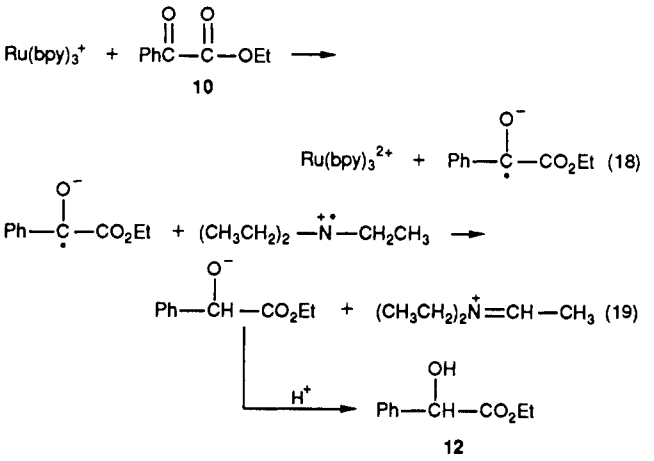
is effectively recycled in the photosensitized reduction of benzil.

Photoinduced reduction of ethyl benzoylformate (**10**) proceeds similarly through photogeneration of $Ru(bpy)_3^+$ that acts as electron-transfer mediator. Illumination of an acetonitrile solution that includes $Ru(bpy)_3^{2+}$ as photosensitizer, triethylamine as electron donor, and **10** as substrate results in the formation of ethyl α-hydroxy benzeneacetate (ethyl mandelate) (**12**). Figure 7 shows the rate of formation of **12** as a function of illumination time. The initial quantum yield of **12** formation corresponds to $\phi = 0.049$. Control experiments reveal that the photosensitizer and TEA are essential components to effect the reduction of the substrate. Exclusion of either $Ru(bpy)_3^{2+}$, TEA, or the illumination prohibits the process. Cyclic voltammetry measurements imply that $Ru(bpy)_3^+$ acts as a primary electron-transfer catalyst for the reduction of **10** (eq 18). The substrate **10** exhibits a reversible one-electron-reduction wave at $E_{1/2} = -1.32$ V. The cyclic voltammogram of $Ru(bpy)_3^{2+}$ in the presence of **10** shows a catalytic cathodic current at the first reduction wave of $Ru(bpy)_3^{2+}$. These results imply that electrogenerated $Ru(bpy)_3^+$ mediates the reduction of **10** (eq 18). The resulting radical anion formed in the photosensitized process is subsequently reduced by $TEA^{\bullet+}$ and yields **12** (eq 19). Table II summarizes the initial rate of **10** reduction and the turnover number of the photosensitizer in the system. The value of the turnover number implies that the photosensitizer is effectively recycled in the reduction process of **10**.



Conclusions

We have demonstrated that photosensitized electron-transfer reactions in organic solvents (acetonitrile) initiated by visible light provide a means to effect debromination of *vic*-dibromides and reduction of activated carbonyl functions. Photogenerated $Ru(bpy)_3^+$ acts in these transformations as an electron-transfer mediator. The complementary electrochemical studies reveal that electroreduction of *vic*-dibromides and of **10** is accompanied by kinetic limitations. Electrogenerated $Ru(bpy)_3^+$ acts as an electron-transfer catalyst that effects these processes. Thus, photochemically or electrochemically induced generation of $Ru(bpy)_3^+$ provides a route for the reduction of organic substrates through electron-transfer catalysis.

Acknowledgment. This research project was supported by the Bundesministerium für Forschung and Technologie (BMFT), West Germany.

Registry No. **1**, 13440-24-9; (±)-**2**, 13027-48-0; **3**, 5464-70-0; **4**, 1196-45-8; **5**, 103-30-0; **6**, 645-49-8; **7**, 4192-77-2; **8**, 873-66-5; **9**, 134-81-6; **10**, 1603-79-8; (±)-**11**, 579-44-2; (±)-**12**, 4358-88-7; $Ru(bpy)_3Cl_2$, 14323-06-9; $(CH_3CH_2)_2NCH_2CH_3$, 121-44-8; $Ru(bpy)^+$, 56977-24-3.

Base-Catalyzed Reactions of Anthrones with Dienophiles[1]

Michael Koerner and Bruce Rickborn*

Department of Chemistry, University of California, Santa Barbara, California 93106

Received October 12, 1989

Anthrone in the presence of an amine functions as a reactive diene in [4 + 2] cycloadditions. Dienophiles which differ in reactivity over a range of ca. 10^5 give products at 25 °C. Thus *N*-methylmaleimide (NMM) gives cycloadduct within minutes in various solvents containing catalytic triethylamine. The reaction of dimethyl fumarate is slower, and a convenient rate with methyl acrylate requires the use of the dienophile as solvent or a primary amine catalyst. The reactions take a different course in methanol solvent, ultimately leading to Michael adduct. Cycloadducts are detected at short reaction times and are shown to be viable precursors to Michael adducts. A 5-alkoxy group on naphthacene directs Diels–Alder reaction mainly to the unsubstituted central ring. The analogous reaction with naphthacen-5-one and amine catalyst affords the bridgehead hydroxyl product. Dithranol (1,8-dihydroxyanthrone) reacts more rapidly than anthrone and exhibits a strong tendency to give Michael adduct. Possible intramolecular protonation of a carbanion (enolate) intermediate was ruled out by the use of deuterated substrate. The product with NMM is deuterated stereoselectively trans to the anthracenyl ring, implying sterically controlled intermolecular reaction. Similar stereoselectivity was observed for the conversion of anthrone–NMM cycloadduct to Michael adduct in MeOD cosolvent. Cycloadducts may be formed either by stepwise (Michael + aldol) reactions, or by oxyanion accelerated concerted Diels–Alder reactions. Arguments favoring the latter mechanism are presented. The reaction is discussed in the context of other base-induced and base-catalyzed cycloadditions of 1-oxido and 2-oxido 1,3-dienes.

Introduction

Diels–Alder reactions are generally viewed as concerted asynchronous processes,[2] although a body of literature ascribes stepwise mechanisms to certain formal [4 + 2] cycloadditions. In particular, the synthetically valuable cycloadditions[3-13] of enolates derived from α,β-unsaturated

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

(2) Loncharich, R. J.; Brown, F. K.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 1129.

0022-3263/90/1955-2662$02.50/0

ketones with electron-poor olefins are usually portrayed as sequential double Michael reactions, although some authors have noted the possibility of an alternative Diels–Alder mechanism,[3,6,10a] and a few appear to prefer the latter pathway.[5,13] The sequential Michael mechanism seems reasonable in light of the speed of these reactions, many of which are complete within minutes at −78 °C. Conversely, there is no history of acceleration of Diels–Alder reactions by oxyanion substituents, although the remarkable effect of this substituent on rates of other pericyclic reactions,[14] including putative retro-Diels–Alder processes,[15] suggests that it would be unwise to discount this possibility.

It is useful to divide oxyanion *influenced* processes into two categories, base *induced* and base *catalyzed*. For base-induced reactions, the pertinent ground and product states are the oxyanions themselves; for base-catalyzed reactions, the pertinent thermodynamic states are the neutral species, typically the conjugate acid of the oxyanion or a keto tautomer. This difference can control the outcome of a reaction. Thus for a cycloaddition the anionic educt may be more stable than the anionic adduct, while the opposite may be true for the corresponding neutrals.

The anthrone system provides a good illustration. Regardless of the mechanistic details, cycloadducts of anthrone and related species are more stable than the educts under the mild base conditions we employ,[1] whereas strong base can cause a cycloadduct (alkoxide) to cleave to form anionic educt (a phenoxide), as shown in the work of Knapp et al.[15] The large pK_a difference between the bridgehead alcohol and 9-anthracenol must be a major factor in inverting the educt/adduct stability picture for base-induced vs base-catalyzed processes in this system.

Most studies of oxyanion-influenced cycloadditions involve base-*induced* procedures, and the majority of these use cross-conjugated dienolates (2-oxido-1,3-butadienes) generated by treatment of an enone with LDA or similar strong base. Both inter- and intramolecular[10] variants have been described, and several different dienophiles (Michael acceptors) have been used. These reactions appear to exhibit complete regiospecificity and two kinds of stereospecificity, i.e., the stereochemistry of the dienophile is retained, and the two oxygen functions of the diene and dienophile are proximal (endo) rather than distal (exo) in the product. The regiochemistry is in keeping with either a sequential Michael or Diels–Alder mechanism, while the more problematic stereospecificity features have been rationalized by postulating Li ion chelation by the two oxygens.[9d,11c]

Linear conjugated dienolates (1-oxido-1,3-butadienes) have been less extensively studied.[5,13,16] For these systems, the Diels–Alder alternative mechanism is given higher priority by some authors.[5,13] Kraus et al. found that the anion derived from 4-methyl-2-butenolide gave a Michael adduct with the "dienophile" bonded to the 4-position. Since other electrophiles, e.g. alkyl halides and carbonyl compounds, are incorporated at the 2-position in reactions with this anion, cycloaddition followed by retroaldol cleavage of the strained ring product was proposed.[5a] In a study of the parent 1-oxido-1,3-butadiene, cycloadducts were isolated. These also had the regiochemistry which required initial γ rather than α attack for a stepwise double Michael mechanism, and on these grounds the concerted process was favored.[5b]

Mechanistic details are not known for a possibly related set of reactions in which an α,β-unsaturated amide[17a] and enones[17b,c] serve as the incipient dienes for intramolecular cycloadditions. These reactions are carried out at relatively high temperatures (160 °C) in sealed tubes, in the presence of Me_3SiCl, Et_3N, and $ZnCl_2$. The Lewis acid and base may serve more than one purpose in these reactions, and the possibility that the cycloaddition step may be a concerted base-catalyzed Diels–Alder reaction involving a 2-oxido 1,3-diene has not been excluded.

