 μL (G), where 1 molar equiv of TFA = ca. 10 μL. Spectrum A exhibited a sharp singlet at 11.0 ppm attributed to the NH proton. In B this peak was broadened but not measurably shifted. This signal was not seen in the other spectra, presumably due to exchange with the TFA.

shift differences of the aromatic ring protons caused by proximity (syn, anti) of the imine proton (NH). These NMR effects are shown in Figure 1. Spectrum A shows the region from ca. 7.6 to 8.8 ppm for material isolated without any purification step from the $LiAlH_4$ reduction procedure. This spectrum was reproducibly observed from various samples of 12 prepared in this manner. When this material is recrystallized (acetone or isopropyl alcohol), or prepared by catalytic reduction of the oxime, spectrum B or similar results. In both spectra the NH proton appears as a singlet at 11.0 ppm, sharp in A and broadened in B.

Figure 1C shows the effect of addition of a small amount (≤0.5 equiv) of trifluoroacetic acid (TFA), and D–G show the changes which result from adding increased amounts

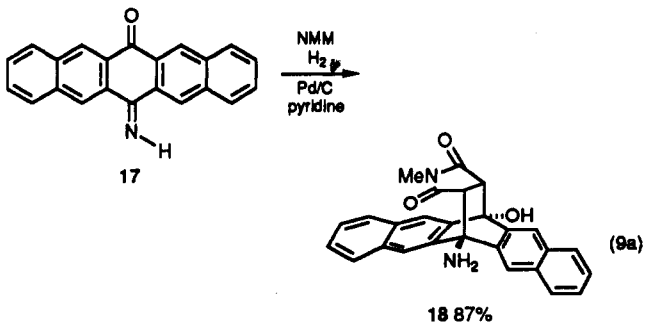
Scheme I



of TFA. The smallest amount of TFA caused the 8 aromatic proton spin system of A to simplify to the 4 proton spin system seen in C, as expected for rapid syn/anti imine interconversion. However, something in addition to syn/anti interconversion must occur, since the new chemical shifts are not simply the averages of the peaks in A or B. Contributions from protonated species are reasonable, but this alone does not seem to explain the shift phenomena observed, i.e., large changes in the triplet shifts caused by a small amount of acid, but no appreciable change as more is added. It appears that a change in the state of aggregation of **12** is also needed to rationalize this behavior.

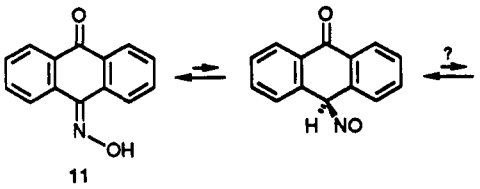
The imine **12** behaves much like anthraquinone when subjected to catalytic reduction (H_2, Pd/C, pyridine) in the presence of reactive dienophiles. Thus NMM, fumaronitrile, maleonitrile, and dimethyl fumarate give the cycloadducts **13**, **14**, **15**, and **16**, respectively. The reactions are stereospecific as shown. The yields are excellent except for the in situ dimethyl fumarate reaction, another parallel between anthraquinone and its monimine. Again the yield of this cycloadduct can be improved by the sequential reduction–cycloaddition approach, showing that the aminophenol has a reasonable lifetime under these conditions.

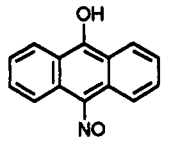
The monimine (**17**) of pentacenequinone was prepared by reduction of the monoxime, which was obtained by treatment of the quinone with hydroxylamine following the literature method for the anthraquinone analogue. The in situ dienophile procedure with NMM gave the bridgehead aminoalcohol derivative **18**.



(9a)

Other Quinone Analogues. The oxime **11** is an interesting candidate for similar reactions, both directly and under reductive conditions. One tautomeric form of **11** is nitrosoanthracenol **19**, and in fact we found that **11** can be prepared by treatment of anthrone with nitrous acid, following a general procedure for nitrosation of active methylene compounds.[12] An initial attempt to effect cycloaddition of **11** with NMM was done in DMF solvent, which had been used previously to effect NMM cycloaddition with unsubstituted anthrone.[2] No reaction was observed, even when the mixture was heated to 100 °C. Pyridine solvent was also used, but again no loss of starting materials was detected. The failure of **11** to undergo base-catalyzed cycloaddition may be due to very unfavorable equilibria, as outlined in eq 10. Only the oxime form **11** is observed in NMR spectra of this material taken in $CDCl_3$.

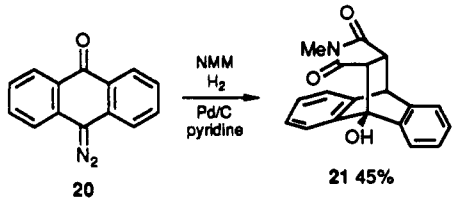




(10)

The use of **11** under reductive conditions was informative even though no new product was obtained. Instead, when an equimolar mixture of **11** and NMM in pyridine was subjected to catalytic hydrogenation, approximately 20% of the cycloadduct **13**, identical with product derived from the monoimine **12**, was formed, while most of the NMM was reduced to *N*-methylsuccinimide. Either the reduction of **11** or the interconversion of its possible intermediate reduction products to **12** occurs more slowly than reduction of NMM. It was independently established that **11** gives **12** under these hydrogenation conditions.

The dark red diazo analogue **20**[16] was also examined under the reductive cyclization conditions with NMM in situ. No bridgehead nitrogen-bearing product was observed. Instead, the cycloadduct **21**, which has been previously prepared[2] by base-catalyzed reaction of anthrone with NMM, was isolated in moderate yield. A control experiment without dienophile established that anthrone is formed rapidly from **20** under these reductive conditions, and the stepwise procedure applied to **20** gave **21** in near quantitative yield.