The earliest example of apparent base-*catalyzed* cycloaddition is found in the work of Buchanan and coworkers.[18] This brief note describes a (further oxidized) product isolated in poor yield from a refluxing mixture of isophorone and β-(dimethylamino)propiophenone. Presumably the reaction is catalyzed by dimethylamine, which can be generated by reversion of the 1,4-addition to phenylvinyl ketone. The product, with structure demonstrated by X-ray analysis, is that derived from the cross-conjugated 2-oxido 1,3-diene of isophorone, even though formation of the 1-oxido 1,3-diene appears to be feasible under these equilibrating conditions. Whether this reflects greater reactivity for the 2-oxido vs 1-oxido diene remains unknown, and alternative explanations may be invoked. It is interesting to note that, unlike all the base-induced examples which lead to the proximal oxygen stereochemistry noted above, the product in this instance has the distal arrangement of these groups. This may not be an intrinsic feature of the cycloaddition mechanism since base catalyzed epimerization of initially formed proximal product may have occurred.

The base/solvent system potassium *tert*-butoxide/Me_2SO was employed in the work of Ban et al.,[19] who used a heavily substituted cyclohexenone as the cross-conjugated diene precursor in reactions with acrylonitrile and

(3) Lee, R. A. *Tetrahedron Lett.* **1973**, 3333.
(4) Hagiwara, H.; Nakayama, K.; Uda, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3769.
(5) (a) Kraus, G. A.; Roth, B. *Tetrahedron Lett.* **1977**, 3129. (b) Kraus, G. A.; Sugimoto, H. *Ibid.* **1977**, 3929.
(6) White, K. B.; Reusch, W. *Tetrahedron* **1978**, *34*, 2439.
(7) Spitzner, D. *Tetrahedron Lett.* **1978**, 3349.
(8) (a) Gibbons, E. G. *J. Org. Chem.* **1980**, *45*, 1540. (b) Gibbons, E. G. *J. Am. Chem. Soc.* **1982**, *104*, 1767.
(9) (a) Quesada, M. L.; Schlessinger, R. H. *J. Org. Chem.* **1978**, *43*, 3968. (b) Roberts, M. R.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 724.
(10) (a) Ihara, M.; Toyota, M.; Fukumoto, K.; Kametani, T. *Tetrahedron Lett.* **1984**, 2167. (b) *Ibid.* **1984**, 3235. (c) *Ibid.* **1985**, 1537. (d) *J. Chem. Soc., Perkin Trans. 1* **1986**, 2151. (e) Ihara, M.; Suzuki, M.; Fukumoto, K.; Kametani, T.; Kabuto, C. *J. Am. Chem. Soc.* **1988**, *110*, 1963.
(11) (a) Ihara, M.; Katogi, M.; Fukumoto, K.; Kametani, T. *J. Chem. Soc., Chem. Commun.* **1987**, 721. (b) Ihara, M.; Takahashi, T.; Shimizu, N.; Ishida, Y.; Sudow, I.; Fukumoto, K.; Kametani, T. *Ibid.* **1987**, 1467.
(12) (a) Nagaoka, H.; Ohsawa, K.; Takata, T.; Yamada, Y. *Tetrahedron Lett.* **1984**, 5389. (b) Nagaoka, H.; Kobayashi, K.; Matsui, T.; Yamada, Y. *Tetrahedron Lett.* **1987**, 2021. (c) Nagaoka, H.; Kobayashi, K.; Okamura, T.; Yamada, Y. *Tetrahedron Lett.* **1987**, 6641.
(13) Marchand, A. P.; Annapurna, P.; Watson, W. H.; Nagl, A. *J. Chem. Soc., Chem. Commun.* **1989**, 281.
(14) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.
(15) Knapp, S.; Ornaf, R. M.; Rodrigues, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 5494. The target conduritol has recently been prepared by a direct thermal (flash vacuum pyrolysis) retro-Diels–Alder procedure; see: Cambie, R. C.; Renner, N. D.; Rutledge, P. S.; Woodgate, P. D. *Synth. Commun.* **1989**, *19*, 537.
(16) The question of stepwise (Michael-aldol) vs concerted cycloaddition also arises in reactions of phthalide anions; see: Rickborn, B. Isobenzofurans. *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, CT, 1989; pp 1–133.
(17) (a) Ihara, M.; Kirihara, T.; Kawaguchi, A.; Fukumoto, K.; Kametani, T. *Tetrahedron Lett.* **1984**, 4541. (b) Ihara, M.; Katogi, M.; Fukumoto, K.; Kametani, T. *J. Chem. Soc., Chem. Commun.* **1987**, 721. (c) Ihara, M.; Takahashi, T.; Shimizu, N.; Ishida, Y.; Sudow, I.; Fukumoto, K.; Kametani, T. *Ibid.* **1987**, 1467.
(18) Brown, H. L.; Buchanan, G. L.; Cameron, A. F.; Ferguson, G. *Chem. Commun.* **1967**, 399.
(19) Ohnuma, T.; Oishi, T.; Ban, Y. *J. Chem. Soc., Chem. Commun.* **1973**, 301.

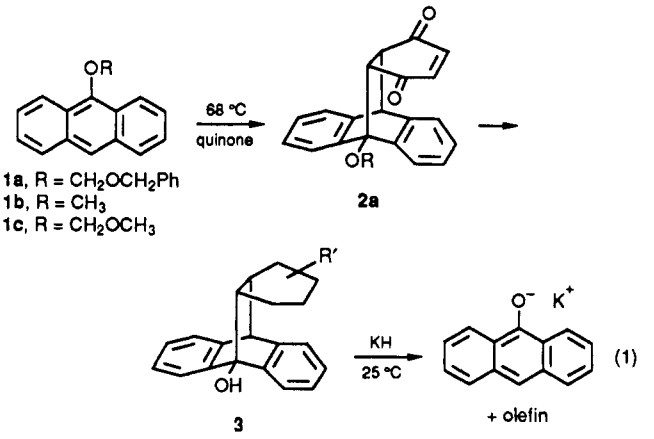
methyl vinyl sulfone. Although the base is substantially stronger than the dialkylamine used in the preceding example, the thermodynamic states are undoubtedly the neutrals, and this constitutes the first clear-cut example of base-catalyzed cycloaddition. Two products were isolated from the acrylonitrile reaction, the cycloadduct and the Michael adduct. Interestingly, the Michael adduct was converted quantitatively to the cycloadduct when resubjected to the same reaction conditions for a longer period. Similar observations are sometimes cited as evidence for a stepwise cycloaddition mechanism, but it should be noted that the Michael product itself is not the intermediate of interest in either base-induced or -catalyzed procedures; rather, it is the conjugate base (enolate) of the Michael adduct, and its kinetic and thermodynamic relationship with the conjugate base of the cycloadduct, which is critical to this mechanistic question.

Results

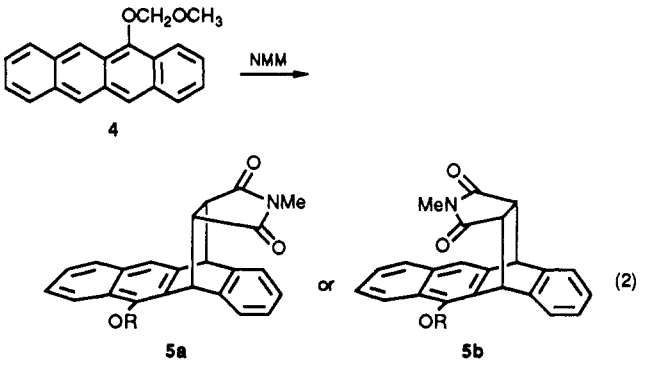
In this paper we describe cycloaddition and Michael reactions of anthrone and some related materials. Weak base treatment of anthrones gives "1-oxido dienes" as reactive intermediates, leading to base-catalyzed Diels–Alder reactions. Variation of base, solvent, dienophile, and substrate structure are used to explore mechanistic features and to control the course of the reaction. These changes can result in the exclusive formation or either cycloadduct or Michael adduct.

This work was initiated with the goal of preparing a diene with the following properties: (a) high reactivity, such that even poor dienophiles, e.g. simple olefins, form cycloadduct at ambient temperature; (b) stability of its cycloadducts toward a range of reagents typically used in syntheses; and (c) facile fragmentation of the (modified) cycloadducts in a low temperature controllable retro-Diels–Alder reaction. Such a diene would be an ideal protecting group for a range of olefins and provide a useful addition to the powerful Diels–Alder repertory. An example which comes close to this ideal is the 9-anthracenyl ether (**1a**) employed by Knapp et al.[15] This "diene" nicely meets requirements (b) and (c), i.e., the aromatic rings of the cycloadduct **2** are inert toward most reagents, and the retro-Diels–Alder expulsion of the embedded dienophile, even when modified to a simple substituted cyclohexene, occurs at room temperature by an oxyanion accelerated mechanism.[15] Unfortunately anthracenes have only modest activity as dienes, and although the use of **1a** with benzoquinone presented no problem,[15] cycloadditions with poor dienophiles[20] would require temperatures too high for practical application.

Sauer et al.[21] studied the effects of 9(10)-substituents on the cycloaddition reactivity of anthracene. The largest increase (k_{rel} = 218) for reaction with maleic anhydride was found for 9,10-dimethylanthracene, which unfortunately is not suitable for anion accelerated retro-Diels–Alder applications. One might expect a 9-alkoxy substituent to significantly enhance reactivity, but a very modest rate increase (k_{rel} = 2.5) was found for the reaction of 9-methoxyanthracene (**1b**) with maleic anhydride.[21] Rates have not been determined for anthracenes bearing alkoxy groups which would be more easily converted to the bridgehead alcohol as in eq 1. We prepared the 9-methoxymethoxy (MOM) derivative (**1c**) to examine this feature and found by competition kinetics experiments that it is somewhat *less* reactive than the parent aromatic with *N*-methylmaleimide (NMM).[22] This approach to the design of a reactive diene therefore does not appear to be promising.



Linear benzannulation is also known to enhance cycloaddition reactivity.[23] With this in mind, 5-(methoxymethoxy)naphthacene[24] (**4**) was prepared, and its reaction with the very reactive[20] dienophile NMM examined. Facile loss of the red-orange color of **4** was observed at room temperature, but NMR analysis of the crude product indicated that cycloaddition had occurred mainly at the unsubstituted central ring to give the exo or endo isomer **5a** and **5b**. Although not verified experimentally, this substitution pattern is not expected to be useful for oxyanion accelerated retro-Diels–Alder reaction.



The small rate effects of 9-alkoxy substituents on anthracene could be associated with peri hydrogen interactions preventing coplanarity of the alkoxy group with the aromatic ring, although it is not obvious that the planar conformation would be more reactive. The hydroxy analogue might exhibit very different reactivity if such steric interactions are important, and it was decided to explore this point.

The phenolic tautomer 9-anthracenol (**8**) is known to be in equilibrium with anthrone (**6**). The equilibrium constant is strongly solvent dependent, with the keto form heavily favored in relatively nonpolar solvents, while good hydrogen bond acceptor solvents lead to substantial equilibrium percentages of **8**. For example, Mills and

(20) A rough working list of estimated dienophile reactivity is as follows: cyclohexene (1), cyclopentene (10^3), norbornene (10^4), 1,4-dihydro-1,4-epoxynaphthalene and 2-butenolide (10^5), methyl acrylate (10^6), dimethyl fumarate (10^8), maleonitrile, fumaronitrile, and benzoquinone (10^9), *N*-methylmaleimimide and maleic anhydride (10^{10}).

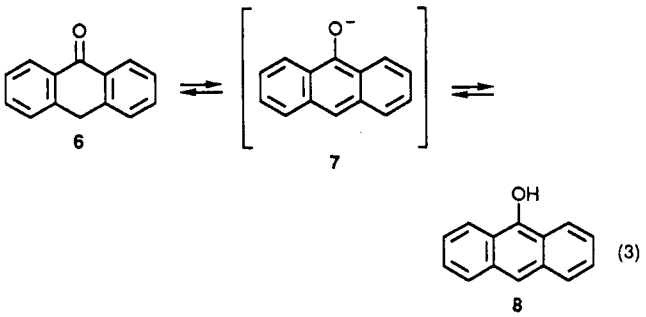
(21) Sauer, J.; Lang, D.; Mielert, A. *Angew. Chem., Int. Ed. Engl.* **1961**, *1*, 268.

(22) The relative rate ratio of **1c**/anthracene for cycloaddition with NMM is 0.36 at 25 °C, and 0.8 at 131 °C.

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

(24) The substituent and typical naphthacene color suggest the trivial name "orange momylate" for **4**.

Beak[25] found K = [8]/[6] values of ≤0.001, 0.2, and 1.3 in chloroform, THF, and DMF, respectively.



(3)

In preliminary studies reactions of anthrone with NMM in DMF solvent were found to be very rapid, complete within a few minutes at room temperature. These rapid rates do not appear to be a characteristic of **8**; instead, the high reactivity is ascribed to the "anion" **7**, for reasons outlined below. The role of added base and the exact nature of oxyanion **7** are not completely understood, but almost certainly **7** does not exist as a free ion in the less polar solvents used in our work. It has been shown[26] that in hydrocarbon solvents the addition of Et_3N displaces the equilibrium toward the hydrogen-bonded enol (ROH···NEt_3), for which one may write a facile equilibrium with the hydrogen bonded enolate (RO^-···$HNEt_3^+$), and this complex may be a more accurate depiction of **7**.

(a) The anthrone–NMM reaction rate in DMF varied widely with the source and history of this solvent, and was inhibited by the addition of HCl. In DMF the reaction is thought to be caused or enhanced by the presence of dimethylamine, a common contaminant of this solvent. In refluxing HOAc solvent, anthrone is in fact less reactive than anthracene.[1] Negligible rates are observed in THF or $CHCl_3$ solvent, unless Et_3N or a similar base is added. Rapid reactions also take place in Et_3N or pyridine solvents.

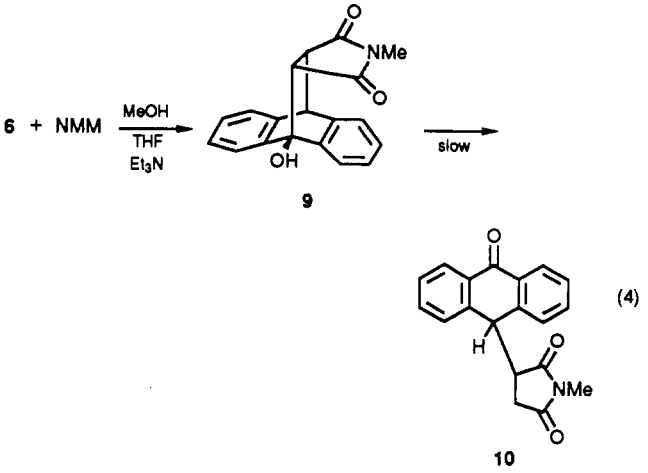
(b) The rate depends on the nature and concentration of the dienophile, showing that the (cyclo)addition step is rate determining except for very reactive dienophiles as described below. The order of reactivity for common dienophiles parallels that observed for more traditional Diels–Alder reactions.[20]

(c) The rate and course of a reaction is sensitive to the base employed. For example, primary amines are more efficient catalysts than Et_3N but may also consume dienophile by conjugate addition under certain conditions. Efforts to increase the rate of cycloaddition by the use of stronger base can be counterproductive. Thus NaOMe in MeOH leads to Michael adduct rather than cycloadduct, and KH in THF causes the retro-Diels–Alder products to be favored, as shown in the work of Knapp.[15]

(d) The Et_3N-catalyzed reactions of anthrone depend upon the concentration of base, and at ca. 0.1 M of substrate and base, they are $\geq 10^4$ faster than cycloadditions with anthracene or 9-methoxyanthracene under analogous conditions.[1] Since **7** must be formed in very low concentration under these weakly basic conditions (there is essentially no change in the NMR spectrum of anthrone in $CDCl_3$ when ca. 1 equiv of Et_3N is added), it must indeed be an extremely reactive "diene", and certainly far more reactive in cycloadditions than previously studied anthracenes. The limitation on tapping this reactivity is noted above, i.e. efforts to increase the concentration of this reactive species also stabilize it relative to cycloadduct.

These points are elaborated in the specific examples which follow.

As reported earlier[1] the reaction of anthrone with NMM gives exclusively the cycloadduct **9** when the reaction is carried out in DMF, Et_3N, or pyridine. No reaction occurs in THF or $CHCl_3$ unless an amine catalyst is added, and then the cycloadduct is formed within the few minutes needed to examine the mixture. Yields are essentially quantitative, and the cycloadduct is stable for at least several hours under these solvent/base conditions. In contrast, methanol as (co)solvent has a marked effect on the outcome, and the product of the Et_3N-catalyzed process is time-dependent. Thus an aliquot from a reaction run in 1:1 MeOH/THF (the THF was used to solubilize the anthrone) examined after 15 min showed that all of the anthrone had been consumed, while the ratio of cycloadduct **9** to Michael adduct **10** was 82:18. After 3.5 h this ratio had changed to 37:63, and in a duplicate experiment, after 16 h only **10** was present. These results show that **10** is a thermodynamic sink under these conditions, and that in methanol, but not in the other solvents examined, Et_3N catalyzes the conversion of cycloadduct to Michael adduct.