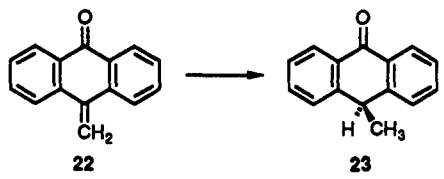


(11)

The methylene derivative **22** was of interest both as a quinone analogue and via reduction as a substituted anthrone (**23**). The usual catalytic hydrogenation of a mixture of **22** and NMM in pyridine gave no cycloadduct. Instead, both starting materials were reduced to give *N*-methylsuccinimide and 10-methylanthrone (**23**), respectively.

The substituted anthrone **23** was subjected to conditions (NMM, THF, Et_3N, 25 °C) which give very rapid cycloadduct formation with anthrone itself,[2] but no reaction was

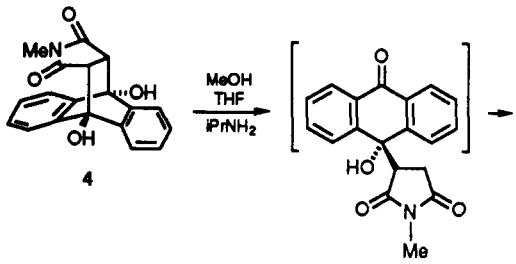
(12) Touster, O. *Org. React.* **1953**, *7*, 327.



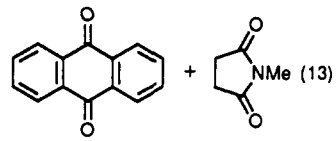
22 23 (12)

observed. The methyl substituent thus prevents reaction, reminiscent of the failure of ethyl crotonate to enter into cycloaddition with anthrone under these conditions.[2] Of the 10-position substituents examined, only hydroxyl and amino groups appear to be well-tolerated in the cycloaddition process under the conditions which we have explored to date.

Double Retro-Aldol Reaction. The cycloadducts of anthrone with several different dienophiles are efficiently converted to the ring-opened Michael adducts by either prolonged exposure to the same conditions used for cycloadduct formation, or by the use of a stronger base in protic solvent.[2] Similar reaction of the anthracenediol derivatives described above would lead to C-10 hydroxy analogues which might be susceptible to further cleavage. Indeed, when cycloadduct 4 was subjected to conditions (MeOH/THF, isopropylamine) which gave facile conversion of the anthrone adduct 21 to its the ring-opened Michael adduct isomer (analogous to 24, but lacking the C-10 hydroxyl), the only products observed were anthraquinone and *N*-methylsuccinimide. This reaction almost certainly occurs in stepwise fashion, with protonation of the intermediate carbanion (imide enolate) formed by initial bond cleavage occurring prior to scission of the second carbon–carbon bond. The overall reaction from 4 is formally a double retro-aldol reaction.



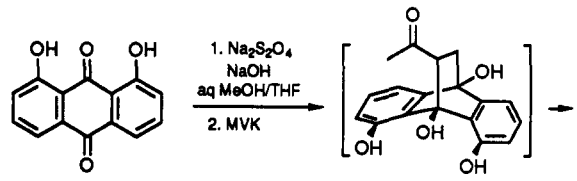
4 24



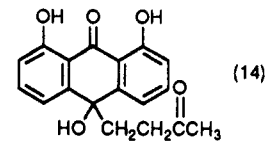
(13)

The net reaction obtained by combining eqs 2 and 13 is the reduction of NMM to *N*-methylsuccinimide, although this occurs by a circuitous route with the hydrogen introduced from a proton source. This feature was demonstrated by carrying out the reaction in MeOD, which led to the formation of *N*-methylsuccinimide-2,3-d_2. Since related "reduction" of the dienophile double bond might account for the reduced yields of cycloadduct in e.g. the dimethyl fumarate reaction (eq 5), a control experiment was carried out which demonstrated that the cycloadduct 7 is stable under the conditions used for its formation. However, it also can be cleaved in analogy to eq 13 under the more forcing conditions of isopropylamine in methanol solvent.

Krohn and Miehe[5a] have reported that anthraquinone and analogues such as 1,8-dihydroxyanthracene-9,10-dione (25) will react with olefins activated by a single electron-withdrawing group to give Michael adducts. For example, 27 is formed as the major product (39%) when 25 is treated with methyl vinyl ketone (MVK) under basic conditions. Although no cycloadducts were observed by Krohn and Miehe, we suggest that cycloadduct 26 may be an intermediate in this process, and note that the factors which make the conversion of dithranol (1,8-dihydroxy-9-anthrone) cycloadducts to Michael adducts[2] more facile than the corresponding anthrone reactions may contribute to this process. It is interesting to note that the minor product (13%) formed from the reagents shown in eq 14 arises from the opposite regioisomer, i.e. the formal Michael adduct is bonded at C-9 rather than C-10; this product may arise from the alternative cycloadduct regioisomer. Formation of both materials may simply reflect modest regioselectivity in the Diels–Alder step.



25 26



27 (39%) (14)

Although the different conditions employed by Krohn and Miehe preclude more direct comparisons, we have been able to isolate cycloadducts from 25 with both NMM and methyl acrylate. We would expect that doubly activated dienophiles such as those employed in the current study would lead to cycloaddition followed by the double retro-aldol process, an overall formal redox disproportionation, i.e., reduction of the dienophile with concomitant oxidation of the anthracenediol to the quinone. The major difference between singly and doubly activated dienophiles is the presence of the adjacent electron-withdrawing group in the (intermediate) Michael adduct from vicinal doubly activated substrate, which allows cleavage of the second C–C bond to occur via formation of a relatively stable ester enolate or similar intermediate.