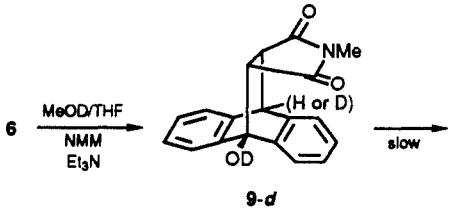


(4)

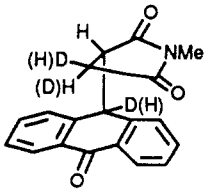
Interesting features were unmasked when similar experiments were carried out in 1:1 MeOD/THF (5 mL each) with Et_3N (3 mL) as the base, as outlined in eq 5. The results are in part dependent upon the order of addition of reagents. When NMM was the final component added to the mixture, the product **9-*d*** was essentially completely deuterated at the bridgehead C-10 position. However, when Et_3N was added last, the **9-*d*** was completely protonated at this site, as judged by comparison of NMR integrals using the NMe peak as a reference. An aliquot taken at 10 min showed that all of the anthrone had been consumed and the product was essentially exclusively **9-*d***. The cycloadduct C-10 incorporation results show that for NMM, the most reactive dienophile employed, the rate-determining step is deprotonation of anthrone. Slower reactions with less active dienophiles indicate a change in rate-determining step.

The product **10-*d*** was formed at longer reaction times, becoming major after ca. 3.5 h. The ^1H NMR spectra of **10-*d*** from both experiments were similar, i.e. the isotopic composition of this material is nearly independent of the order of addition of reagents. The amount of deuterium at C-10 was somewhat erratic (75–90%), presumably because of exchange with adventitious moisture on workup. In the succinimide ring, no deuterium was detected at the methine site, as shown by integration (1.0) of this NMR

(25) Mills, S. G.; Beak, P. *J. Org. Chem.* **1985**, *50*, 1216.
(26) (a) Baba, H.; Takemura, T. *Tetrahedron* **1968**, *24*, 4779. (b) Takemura, T.; Baba, H. *Tetrahedron* **1968**, *24*, 5311.



9-*d*



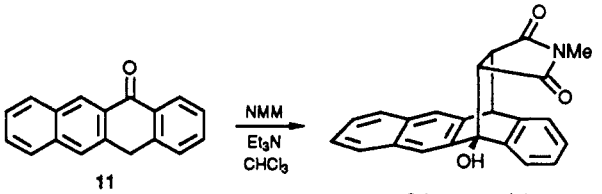
10-*d* (5)

absorption relative to the NMe peak (3.0).

The analysis of the methylene group isotopic composition was more complicated. The sum of the integrals for cis and trans protons combined was somewhat less than 1.0, implying that some CD_2 product had been formed. This presumably reflects partial exchange after cleavage to the Michael adduct, since no deuterium was found at the ring fusion positions of the cycloadduct. However, overall more deuterium had been introduced trans than cis to the anthracenyl ring. This ratio was estimated by ^1H NMR to be 85/15, and reinforced by examination of the ^2H NMR spectrum, which showed absorptions at 1.9 (cis, 15 ± 5%) and 2.2 ppm (trans, 85 ± 5%).

Deuteration of the intermediate succinimide carbanion trans to the anthracenyl ring may simply be caused by steric shielding of the cis face. The depiction of product in eq 5 is not meant to imply that deuteration must occur in this conformation, since steric shielding may also be invoked for other conformers formed by rotation about the anthrone–succinimide bond.

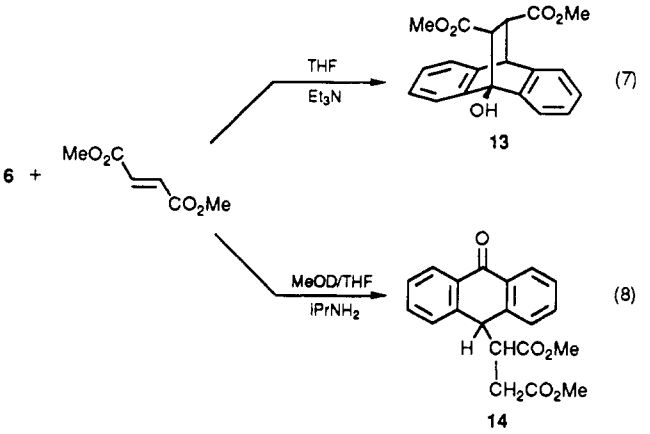
The benzologue 5-naphthacenone (11) also gives a cycloadduct with NMM in DMF solvent. Although the intermediate phenoxide may be even more reactive in this system, operationally the reaction was found to be slower than with anthrone under the same conditions. A lower concentration of reactive intermediate is expected for 11, since the factors which enhance reactivity will also diminish its stability. The significant result with 11 is that cycloaddition takes place at the substituted ring as shown in eq 6, in contrast to the results of the related ether shown in eq 2.



11 12 (exo + endo) (6)

The product 12 is a mixture of exo (shown) and endo isomers, as indicated by NMR spectroscopy. The very similar spectra of the two do not allow assignment of the major and minor isomers of this 2/1 mixture.

Anthrone with Other Dienophiles. The high reactivity of the anion 7 allows the use of much less reactive dienophiles than NMM. Thus dimethyl fumarate, which is ca. 10^{-2} as reactive as NMM in other cycloaddition reactions, gives cycloadduct 13 in excellent yield but in a noticeably slower reaction which requires hours instead of minutes for completion. The stereochemistry of the dienophile is retained, as judged by the coupling constant, and none of the cis stereoisomer was detected.



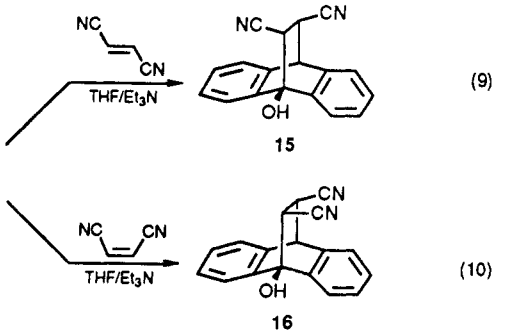
13 (7)

14 (8)

The influence of methanol solvent is again evident in the reaction of dimethyl fumarate. An aliquot taken at 3.5 h from a reaction run in MeOH/THF with isopropylamine catalyst showed that starting material had been consumed, and both cycloadduct 13 and Michael adduct 14 were present, in a ratio of 1/3; 14 is the exclusive product when the reaction is carried out for 24 h.

Attempts to examine the stereochemistry of cycloaddition with dimethyl maleate were thwarted by the greatly diminished reactivity of this dienophile. Even when the diester was used as solvent, no product was observed after a day with Et_3N catalyst. In an effort to speed the reaction piperidine was used, but this caused the exothermic conversion of maleate to fumarate. No reaction was observed between anthrone and dimethyl maleate in pyridine solvent at room temperature (12 h). This solution was subsequently refluxed for 3 days. Extensive oxidation (formation of anthraquinone) occurred, in spite of normal precautions to exclude air, and no adducts were evident in the crude product.

Unlike the diesters, fumaronitrile and maleonitrile exhibit similar reactivity, and both are more reactive than dimethyl fumarate.[27] The Et_3N-catalyzed reactions of the dinitriles with anthrone in THF were both complete within 1 h. These cycloadditions are essentially quantitative and completely stereospecific, occurring with retention of dienophile geometry to give products 15 and 16, respectively. Most of the cycloadducts described in this paper are stable toward chromatography on silica gel, but 15 proved to be an exception and was completely converted to Michael adduct 17 by such treatment (16 was not examined in this context).



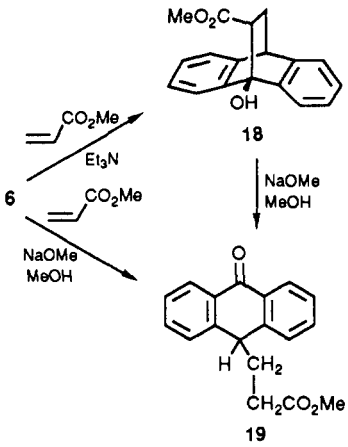
15 (9)

16 (10)

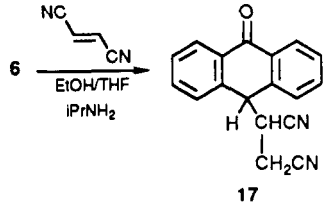
The reaction of 6 with fumaronitrile under protic solvent conditions (1/1 EtOH/THF) catalyzed by isopropylamine was time dependent. An aliquot taken at 25 min showed that the starting materials had been consumed, to give

(27) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16. We thank Prof. Richard Glass (University of Arizona) for helpful correspondence regarding fumaronitrile and maleonitrile.

Scheme I



exclusively **15**. Continued stirring for 23 h led to the exclusive formation of Michael adduct **17**.

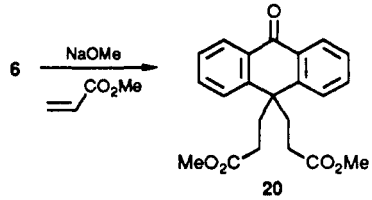


(11)

The diminished reactivity of methyl acrylate[20] became evident in attempts to form cycloadduct with anthrone under typical conditions. No reaction was observed after 29 h in THF when anthrone, dienophile, and Et_3N were used in approximately equal concentration (0.2 M). However, cycloaddition could be effected within 1 day by using the dienophile as solvent, thereby increasing its concentration by ca. 10^2. Primary amines also proved to be more effective catalysts than Et_3N, and reactions were successfully carried out in THF with e.g. isopropylamine as the catalyst. The cycloadduct **18** (Scheme I) is formed completely regiospecifically and essentially quantitatively under both sets of conditions.

In an effort to speed the reaction, variations of solvent and base were examined. For example, NaOMe in THF gave **18** cleanly, and the stronger base clearly enhanced the rate. Rapid reaction was also observed when NaOMe in methanol was employed, but the exclusive product in this solvent is the Michael adduct **19**. This product is also formed when isolated cycloadduct **18** is subjected to the same conditions, showing that **18** is a permissable intermediate in the formation of **19**.

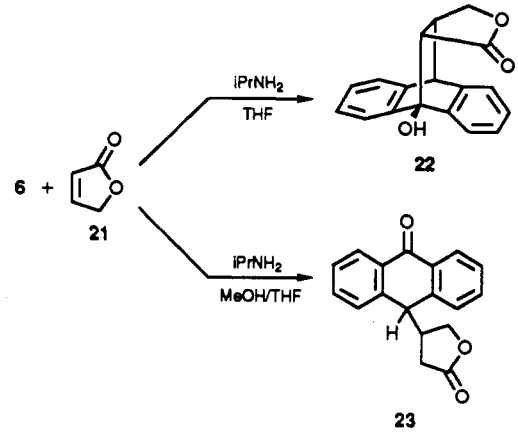
As noted above, **18** is formed smoothly when anthrone is dissolved in methyl acrylate solvent containing Et_3N catalyst. The use of NaOMe in this dienophile as solvent, or in methanol with excess (5 equiv) of methyl acrylate, gives the known[33] bis-Michael adduct **20**, which is also formed when cycloadduct **18** is subjected to the same conditions.



(12)

No reaction between methyl acrylate and anthrone was observed in MeOH solvent with Et_3N as the catalyst. When isopropylamine was employed under these conditions, the dienophile was consumed by conjugate addition of the amine, and the anthrone was recovered unchanged.

The least reactive dienophile[20] with which we have been able to form cycloadduct is 2-butenolide (**21**). Although slower than the reactions described above, **21** reacts with **6** to give cycloadduct **22** in good yield when the reaction is carried out in THF with isopropylamine (40 h). As with methyl acrylate, a single regioisomer is formed. With all other reagents including the amine the same, simply changing the solvent to MeOH/THF led to the exclusive formation of Michael adduct **23** (95 h). This product is also formed when **22** is subjected to the same conditions.

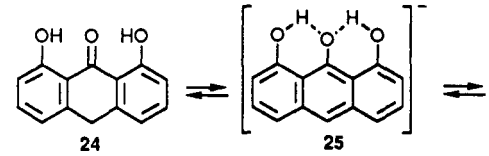


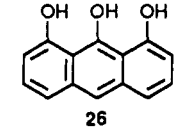
(13)

(14)

Attempted cycloadditions with the less reactive dienophiles ethyl crotonate, 1,4-dihydro-1,4-epoxynaphthalene, and norbornene were unsuccessful, in spite of changes in base and concentration such as those described above to enhance rates, as well as heating in some instances. Although there is obviously a limitation based on dienophile structure, those which have been successfully employed at room temperature span an impressive reactivity range of ca. 10^5. The anthrone/base system is clearly the most reactive "diene" in the anthracene family.

Reactions of Dithranol. In 1977 Schultz and Frey[28] described reactions of dithranol (1,8-dihydroxy-9-anthrone, **24**) with dimethyl acetylenedicarboxylate. No reaction was observed in refluxing acetic acid, but the addition of LiOMe to THF or $CHCl_3$ solutions led to cycloadduct and Michael adduct, respectively. These authors attributed the reactions to base-catalyzed formation of the enol (phenol) tautomer **26**. In light of our anthrone results, we would interpret these products as arising from reaction of the enolate (phenoxide) species, e.g. **25**.





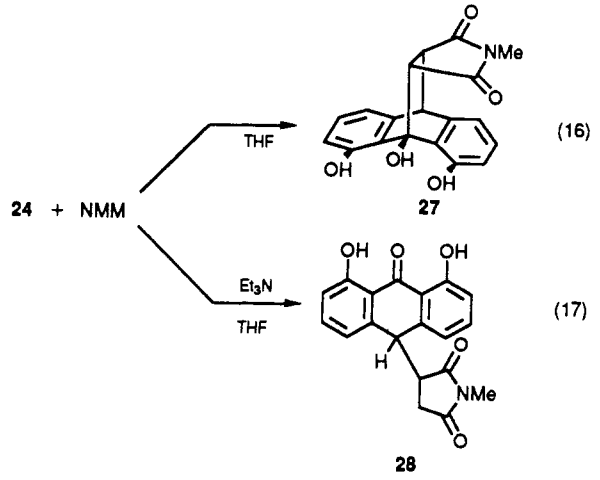
(15)

Under our typical amine-catalyzed conditions, the reactions of dithranol occur more rapidly than those of anthrone. This enhanced reactivity may be associated with the intramolecular hydrogen bonding which is available to the dithranol structure, or a variant involving a complex

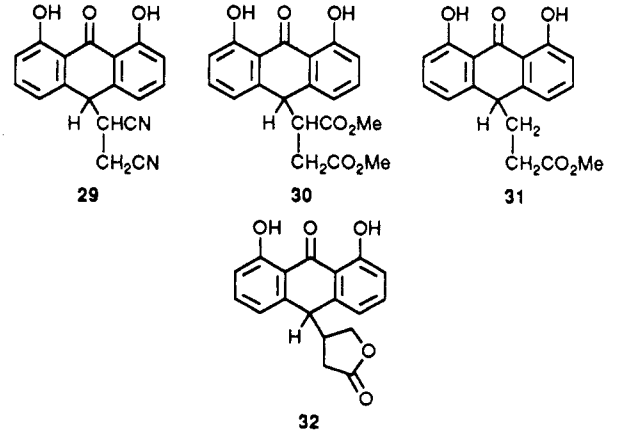
(28) Schultz, O. E.; Frey, G. *Arch. Pharm. (Weinheim)* **1977**, *310*, 776.

with the amine. To the extent that this is more stabilizing for the anion (as shown in structure **25**) than for the neutrals, the concentration of **25** may be increased relative to the anion (**7**) derived from anthrone under the same conditions, and greater apparent reactivity could be due to this concentration effect. Perhaps reflecting this difference, dithranol/amine solutions in THF are much more intensely colored (orange-red) than analogous anthrone/amine solutions (yellow).

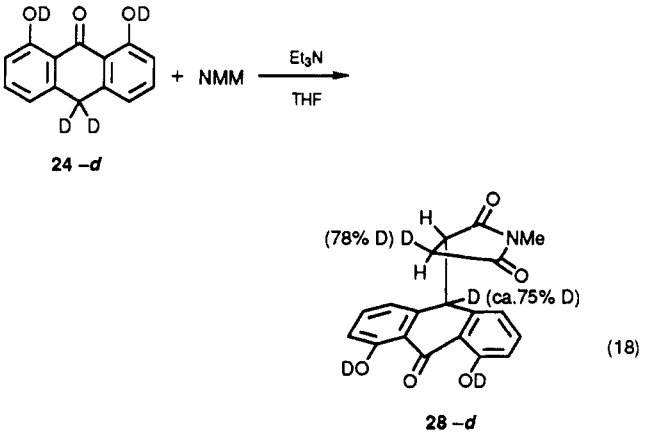
The second major difference between anthrone and dithranol is the facile formation of Michael adducts with the latter. In fact, we have isolated a cycloadduct (**27**) from dithranol only with NMM in THF (but not in $CHCl_3$, where no reaction occurs), and then only when no base was (intentionally) added. This reaction is relatively slow, requiring 4 days to go to completion. Under the same conditions but with Et_3N added, Michael adduct **28** is the exclusive product after just 30 min. Treatment of isolated **27** under the latter conditions also causes rapid conversion to **28**, showing that **27** is a viable intermediate on the pathway to Michael adduct.



Conditions (THF, amine) which with anthrone and the dienophiles fumaronitrile, dimethyl fumarate, methyl acrylate, and butenolide lead exclusively to cycloadducts, give only the Michael adducts **29–32** when dithranol is used.