Conclusions. Cycloadducts are formed between anthracenediols (and related aminoanthracenols) and reactive dienophiles under mild base conditions. Stronger base/protic medium can lead to a formal redox disproportionation, which is believed to occur mechanistically as a double retro-aldol reaction. The fundamental chemistry appears to be analogous to that described previously for anthrones,[2] in which base-catalyzed Diels–Alder reactions were shown to occur more rapidly than Michael additions. Cycloadditions may be carried out by either a one-step (in situ dienophile) or a two-step experimental procedure, with advantages to both. As in the anthrone reactions, the ultimate product can depend strongly on apparently minor changes in reaction conditions.

Experimental Section

Reductions were carried out under an atmosphere of H_2 maintained by a balloon, which was attached by a syringe tip through a septum. The catalyst was 10% Pd/C from two different lots. Unless otherwise noted, ^1H spectra were recorded at 500 MHz, and ^{13}C NMR spectra at 75 MHz, both with $CDCl_3$ solutions. MS, MS (CI) (chemically induced, methane), and MS (DCI) (desorption chemical ionization) data were obtained by Dr. Hugh Webb. Melting points were taken in open capillary tubes and are uncorrected. Combustion analyses were performed by Desert Analytics, Tucson, AZ, and by Galbraith Laboratories, Knoxville,

TN. The pyridine was Fisher Scientific reagent grade, used as received. Starting materials were either commercial reagents or prepared as described earlier.[2]

4,9[1′,2′]-Benzeno-3a,4,9,9a-tetrahydro-4,9-dihydroxy-2-methyl-1*H*-benz[*f*]isoindole-1,3(2*H*)-dione (4). A suspension of 612 mg (2.94 mmol) of anthraquinone, 330 mg (2.97 mmol) of NMM, and 25 mg of 10% Pd/C in 25 mL of pyridine was vigorously stirred while H_2 gas was introduced from a balloon (ca. 0.5 L) via a syringe tip with the needle introduced through a septum and extending below the surface of the liquid. Flow was maintained by allowing gas to exit via a narrow-gauge needle. After 0.5 h, the mixture was suction filtered and the filtrate was evaporated under vacuum. The residue was washed with cold methanol to give 893 mg (95%) of a colorless solid: mp 258–260.5 °C; ^{1}H NMR δ 2.51 (s, 3 H), 3.24 (s, 2 H), 4.35 (s, 2 H), 7.25 (m, 4 H), 7.45 (m, 2 H), and 7.67 (m, 2 H) ppm; ^{13}C NMR δ 24.4, 51.7, 120.2, 120.5, 126.8, 127.3, 138.4, 140.0, and 177.4 ppm; IR (KBr) 3420 (br, s), 3080 (w), 3000 (w), 2945 (w), 1680 (vs), 1430 (m), 1375 (m), 1200 (m), 1130 (m), 1025 (m) cm^{-1}; MS (CI) 322 (P + H, 5), 211 (60), 210 (58), 195 (26), 112 (100); calcd for $C_{19}H_{16}NO_4$ (P + H) 322.1039, found 322.1059.

***trans*-11,12-Dicyano-9,10-ethano-9,10-dihydro-9,10-dihydroxyanthracene (5).** Similar hydrogenation was carried out over a period of 2 h of a suspension of anthraquinone (280 mg, 1.35 mmol), fumaronitrile (106 mg, 1.36 mmol), and 15 mg of 10% Pd/C in 5.0 mL of pyridine. Suction filtration followed by evaporation of volatiles gave a residue which was recrystallized from $CHCl_3$ to give 361 mg (94%) of tan cubic crystals: mp 180–184 °C dec; ^{1}H NMR (acetone-d_6) δ 3.47 (s, 2 H), 7.37 (m, 4 H), 7.68 (m, 2 H), and 7.75 (m, 2 H) ppm; ^{13}C NMR (acetone-d_6) δ 43.7, 75.6, 118.4, 121.0, 122.3, 128.1, 140.0, and 141.2 ppm; IR (KBr) 3350 (br, s), 3060 (w), 2924 (w), 2250 (m), 1445 (w), 1360 (vs), 1280 (m), 1255 (m), 1021 (s) cm^{-1}; MS (DCI) 210 (P − 78, 100), 181 (29), 152 (18), 81 (49). Anal. Calcd for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20. Found: C, 74.72; H, 4.18.

***cis*-11,12-Dicyano-9,10-ethano-9,10-dihydro-9,10-dihydroxyanthracene (6).** Analogous treatment of a mixture of 220 mg (1.06 mmol) of anthraquinone, 81 mg (1.04 mmol) of maleonitrile, and 10 mg of 10% Pd/C in 4.0 mL of pyridine for 2 h gave after workup and recrystallization from $CHCl_3$ 294 mg (98%) of a colorless solid: mp 214–217 °C dec; ^{1}H NMR (acetone-d_6) δ 3.77 (s, 2 H), 7.32 (m, 2 H), 7.37 (m, 2 H), 7.65 (m, 2 H), and 7.76 (m, 2 H) ppm; ^{13}C NMR (acetone-d_6) δ 42.8, 75.5, 117.5, 120.8, 122.1, 127.8, 128.0, 139.9, and 141.8 ppm; IR (KBr) 3400 (br, vs), 3075 (w), 2920 (m), 2240 (m), 1455 (m), 1230 (m) cm^{-1}; MS (DCI) 210 (P − 78, 46), 180 (15), 152 (15), 79 (100). Several attempts to obtain combustion analyses resulted in low carbon percentages (ca. 2%) for reasons that are not understood; all MS efforts failed to give a parent ion.