The reactions of dithranol/amine/THF thus resemble those of anthrone/amine/methanol, in that both tend to give Michael adducts. Both systems have proton sources that are not available to anthrone/amine/THF, from the hydroxyl groups of dithranol in the former, and from the solvent in the latter. This raises the interesting possibility of intramolecular proton transfer from the 1,8-hydroxy groups of dithranol to the carbanion which would be generated as an intermediate in Michael addition, if indeed Michael adducts are formed by this mechanism. In order to probe this question, a sample of dithranol was deuterated by treatment with D_2O in THF with Et_3N catalyst. The product (**24-*d***) obtained by vacuum evaporation of volatiles was extensively deuterated in the positions shown, as indicated by its ^1H NMR spectrum.



Intramolecular transfer would lead to introduction of deuterium on the succinimide ring cis to the anthracenyl substituent. However, no cis deuteration is detected. Instead, stereoselective trans deuteration occurs to give **28-*d***. This outcome parallels that observed in the ring opening of anthrone–NMM cycloadduct (eq 5), and presumably the same (steric) factors dictate the stereochemical course of both reactions. The nearly identical percentage of deuterium found at the two carbon sites of compound **28-*d*** is believed to be due to equilibration at C-10 after formation of Michael adduct, i.e., this figure represents the D/H (adventitious) pool available for reaction.

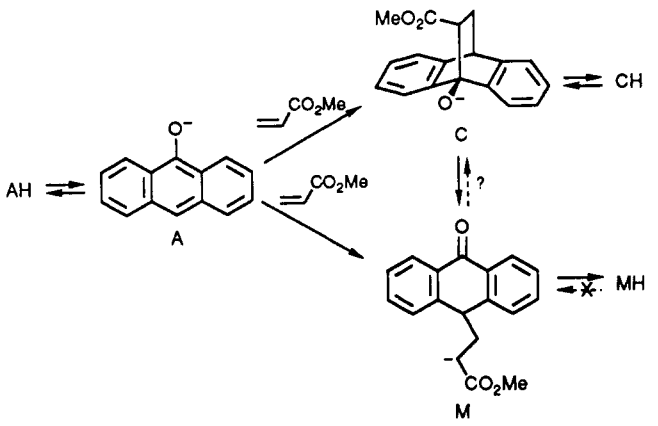
An alternative explanation for the facile conversion of dithranol to Michael adduct is that cycloadduct is formed first, and being inherently more acidic due to the phenolic hydroxyl groups, leads in the presence of base to a significant concentration of anionic form. The proximity of the bridgehead hydroxyl group allows an effective intramolecular proton transfer between two heteroatoms which opens up a pathway for cleavage to the carbanion precursor of Michael adduct.

Mechanism

The principal mechanistic issue in base-catalyzed anthrone cycloadditions is whether these occur as concerted Diels–Alder processes, or as two-step (Michael + aldol) sequences. This same fundamental question arises in other 1-oxido and 2-oxido diene cycloadditions discussed earlier, whether these are base-induced or -catalyzed reactions.

The alternative routes for anthrone are illustrated in Scheme II, with methyl acrylate as a typical dienophile. The three putative intermediate anions are labeled A, M, and C, and it is assumed that of the two mechanistic options A → C, and A → M → C, one occurs to the exclusion of the other. The step C → M appears to be confirmed by the observation that CH can be converted to MH (where the H refers to the neutral protonated forms of the corresponding anion) without reverting to AH (as shown with NMM as dienophile by conversion of cycloadduct to Michael adduct without incorporation of deuterium at the bridgehead position of cycloadduct; cf. discussion of eq 5). The irreversible formation of NMM cycloadduct was also demonstrated in DMF, by stirring a mixture of the adduct and 1,3-diphenylisobenzofuran in this solvent for 3 days.

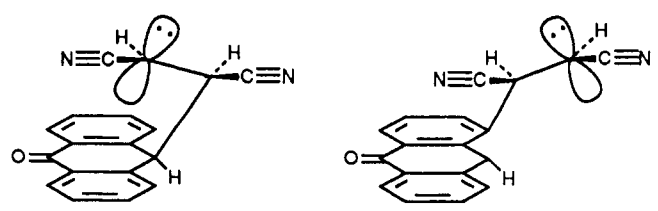
Scheme II



Any NMM regenerated under these conditions would have been rapidly and irreversibly trapped by the diphenylisobenzofuran, and none of this cycloadduct was detected. Under the weak base conditions employed in this study, there is no evidence for the occurrence of the reverse reaction (MH → CH). However, since MH may not be readily deprotonated to M under these conditions, this may not illuminate the mechanistically critical step (does M → C?).

The effect of alcohol on product distribution is subject to at least two rational interpretations. In those instances which give MH rapidly when methanol is present but not in THF alone, it is tempting to conclude that M is formed directly from A + dienophile, with the role of protic solvent being interception of M before closure to C can occur. However, the time dependence of the CH/MH ratios from several reactions (e.g. with NMM, dimethyl furarate, fumaronitrile) shows that such a conclusion would be an oversimplification. In these reactions CH is formed first, and converted to MH under the same conditions in a slower reaction. From this one might reasonably conclude that A plus dienophile gives C in concerted fashion. Initial formation of M cannot be rigorously excluded, provided that the rate of closure of M to C is faster (much faster in the case of NMM and fumaronitrile, which at short reaction times give cycloadducts as the only measurable products) than protonation to MH can occur. We view this as unlikely in polar protic medium, but difficult to disprove experimentally.

Finally, the stereospecificity of cycloaddition found for dimethyl fumarate and the *E* and *Z* dinitriles requires either a concerted Diels–Alder mechanism, or a stepwise process in which the second (ring closure) step is much faster than rotation about the single bond (former double bond) generated by Michael addition to the dienophile. This outcome would seem to require that the Michael addition occur to give the syn intermediate **33** rather than the anti intermediate **34**.



33 **34**

In order for **34** to undergo ring closure, 180° rotation about the C(10)-dienophile bond must occur. It is not obvious how the time could be available for this rotation and not for similar rotation about the product stereoisomer-determining bond. Faced with a similar need to rationalize stereospecifically formed products from 2-oxido diene reactions which were believed to be sequential "Michael + Michael" processes, earlier workers have called upon lithium ion coordination between the heteroatoms of diene and dienophile. The alkylammonium ion involved in the present study does not lend itself to similar interpretation and certainly shows that a good oxygen coordinating cation such as lithium is not needed to effect stereospecific reaction. We conclude that the base catalyzed reactions of anthrones with dienophiles are concerted Diels–Alder processes. The body of reactions involving 1-oxido and 2-oxido 1,3-dienes may likewise fall under the umbrella of concerted cycloadditions, although, as previous workers have recognized, there is no a priori reason to believe that all must occur by a common mechanism.

The work of Ban et al.,[19] in which both cycloadduct and Michael adduct are formed in a base-catalyzed reaction between a complex heterocyclic "diene" precursor and acrylonitrile, appears to counter the concerted mechanism view. One would normally expect ring strain in a cycloadduct to favor Michael adduct if there is a pathway for equilibration of the two and no overriding pK_a differences are involved, but in this instance it was reported that the Michael adduct was converted to cycloadduct when resubjected to the same reaction conditions. In order to classify cycloaddition as concerted for this 2-oxido diene, the two products would have to arise from competing rather than sequential reactions of the diene + dienophile, and the Michael adduct would have to revert to educts in order to form cycloadduct.

Experimental Section

The *N*-methylmaleimide (NMM), fumaronitrile, dimethyl fumarate, methyl acrylate, 9-anthrone, and dithranol were commercial materials used as received. The 2-butenolide was prepared following a literature procedure,[29] and maleonitrile was isolated after equilibration with fumaronitrile as described by Ficken et al.[30] The solvents were used without purification except for THF, which was distilled from sodium benzophenone ketyl immediately before use. All reactions were carried out under an inert atmosphere of N_2 or Ar, an important precaution because of the facile air oxidation of anthrones to the corresponding anthraquinones under basic conditions. Proton and carbon NMR spectra were obtained on a GE GN-500 instrument in $CDCl_3$ solvent unless otherwise specified. The purity of titled compounds was estimated to be ≥95% by examination of the NMR spectra. MS and MS(CI) (chemically induced, methane flow gas) data were obtained on a VG 70-250 instrument by Dr. Hugh Webb. Perkin-Elmer Model 283 or 1330 spectrometers were used for IR spectra. Combustion analysis was performed by Desert Analytics, Tucson, AZ.