Dimethyl 9,10-Ethano-9,10-dihydro-9,10-dihydroxyanthracene-11,12-*trans*-dicarboxylate (7). A mixture of 585 mg (2.81 mmol) of anthraquinone, 410 mg (2.85 mmol) of dimethy fumarate, and 20 mg of 10% Pd/C in 10 mL of pyridine was hydrogenated for 3 h. The usual workup gave a residue which by ^{1}H NMR exhibited singlets at 3.70 and 2.64 ppm due to dimethyl succinate in addition to absorptions for the product described below. Recrystallization from methanol gave 597 mg (60%) of 7 as a colorless solid: mp 140–141.5 °C; ^{1}H NMR δ 3.59 (s, 6 H), 5.4 (br s, 2 H), 7.22 (m, 4 H), 7.47 (m, 2 H), and 7.65 ppm (m, 2 H); ^{13}C NMR δ 52.39, 55.03, 76.35, 120.1, 121.5, 126.8, 141.4, 143.4, and 172.6 ppm; IR (KBr) 3360 (br, vs), 3080 (m), 3020 (m), 1740 (vs), 1482 (s), 1345 (s), 1255 (vs) cm^{-1}; MS (CI) 210 (P − 144, 61), 194 (30), 180 (29), 152 (27), 145 (76), 113 (100), 85 (37). Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.54; H, 5.04.

This product (7) was also prepared, in 80% yield, by stepwise reduction (1 h), replacement of the H_2 atmosphere by Ar, followed by addition of dimethyl fumarate.

***endo*- and *exo*-3a,4,9,9a-Tetrahydro-4,9[2′,3′]-benzeno-4,9-dihydroxy-2-methylnaphthaleno-1*H*-benz[*f*]isoindole-1,3(2*H*)-dione (8a,b).** A suspension of 90 mg (0.35 mmol) of naphthacenequinone, 60 mg (0.54 mmol) of NMM, and 15 mg of 10% Pd/C in 15 mL of pyridine was hydrogenated in the usual way. The heterogeneous yellow mixture developed a dark burgundy red color at the start of the reaction, and the color faded to pale orange if the reduction was interrupted. After 0.5 h the red color no longer appeared when additional H_2 was passed through solution, and this was taken as an indication of completion. Suction filtration and evaporation gave crude product which exhibited peaks attributed to **8a,b** in a ratio of ca. 65/35. Recrystallization from methanol gave 77 mg (65%) of the major isomer in essentially pure form as a colorless solid, mp 237–240 °C dec; ^{1}H NMR δ 2.44 (s, 3 H), 3.32 (s, 2 H), 4.44 (br s, 2 H), 7.30 (m, 2 H), 7.47 (m, 2 H), 7.69 (m, 2 H), 7.82 (m, 2 H), and 7.87 ppm (s, 2 H); ^{13}C NMR (acetone-d_6) δ 52.8, 120.6, 120.9, 127.0, 127.4, 128.8, 133.0, and 176.8 ppm; IR (KBr) 3400 (br, s), 3022 (w), 1655 (br, s), 1430, (m), 1275 (m), 1125 (m), 872 cm^{-1}; MS 371 (P, 2), 261 (19), 260 (100), 231 (14), 202 (28); MS (CI) calcd for $C_{23}H_{18}NO_4$ (P + H) 372.1257, found 372.1246. Identification of the minor isomer rests on the NMR of the crude mixture, which exhibited peaks that closely paralleled those of the major product.

6,13-Dihydro-6,13-dihydroxy-15*H*,19*H*-6,13[3′,4′]-pyrrolopentacene-16,18(17*H*)-dione (9). (a) In Situ NMM. A mixture of 101 mg (0.33 mmol) of 6,13-pentacenedione, 44 mg (0.40 mmol) of NMM, and 15 mg of 10% Pd/C in 15 mL of pyridine was hydrogenated in the usual manner for 0.5 h and then stirred overnight at room temperature. Examination of the crude residue after filtration and evaporation of volatiles showed that **9** was the major product, along with *N*-methylsuccinimide. Further vacuum treatment (1 Torr) removed the latter material to give 58 mg (42%) of essentially pure **9**, as a colorless solid, mp 269–270 °C. The NMR of this material was identical with that described below.

(b) Stepwise Procedure. Reduction was carried out by bubbling H_2 through a mixture of 9,13-pentacenedione (90 mg, 0.29 mmol) and 10 mg of Pd/C in 12 mL of pyridine for 0.75 h. Methanol (2 mL) was added, and the mixture was suction filtered to remove the catalyst. Vacuum evaporation of the volatiles gave 87 mg (96%) of a pale yellow solid, mp 330 °C, identified as 13-hydroxypentacene-9(13*H*)-one (**10**) on the basis of its spectral properties: ^{1}H NMR δ 2.45 (d, 1 H, J = 8.5 Hz), 6.15 (d, 1 H, J = 8.5 Hz), 7.58 (t, 2 H, J = 8 Hz), 7.65 (t, 2 H, J = 8 Hz), 7.97 (d, 2 H, J = 8 Hz), 8.06 (d, 2 H, J = 8 Hz), 8.36 (s, 2 H), and 8.90 (s, 2 H); IR (KBr) 3420 (br, m), 3060 (w), 1652 (m), 1605 (s), 1590 (s), 1445 (s), 1390 (m), 1370 (s), 1285 (vs), and 1191 (vs) cm^{-1}.