5(12*H*)-Naphthacenone (11). This benzologue was prepared by reduction of 5,12-naphthacenedione as described by Fieser.[31] The quinone was formed by cycloaddition of 1,4-naphthaquinone with isobenzofuran (formed in situ from 1,3-dihydro-1-ethoxyisobenzofuran)[16] in refluxing acetic acid, conditions which also effect dehydration as described by Smith and Dibble.[32]

5-(Methoxymethoxy)naphthacene (4). A stirred suspension of 175 mg (0.710 mmol) of 11 in 10 mL of THF was cooled to −40 °C under an Ar atmosphere. A solution of LTMP (1.1 mmol, prepared from 2,2,6,6-tetramethylpiperidine and *n*-BuLi at −78 °C) in 5 mL of THF was added via syringe. After 10 min, the dark purple solution was treated with 0.110 mL (1.4 mmol) of chloromethyl methyl ether, and the mixture was allowed to warm to room temperature (2.5 h). Without any workup, solvent was removed in vacuo, and a portion of the brilliant orange, very air

(29) Takano, S.; Ogasawara, K. *Synthesis* **1974**, 42.
(30) Ficken, G. E.; Linstead, R. P.; Stephen, E.; Whalley, M. *J. Chem. Soc.* **1958**, 2879.
(31) Fieser, L. F. *J. Am. Chem. Soc.* **1931**, *53*, 2329.
(32) Smith, J. G.; Dibble, P. W. *J. Org. Chem.* **1983**, *48*, 5361.

sensitive product was examined by NMR under Ar. Other than naphthacenequinone which was formed rapidly on contact with air, the material appeared to be quite pure: ^{1}H NMR (300 MHz) δ 3.79 (s, 3 H), 5.47 (s, 2 H), 7.40 (m, 4 H), 7.97 (m, 3 H), 8.31 (m, 1 H), 8.47 (s, 1 H), 8.64 (s, 1 H), and 8.95 ppm (s, 1 H).

Reaction of 4 with NMM: 5a or 5b. A solution of **4** was prepared from 440 mg (1.80 mmol) of **11** in 70 mL of THF. NMM (285 mg, 2.50 mmol) was added, and the mixture was stirred for 12 h at room temperature. Water was added, and the product was extracted into CH_2Cl_2, which was dried over $MgSO_4$ and vacuum evaporated to give 640 mg (89%) of a brown solid. The NMR spectrum of this crude product showed that it contained ca. 60% of the single isomer described below. The material was recrystallized from EtOAc/hexanes to give 310 mg (43%) of this major product as an off-white solid, mp 197–199.5 °C. The NMR spectrum contains two doublets attributed to bridgehead protons and only one aromatic singlet, indicating structure **5a** or **5b**: ^{1}H NMR (300 MHz) δ 2.54 (s, 3 H), 3.28 (leaning dd, 1 H, J = 9, 3 Hz), 3.31 (leaning dd, 1 H, J = 9, 3 Hz), 3.83 (s, 3 H), 4.89 (d, 1 H, J = 3 Hz), 5.19–5.25 (AB q, 2 H, OCH_2OMe), 5.32 (d, 1 H, J = 3 Hz), 7.15 (m, 2 H), 7.30 (m, 2 H), 7.48 (m, 2 H), 7.64 (s, 1 H), 7.79 (d, 1 H, J = 7.5 Hz), 8.02 (d, 1 H, J = 8 Hz); IR (KBr) 3040 (w), 2959 (w), 1782 (w), 1702 (s), 1440 (m), 1387 (m), 1292 (m), 1045 cm^{-1} (m); MS calcd for $C_{25}H_{21}NO_4$ 399.1436, found 399.1453.

4-Hydroxy-2-methyl-3a,4,9,9a-tetrahydro-4,9[1′,2′]-benzeno-1*H*-benz[*f*]isoindole-1,3(2*H*)-dione (9). To a solution of 239 mg of anthrone (1.23 mmol) and 136 mg (1.23 mmol) of NMM in 12 mL of THF was added 0.10 mL (0.72 mmol) of Et_3N, which caused a yellow color to develop. The mixture was stirred at ambient temperature (24 ± 2 °C) for 15 min. Vacuum evaporation of the solvent gave 374 mg (100%) of a colorless solid: mp 194–197 °C; ^{1}H NMR δ 2.50 (s, 3 H), 3.11 (d, 1 H, J = 8.5 Hz), 3.31 (dd, 1 H, J = 8.5, 3.5 Hz), 4.48 (s, 1 H), 4.71 (d, 1 H, J = 3.5 Hz), 7.21 (m, 5 H), 7.36 (d, 1 H, J = 7.5 Hz), 7.47 (d, 1 H, J = 7.5 Hz), and 7.68 ppm (d, 1 H, J = 7.5 Hz); ^{13}C NMR δ 24.29, 44.51, 47.63, 50.75, 120.73, 120.82, 123.69, 124.42, 126.71, 126.82, 127.07, 127.20, 136.38, 138.96, 140.63, 142.40, 176.45, and 177.85 ppm; MS (CI) 306 (P + H, 5.9), 195 (95.8), 194 (100), 165 (28.5), 112 (48.9); IR ($CHCl_3$) 3522 (br, m), 3026 (vs), 1684 (s), 1439 (m), and 1220 (br s) cm^{-1}; MS (CI) calcd for P + H 306.1122, found 306.1130.

Anal. Calcd for $C_{19}H_{15}NO_3$: C, 74.77; H, 4.95. Found: C, 74.66; H, 4.81.

10-(1-Methyl-2,5-dioxopyrrolidin-3-yl)-9(10*H*)-anthracenone (10). A solution of 526 mg (2.71 mmol) of anthrone and 302 mg (2.72 mmol) of NMM in a mixed solvent consisting of 15 mL each of methanol and THF was treated with 4.0 mL (28.7 mmol) of Et_3N, giving a bright yellow solution. After 16 h the volatile materials were vacuum evaporated, and the residue was chromatographed (silica gel, CH_2Cl_2) to give 787 mg (96%) of a colorless solid: mp 122–122.5 °C; ^{1}H NMR δ 1.87 (dd, 1 H, J = 18.5, 5 Hz), 2.22 (dd, 1 H, J = 18.5, 9 Hz), 3.45 (ddd, 1 H, J = 9, 5, 3.5 Hz), 5.15 (d, 1 H, J = 3.5 Hz), 7.38 (d, 1 H, J = 7.5 Hz), 7.51 (m, 3 H), 7.60 (d, 1 H, J = 7.5 Hz), 7.66 (t, 1 H, J = 7.5 Hz), and 8.29 ppm (app t, 2 H, J = 8 Hz); ^{13}C NMR (75 MHz) δ 22.34, 26.45, 39.16, 47.60, 125.24, 125.40, 125.48, 126.10, 129.86, 130.94, 130.70, 131.30, 135.74, 139.95, 172.57, 175.54, and 181.30 ppm; MS (CI) 306 (P + H, 82), 196 (15), 195 (100), 194 (80), 193 (95), 165 (31), 114 (25), 112 (50); IR (film) 3055 (w), 2962 (m), 2920 (w), 2860 (w), 1772 (m), 1700 (vs), 1660 (s), 1595 (s), 1432 (m), 1380 (m), 1311 (m), and 1120 (m) cm^{-1}; MS (CI) calcd for $C_{19}H_{16}NO_3$ (P + H) 306.1131, found 306.1117.

Reaction in MeOD: 9-*d* and 10-*d*. (a) Et_3N Added Last. A solution of anthrone (363 mg, 1.87 mmol) and NMM (207 mg, 1.86 mmol) in a mixture of 5 mL of MeOD and 5 mL of THF was prepared, and Et_3N (3 mL) was added in one portion. After 3.3 h an aliquot was removed, evaporated under vacuum, and examined by ^{1}H NMR spectroscopy. At this point the mixture consisted of 45% **9-*d*** and 55% **10-*d***, as measured by integration of the respective NMe peaks. For **9-*d***, the bridgehead (d) at 4.7 ppm, as well as the ring fusion (dd) at 3.3 and (d) at 3.1 ppm exhibited integrals of 1.0 relative to the NMe (3.0), showing that no measurable deuterium had been incorporated at these sites. In **10-*d***, the relative areas were NMe (3.0), C-10 (1.0), succinimide methine (1.0), succinimide methylene cis to anthracenyl ring (dd at 1.87 ppm, 0.8), and trans (dd at 2.2 ppm, 0.1). After 6 h, **10-*d*** was the exclusive product and exhibited a very similar NMR spectrum.

(b) NMM Added Last. Essentially the same amounts of materials were used in a larger solvent volume (7 mL each of THF and MeOD); the NMM was added in one portion after the other reagents had been stirred for 5 min. An aliquot taken after 10 min was treated as above. Starting materials had been consumed at this point, and the product was exclusively cycloadduct (**9-*d***). No absorption was detected at 4.7 ppm, and from the magnitude of the NMe peak it was estimated that the C-10 position of **9-*d*** was ≥95% deuterated. No deuterium was detected in the succinimide ring, as judged by integration of the ring fusion protons (1.0 for each doublet) vs the NMe (3.0). Conversion of **9-*d*** to Michael adduct (**10-*d***) was slower (lower concentrations) than in the preceding run, and when quenched after 24 h the product consisted of 90% **10-*d*** with ca. 10% residual **9-*d***.

The **10-*d*** exhibited ^{1}H NMR integrals as follows: NMe (3.0), succinimide methine (1.0), cis to anthracene (0.8), and trans (0.1). The proton at C-10 in different aliquots varied from 0.1 to 0.3, presumably because of exchange with adventitious water on workup. The proton decoupled ^{2}H NMR spectrum had peaks centered at 2.2 and 1.9 ppm, with relative areas of 9 and 1, respectively.