A solution of 72 mg (0.114 mmol) of **10** and 13 mg (0.117 mmol) of NMM in 5 mL of THF was treated with 4 drops of triethylamine and allowed to stand overnight. The solvent was vacuum evaporated to give 41 mg (84%) of **9** as a colorless solid: mp 269–271 °C; ^{1}H NMR δ 2.49 (s, 3 H), 3.42 (s, 2 H), 4.58 (s, 2 H), 7.47 (m, 4 H), 7.83 (m, 2 H), 7.88 (m, 2 H), 7.92 (s, 2 H), and 8.11 ppm (s, 2 H); ^{13}C NMR (THF-d_8) δ 30.76, 52.86, 76.05, 119.82, 119.87, 120.69, 126.64, 128.73, 133.36, 133.43, 138.13, 140.78, 176.57; IR (KBr) 3400 (br, s), 2070 (w), 2810 (w), 1695 (vs), 1445 (s), 1390 (s), 1285 (s), 1135 (s) cm^{-1}; MS 421 (P, 1), 311 (23), 310 (P − 111, 100), 308 (38), 252 (22), 155 (12), 126 (14); MS (CI) calcd for $C_{27}H_{20}NO_4$ (P + H) 422.1430, found 422.1412.

Anthraquinone Monoxime (11). This material was prepared by two different methods in essentially quantitative yield. The literature procedure[13] utilizes anthraquinone and hydroxylamine. The alternative described here involves nitrosation of anthrone, following a general procedure outlined by Touster for active methylene compounds.[12] To a solution of 1.00 g (5.15 mmol) of 9-anthrone in 50 mL of DMF was added 10 mL of water and 20 mL of concentrated HCl. The ice bath cooled, and the stirred mixture was treated in several portions with 1.11 g (13 mmol) of $NaNO_2$, and stirring was continued with the bath removed for 12 h. The colorless precipitate was suction filtered and recrystallized from ethanol to give 1.11 g (98%) of **11**: mp 224.5–225 °C (lit.[14] mp 224 °C); ^{1}H NMR δ 7.58 (t, 1 H, J − 8 Hz), 7.66 (t, 2 H, J = 8 Hz), 7.74 (t, 1 H, J = 8 Hz), 8.20 (d, 1 H, J = 8 Hz), 8.28 (d, 1 H, J = 8 Hz), 8.42 (d, 1 H, J = 8 Hz), 8.90 (br s, 1 H), and 9.02 ppm (d, 1 H, J = 8 Hz); ^{13}C NMR (acetone-d_6) δ 125.3, 127.1, 127.9, 128.0, 130.1, 131.2, 131.9, 132.2, 134.0, 134.1, 137.2, 143.2, and 183.5 ppm; MS 223 (P, 100), 207 (25), 193 (28), 179 (23), 165 (26), 121 (19), 76 (26); IR (KBr) 3280 (br, s), 3075 (w), 2980 (w), 1650 (vs), 1600 (vs), 1444 (s), 1360 (vs), and 1030 (s) cm^{-1}.

Anthraquinone Monimine (12). The reduction of **11** was carried out as described by Costa et al.[11] A solution of **11** (2.76

(13) Haq, M. A.; Ray, J. N.; Tuffail-Malkana, M. *J. Chem. Soc.* **1934**, 1326.

(14) Schunck, E.; Marchlewski, L. *Chem. Ber.* **1894**, *27*, 2125.

g, 12.4 mmol) in 130 mL of THF was cooled in an ice bath, and 2.54 g (67.1 mmol) of $LiAlH_4$ was added. The mixture was then refluxed for 5 h, cooled, and quenched by careful addition of water (11 mL). After stirring overnight, the mixture was filtered and the filtrate with THF washes was evaporated in vacuo to give 2.49 g (97%) of tan solid, mp 225.5–226 °C (lit.[15] mp 224–225 °C). Material formed in this way reproducibly exhibited NMR spectra expected for **12** not undergoing rapid (NMR time frame) syn/anti interconversion (see Figure 1A): ^1H NMR δ 7.71 (m, 2 H), 7.79 (m, 2 H), 7.97 (d, 1 H, J = 8 Hz), 8.33 (d, 1 H, J = 8 Hz), 8.40 (d, 1 H, J = 8 Hz), 8.64 (d, 1 H, J = 8 Hz), and 11.0 ppm (s, 1 H, exchanges with D_2O); ^{13}C NMR δ 123.3, 126.0, 126.9, 127.9, 131.6, 131.7, 133.5, 133.7, 163.1, and 183.3 ppm; MS(CI): 236 (P + 29, 11), 209 (23), 208 (P + H, 100), 207 (33), 179 (9); IR (KBr) 3055 (w), 1660 (m), 1582 (s), 1361 (s), 1310 (vs), 1184 (s) cm^{-1}. The effect of added trifluoroacetic acid on the ^1H NMR is shown in Figure 1.

Recrystallization of this product from acetone gave material which exhibited (broadened) spectra such as that shown in Figure 1B, as did material prepared by catalytic reduction. Thus hydrogenation in the usual manner of a solution of 115 mg (0.52 mmol) of **11** and 10 mg of 10% Pd/C in 7 mL of pyridine for 1 h gave, after vacuum evaporation, 96 mg (90%) of an off-white solid: mp 223–224 °C; ^1H NMR δ 7.71 (t, 2 H, J = 8 Hz), 7.78 (t, 2 H, J = 8 Hz), 8.0 (very broad s, 1 H), 8.36 (broadened d, 2 H, J = 8 Hz), 8.5 (very broad s, 1 H), and 11.0 ppm (broad s, 1 H); ^{13}C NMR δ 127.3, 127.4, 131.6, 131.7, 163.0, and 183.3 ppm. The MS (CI) and IR spectra were essentially identical with those described above. Monimine **12** from both procedures gave the same cycloadduct with NMM.

4-Amino-4,9[1′,2′]-benzeno-3a,4,9,9a-tetrahydro-9-hydroxy-2-methyl-1*H*-benz[*f*]isoindole-1,3(2*H*)-dione (13). A mixture of 70 mg (0.314 mmol) of **12**, 36 mg (0.324 mmol) of NMM, and 10 mg of 10% Pd/C in 4.0 mL of pyridine was vigorously stirred while the contents of a H_2-filled balloon was bubbled into the solution by means of a syringe needle tip immersed below the surface. A slow flow was maintained by allowing excess gas pressure to exit via a narrow gauge needle. After 2 h the mixture was filtered, and the filtrate was evaporated to give 107 mg (100%) of an off-white solid: mp 107–200 °C dec; ^1H NMR δ 2.50 (s, 3 H), 2.72 (s, 2 H), 3.10 (d, 1 H, J = 9 Hz), 3.22 (d, 1 H, J = 9 Hz), 4.50 (s, 1 H), 7.23 (m, 1 H), 7.24 (m, 2 H), 7.29 (m, 1 H), 7.39 (m, 1 H), 7.48 (m, 1 H), 7.55 (m, 1 H), and 7.70 ppm (m, 1 H); ^{13}C NMR (75 MHz) δ 25.4, 52.0, 52.4, 59.5, 64.4, 120.3, 120.5, 120.7, 126.9, 127.1, 127.2, 139.4, 139.5, 141.0, and 141.3 ppm; IR (KBr) 3320 (m), 3295 (m), 3200 (br, s), 3060 (m), 3005 (m), 1680 (vs), 1440 (s), 1290 (s), 1140 (s), 1010 cm^{-1}; MS (CI) 321 (P + H, 6), 231 (9), 208 (100), 180 (18), 112 (59); calcd for $C_{19}H_{17}N_2O_3$ (P + H) 321.1223, found 321.1231.

9-Amino-*trans*-11,12-dicyano-9,10-ethano-9,10-dihydro-10-hydroxyanthracene (14). Similar treatment of a mixture of **12** (87 mg, 0.39 mmol), fumaronitrile (30 mg, 0.39 mmol), and 10 mg of 10% Pd/C in 5.0 mL of pyridine for 40 min gave, after recrystallization from $CHCl_3$, 105 mg (90%) of an off-white solid: mp 176–178.5 °C dec; ^1H NMR (acetone-d_6) δ 3.07 (br s, 3 H), 3.44 (d, 1 H, J = 5 Hz), 3.47 (d, 1 H, J = 5 Hz), 7.35 (m, 4 H), 7.69 (m, 3 H), and 7.75 ppm (m, 1 H); ^{13}C NMR (acetone-d_6) δ 43.9, 45.1, 59.9, 75.7, 118.9, 121.0, 121.7, 122.1, 122.5, 127.7, 127.8, 127.9, 128.0, 140.5, 140.7, 141.6, and 142.2 ppm; IR (KBr) 3500 (m), 3400 (m), 3250 (br, s), 3082 (m), 2945 (m), 2250 (m), 1455 (m), 1300 (s), 750 (s) cm^{-1}; MS (CI) calcd for $C_{18}H_{14}N_3O$ (P + H) 288.1117, found 288.1127.

9-Amino-*cis*-11,12-dicyano-9,10-ethano-9,10-dihydro-10-hydroxyanthracene (15). A solution of 100 mg (0.480 mmol) of **12**, 40 mg of maleonitrile (0.51 mmol), and 10 mg of 10% Pd/C in 5.0 mL of pyridine was hydrogenated for 40 min. The solvent was vacuum evaporated, and the residue was recrystallized from $CHCl_3$ to give 127 mg (92%) of tan solid: mp 164–166 °C dec; ^1H NMR (acetone-d_6) δ 3.05 (br s, 2 H), 3.64 (d, 1 H, J = 10.5 Hz), 3.75 (d, 1 H, J = 10.5 Hz), 6.50 (s, 1 H), 7.31 (m, 2 H), 7.37 (m, 2 H), 7.64 (m, 2 H), 7.71 (m, 1 H), and 7.77 ppm (m, 1 H); ^{13}C NMR (acetone-d_6) δ 43.1, 44.5, 117.8, 118.0, 120.8, 121.6, 122.2, 122.4, 127.7, 127.8, 140.5, and 142.0 ppm; IR (KBr) 3340 (m), 3280 (m), 3150 (br, s), 2940 (m), 2250 (m), 1600 (m), 1460 (s), 1225 (s), 1005 (s) cm^{-1}; MS (CI) 288 (P + H, 0.1), 209 (100), 193 (12), 180 (26), 130 (9), 76 (67); calcd for $C_{18}H_{14}N_3O$ (P + H) 288.1177, found 288.1157.

Dimethyl 9-Amino-9,10-ethano-9,10-dihydro-10-hydroxyanthracene-*trans*-11,12-dicarboxylate (16). A mixture of the monimine **12** (322 mg, 1.55 mmol), dimethyl fumarate (225 mg, 1.56 mmol), and 20 mg of 10% Pd/C in 10 mL of pyridine was vigorously stirred while H_2 gas was bubbled through the solution. After 1.5 h, the mixture was filtered and then vacuum evaporated. Analysis of the crude product by ^1H NMR showed the presence of cycloadduct **16** (30%), starting material **12** (70%), and dimethyl succinate (70%).

The yield was raised to 60% by repeating the procedure with 5 equiv of dimethyl fumarate, and 60% was also obtained by the stepwise reduction–cycloaddition as described for the analogous quinone. Compound **16** was isolated by silica gel chromatography (90/10 CH_2Cl_2/acetone) as a colorless solid: mp 116–118 °C dec; ^1H NMR δ 2.60 (br s, 2 H), 3.26 (d, 1 H, J = 5 Hz), 3.37 (d, 1 H, J = 5 Hz), 3.57 (s, 3 H), 3.58 (s, 3 H), 7.23 (m, 4 H), 7.38 (m, 1 H), 7.49 (m, 1 H), 7.53 (m, 1 H), and 7.67 ppm (m, 1 H); ^{13}C NMR δ 119.5, 120.0, 120.5, 126.4, 126.5, 140.2, 141.4, 141.7, 142.1, 171.7, and 172.9 ppm; IR (KBr) 3480 (br), 3390 (m), 3210 (m), 3080 (m), 2970 (m), 1735 (s), 1595 (m), 1270 (m) cm^{-1}; MS (CI) 354 (P + H, 2), 210 (58), 209 (100), 208 (44), 180 (14), 145 (57), 113 (33), 85 (13); calcd for $C_{20}H_{20}NO_5$ (P + H) 354.1355, found 354.1348.

Pentacenequinone Monoimine (17). The monoxime of 9,13-pentacenedione was prepared by appropriate modification of the literature method for the anthraquinone analogue.[11] A mixture of the quinone (260 gm, 0.844 mmol) and 1.7 g (30 mmol) of KOH in 170 mL of ethanol was treated with 610 mg (8,77 mmol) of hydroxylamine hydrochloride dissolved in 0.5 mL of water. The yellow suspension was refluxed for 20 h, at which time it was dark red and appeared to be homogeneous. After cooling to room temperature, the mixture was treated with acetic acid, and the resulting yellow suspension was reduced to about half volume on a hot plate, after which water was added. Filtration followed by recrystallization from ethanol/water gave 222 mg (82%) of the *oxime* as a yellow solid: mp 269–271 °C; ^1H NMR (acetone-d_6) δ 7.70 (m, 4 H), 8.10 (d, 1 H, J = 8 Hz), 8.17 (d, 1 H, J = 8 Hz), 8.20 (d, 1 H, J = 8 Hz), 8.24 (d, 1 H, J = 8 Hz), 8.79 (s, 1 H), 8.88 (s, 1 H), 8.98 (s, 1 H), 9.82 (s, 1 H), and 12.0 ppm (br s, 1 H); ^{13}C NMR (THF-d_8) δ 124.9, 127.8, 128.8, 129.0, 129.3, 129.5, 130.0, 130.3, 130.4, 133.1, 133.8, 133.9, 136.3, 136.6, and 143.8 ppm; IR (KBr) 3290 (br), 1640 (m), 1360 (m), 1295 (m), 1195 (m) cm^{-1}; MS (CI) 309 (31), 308 (P − 15, 100), 307 (85), 295 (29), 294 (31), 293 (13).

Reduction of the oxime (35 mg, 0.108 mmol) was carried out in THF by adding $LiAlH_4$ (38 mg, 1.0 mmol) at 0 °C, followed by 5 h at reflux. Water (5 drops) was added to quench the excess hydride, and the mixture was filtered to remove inorganic material. Evaporation and recrystallization of the residue from ethanol gave 33 mg (99%) of **17** as pale yellow needles: mp 322 °C dec; IR (KBr) 3060 (w), 1661 (s), 1640 (m), 1570 (s), 1445 (s), 1390 (s), 1308 (vs), 1190 (s), 1175 (s), and 968 (s) cm^{-1}; MS 308 (26), 307 (P, 100), 277 (14), 252 (10), 126 (19), 125 (15); calcd for $C_{22}H_{13}NO$ 307.0986, found 307.0992. Like the anthraquinone monoimine discussed in greater detail in the text, **17** exhibited NMR characteristics which depended upon the sample history, again attributed to syn/anti interconversion rates: ^1H NMR (slow interconversion) δ 7.67 (m, 4 H), 8.09 (m, 4 H), 8.47, (s, 1 H), 8.96 (s, 1 H), 9.00 (s, 1 H), 9.20 (s, 1 H), and 10.95 ppm (br s, 1 H); (rapid interconversion) δ 7.67 (m, 4 H), 8.09 (m, 4 H), 8.85 (br s, 2 H), 8.98 (s, 2 H).

Cycloadduct of 17 + NMM (18). A mixture of **17** (24 mg, 0.078 mmol), NMM (20 mg, 0.18 mmol), and 5 mg of Pd/C in 6 mL of pyridine was subjected to H_2 bubbling for 0.5 h and then allowed to stand overnight. The crude residue from the initial filtration and evaporation was taken up in THF and filtered through a short plug of neutral alumina (1 g), and then volatiles including *N*-methylsuccinimide were removed by full pump vacuum with mild heating. Essentially pure **18** was obtained (29 mg, 87%) as a colorless solid: mp 259.5–260 °C; ^1H NMR δ 2.47 (s, 3 H), 3.00 (br s, 2 H), 3.26 (d, 1 H, J = 9 Hz), 3.37 (d, 1 H, J = 9 Hz), 4.73 (s, 1 H), 7.47 (m, 4 H), 7.84 (m, 5 H), 7.95 (s, 1

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H), 7.99 (s, 1 H), and 8.13 ppm (s, 1 H); ^{13}C NMR 24.51, 51.60, 52.12, 59.10, 119.26, 119.33, 119.62, 120.00, 120.17, 120.33, 126.42, 128.04, 132.26, 136.83, 138.34, 138.58, 176.43, 177.62; IR (KBr) 3400 (br, s), 3380 (m), 3210 (m), 3047 (m), 2942 (w), 1680 (vs), 1440 (vs), 1285 (vs), 1140 (s) cm^{-1}; MS (CI) 421 (P, 1), 323 (5), 295 (16), 294 (13), 114 (12), 112 (71), 111 (12), 55 (12), 43 (100); MS (CI) calcd for $C_{27}H_{21}N_2O_3$ (P + H) 421.1530, found 421.1541.

Reaction of 20. The procedure of Regitz[16] was used to prepare 10-diaza-9-anthrone (**20**) from 9-anthrone and *p*-toluenesulfonyl azide[17] in 90% yield. Bright red **20** (mp >300 °C) has ^{1}H NMR δ 7.33 (d, 2 H, J = 8 Hz), 7.41 (t, 2 H, J = 8 Hz), 7.70 (t, 2 H, J = 8 Hz), and 8.54 ppm (d, 2 H, J = 8 Hz).

A solution of **20** (126 mg, 0.594 mmol) and NMM (68 mg, 0.613 mmol) in 7 mL of pyridine was reduced in the usual manner with 15 mg of 10% Pd/C catalyst. After 1 h of vigorous stirring with H_2, and 5 h of additional stirring, the mixture was worked up in the usual manner. The deazotized cycloadduct **21** was estimated by NMR to have been formed in 45% yield, along with *N*-methylsuccinimide and 9-anthrone. An essentially quantitative yield of **21** was formed when this procedure was carried out by stepwise reduction–cycloaddition. The product **21** was identical with material prepared by direct reaction of anthrone with NMM, as recently described.[2]

Reaction of 22. The procedure of Clar was used to prepare 10-methylene-9-anthrone[18] (**22**) from 9-anthrone and aqueous formaldehyde. Compound **22** was obtained in 91% yield as colorless crystals: mp 146.5–147 °C (lit.[19] mp 145–147.5 °C); ^{1}H NMR δ 6.34 (s, 2 H), 7.54 (t, 2 H, J = 7 Hz), 7.65 (t, 2 H, J = 8 Hz), 8.01 (d, 2 H, J = 8 Hz), and 8.35 ppm (d, 2 H, J = 7 Hz).

A mixture of **22** (212 mg, 1.02 mmol), NMM (126 mg, 1.14 mmol), and 10 mg of 10% Pd/C in 10 mL of pyridine was hydrogenated for 40 min, stirred an additional 30 min, and then worked up in the usual manner. Analysis of the crude residue by NMR showed no absorptions anticipated for cycloadduct; instead, major amounts of *N*-methylsuccinimide and 10-methyl-9-anthrone (**23**) were formed. The latter was identical with **23** that had been independently prepared by methylation of anthrone and also by reduction of **22**: 10-methyl-9-anthrone (**23**) has mp 64–66 °C (lit.[19] mp 64.5–66.5 °C); ^{1}H NMR δ 1.59 (d, 3 H, J = 7.5 Hz), 4.30 (q, 1 H, J = 7.5 Hz), 7.44 (t, 2 H, J = 7.5 Hz), 7.50 (d, 2 H, J = 7.5 Hz), 7.62 (t, 2 H, J = 7.5 Hz), and 8.31 ppm (d, 2 H, J = 7.5 Hz).

Double Retro-Aldol Reaction of 4 in MeOD. A solution of 321 mg (1.0 mmol) of cycloadduct **4** in a solvent consisting of 7 mL each of MeOD and THF was treated with 1 mL of isopropylamine. After 24 h at room temperature, the solution was separated from the yellow needles of anthrquinone which had precipitated, and the solvent was removed under vacuum, with care to retain the relatively volatile *N*-methylsuccinimide. The ^{1}H NMR spectrum of the residue showed a singlet at 3.00 ppm (N-Me; relative area = 3) and a broadened triplet-like absorption at 2.72 ppm (relative area = 2.1, compared to 4.0 for the undeuterated *N*-methylsuccinimide methylene absorption), signifying formation of the dideuterio compound with high efficiency.

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Supplementary Material Available: ^{1}H NMR spectra of **4**, **6**, **8a** + **8b**, **10**, and **13–18** and ^{13}C NMR spectra of **4**, **6**, **8a** + **8b**, **13–16**, and **18** (67 pages). Ordering information is given on any current masthead page.

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Pentaalkylstiboranes. 1. Synthesis of Homobenzylic Alcohols, Homoallylic Alcohols, Ethyl 5-Aryl-5-hydroxypent-2-enoates, and β-Hydroxypropionic Acid Derivatives via Pentaalkylstiboranes†

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Although pentaalkylstiboranes have long been known, their applications in organic synthesis have not been exploited. It has been found that quaternary stibonium salts $(n\text{-}Bu_3SbCH_2E]^+X^-$ (E = Ph, CH=CH_2, CH=$CHCO_2Et$, CO_2Et, CN; X = Br, I, BPh_4) on treatment with RLi (R = *n*-Bu, *t*-Bu, Ph) afford pentaalkylstiboranes, $n\text{-}Bu_3Sb(R)CH_2E$, which react with aromatic aldehydes to give, after subsequent hydrolysis, homobenzylic alcohols, homoallylic alcohols, ethyl 5-aryl-5-hydroxypent-2-enoates, ethyl β-aryl-β-hydroxypropionates, and β-aryl-β-hydroxypropionitriles, respectively, in good to excellent yields. The reaction is chemoselective for aldehydes.

Introduction

Few reports[1] concerning the application of organoantimony compounds in organic synthesis have appeared in the literature. Henry and Wittig[2] claimed that triphenylstibonium methylide, prepared from methyltriphenylstibonium iodide and phenyllithium, reacted with benzophenone to form acetaldehyde. However, Doleshall et al.[3] later reported a quite different result: that reaction of methyltriphenylstibonium iodide or tetraphenylborate with phenyllithium followed by introduction of benzophenone into the reaction mixtures gave a pentaorganylstiborane, methyltetraphenylstiborane, and unreacted benzophenone. On the other hand, Wittig and Laib[4] reported that $Me_2Sb(CH_2Ph)_2Br$ reacted with PhLi to yield $Me_2SbCH(CH_2Ph)Ph$, a product hypothesized to result from the rearrangement of an antimony ylide. The only successful Wittig-type process reported for an antimony ylide was the reaction of triphenylstibonium tetraphenylcyclopentadienylide, formed from triphenylstibine

† This paper is the 85th report of the synthetic application of elementoorganic compounds of group 15 and 16.

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