***endo*- and *exo*-4-Hydroxy-2-methyl-3a,4,9,9a-tetrahydro-4,9[2′,3′]-naphthaleno-1*H*-benz[*f*]isoindole-1,3(2*H*)-dione (12).** An aliquot removed from a mixture of 176 mg (0.721 mmol) of **11**, 93 mg of NMM (0.84 mmol), and 0.1 mL of Et_3N after 15 min was examined by NMR spectroscopy, which indicated that the reaction had proceeded 70% to completion to afford a mixture of exo/endo isomers in a ca. 2/1 ratio. The minor isomer gave peaks which shadowed those of the major isomer reported below. After 12 h the reaction was complete, with the ratio unchanged. The solid residues from both samples were combined and recrystallized from $CHCl_3$ to afford 158 mg (62%) of the major isomer: mp 281–283 °C; ^{1}H NMR δ 2.52 (s, 3 H), 3.19 (d, 1 H, J = 9 Hz), 4.00 (dd, 1 H, J = 9, 4 Hz), 4.59 (s, 1 H), 4.85 (d, 1 H, J = 4 Hz), 7.17 (m, 1 H), 7.26 (m, 2 H), 7.47 (m, 2 H), 7.52 (d, 1 H, J = 8 Hz), 7.79 (s, 1 H), 7.81 (m, 1 H), 7.87 (m, 1 H), and 8.10 ppm (s, 1 H); IR (KBr) 3450 (br, s), 3370 (br, s), 3040 (w), 2944 (w), 1772 (m), 1682 (br, vs), 1440 (s), 1385 (s), 1280 (s), 1132 (s), 1010 (m), 972 cm^{-1} (m); MS (CI) calcd for $C_{23}H_{18}NO_3$ (P + H) 356.1299, found 356.1293.

Dimethyl 9,10-Dihydro-9-hydroxy-9,10-ethanoanthracene-11,12-*trans*-dicarboxylate (13). The (yellow upon addition of amine) solution of anthrone (1.28 g, 6.58 mmol), dimethyl fumarate (0.97 g, 6.72 mmol), and Et_3N (3.0 mL, 21.5 mmol) was stirred for 24 h and then rotary evaporated. Recrystallization of the residue from methanol gave 2.18 g (97%) of a colorless solid: mp 145–146 °C; ^{1}H NMR δ 3.42 (dd, 1 H, J = 5, 3 Hz), 3.46 (d, 1 H, J = 5 Hz), 3.58 (s, 3 H), 3.65 (s, 3 H), 4.67 (d, 1 H, J = 3 Hz), 5.30 (s, 1 H), 7.13 (m, 2 H), 7.21 (m, 3 H), 7.32 (d, 1 H, J = 7 Hz), 7.53 (d, 1 H, J = 7.5 Hz), and 7.66 ppm (d, 1 H, J = 7.5 Hz); ^{13}C NMR δ 45.63, 49.23, 51.19, 52.45, 52.57, 120.54, 120.96, 123.36, 123.68, 126.45, 126.51, 126.60, 138.13, 139.92, 142.36, 142.66, 172.04, and 173.49 ppm; MS(CI) 339 (P + H, 1.5), 223 (11.7), 196 (16), 195 (100), 194 (52), 165 (12), 145 (53.3); IR (KBr) 3031 (vs), 2986 (m), 2901 (w), 1744 (m), 1525 (w), 1449 (w), 1230 (br, vs) cm^{-1}; MS(CI) calcd for $C_{20}H_{19}O_5$ (P + H) 339.1232, found 339.1228.

10-(1,2-Bis(methoxycarbonyl)ethyl)-9(10*H*)-anthracenone (14). To a solution of 400 mg (2.06 mmol) of anthrone and 300 mg of dimethyl fumarate (2.08 mmol) in a mixed solvent consisting of 7 mL each of MeOH and THF was added 0.50 mL of isopropylamine (5.9 mmol). Upon addition of the amine the clear colorless solution turned orange. After the solution was stirred for 24 h at ambient temperature the solvent was removed in vacuo. The residue was chromatographed (silica gel, CH_2Cl_2) to give 677 mg (96%) of a colorless solid: mp 117.5–119 °C; ^{1}H NMR δ 1.86 (dd, 1 H, J = 17, 4 Hz), 2.17 (dd, 1 H, J = 17, 11 Hz), 3.47 (m, 1 H), 3.49 (s, 3 H), 3.75 (s, 3 H), 4.87 (d, 1 H, J = 4 Hz), 7.22 (d, 1 H, J = 7.5 Hz), 7.48 (t, 2 H, J = 7.5 Hz), 7.54 (m, 1 H), 7.62 (m, 2 H), and 8.26 ppm (m, 2 H); ^{13}C NMR (75 MHz) δ 27.79, 41.17, 48.27, 49.29, 49.79, 124.81, 125.09, 125.29, 125.43, 125.57, 125.86, 130.38, 130.42, 130.88, 137.70, 139.59, 169.47, 170.09, and 181.70 ppm; MS 338 (P, 5.8), 194 (17), 193 (100), 165 (20), 84 (11);

IR ($CHCl_3$) 3038 (s), 3020 (s), 1762 (s), 1667 (m), 1600 (m), 1400 (br, s), 1330 (br, m), 1205 (m) cm^{-1}; MS calcd for $C_{20}H_{18}O_5$ 338.1154, found 338.1169.

***trans*-11,12-Dicyano-9,10-dihydro-9-hydroxy-9,10-ethanoanthracene (15).** A solution of 197 mg (1.02 mmol) of anthrone, 81 mg (1.04 mmol) of fumaronitrile, and 0.10 mL (0.72 mmol) of Et_3N in 10 mL of THF (bright yellow) was vacuum evaporated after standing for 20 min. Recrystallization from $CHCl_3$ gave 277 mg (99%) of pale yellow needles: mp 209–211 °C; ^1H NMR δ 3.17 (d, 1 H, J = 5 Hz), 3.22 (dd, 1 H, J = 5, 2.5 Hz), 3.55 (br s, 1 H), 4.61 (d, 1 H, J = 2.5 Hz), 7.34 (m, 5 H), 7.47 (d, 1 H, J = 7 Hz), and 7.60 ppm (d, 1 H, J = 7.5 Hz); ^{13}C NMR (75 MHz) δ 33.51, 39.89, 43.01, 114.91, 115.62, 117.57, 118.68, 121.55, 122.86, 125.39, 125.50, 125.64, and 125.82 ppm; MS 195 (15), 194 (100), 193 (46), 165 (74), 78 (17); IR (KBr) 3505 (br, s), 3083 (m), 3058 (m), 3018 (w), 2944 (s), 2258 (s), 1462 (s), 1193 (s), 1078 (m) cm^{-1}; MS (CI) calcd for $C_{18}H_{13}N_2O$ (P + H) 273.1028, found 273.1044.

***cis*-11,12-Dicyano-9,10-dihydro-9-hydroxy-9,10-ethanoanthracene (16).** In the same manner, a mixture of 93 mg (0.48 mmol) of anthrone, 37 mg (0.47 mmol) of maleonitrile, and 0.50 mL of Et_3N in 5 mL of THF was vacuum evaporated after standing for 1 h. The residue was recrystallized from $CHCl_3$ to give 131 mg (100%) of a colorless solid: mp 210.5–214 °C; ^1H NMR δ 3.66 (d, 1 H, J = 10 Hz), 3.82 (dd, 1 H, J = 10, 2.5 Hz), 4.88 (d, 1 H, J = 2.5 Hz), 6.60 (br s, 1 H), 7.25 (t, 1 H, J = 7.5 Hz), 7.30 (t, 1 H, J = 7 Hz), 7.31 (t, 1 H, J = 7 Hz), 7.36 (t, 1 H, J = 7.5 Hz), 7.47 (d, 1 H, J = 7 Hz), 7.54 (d, 1 H, J = 7.5 Hz), 7.64 (d, 1 H, J = 7 Hz), and 7.77 ppm (d, 1 H, J = 7.5 Hz); ^{13}C NMR δ 35.78, 41.84, 46.13, 117.78, 118.78, 121.37, 122.58, 124.87, 125.89, 127.84, 127.94, 128.09, 138.37, 139.75, 141.66, and 143.26 ppm; MS (CI) 223 (7), 196 (13), 195 (84), 194 (17), 79 (100); IR (KBr) 3410 (br, s), 3080 (m), 3035 (m), 2970 (w), 2940 (m), 2260 (m), 1462 (s), 1250 (s), 1078 (m) cm^{-1}; MS (CI) calcd for $C_{18}H_{13}N_2O$ (P + H) 273.1028, found 273.1028.

10-(1,2-Dicyanoethyl)-9(10*H*)-anthracenone (17). To a solution of 313 mg (1.61 mmol) of anthrone and 131 mg (1.68 mmol) of fumaronitrile in a solvent consisting of 10 mL each of ethanol and THF was added 0.10 mL (1.17 mmol) of isopropylamine. The resultant yellow-orange solution darkened on standing for 24 h, at which point the volatiles were vacuum evaporated. Chromatography (silica gel, CH_2Cl_2) afforded 420 mg (95%) of colorless solid: mp 195–196.5 °C; ^1H NMR δ 2.35 (m, 2 H), 3.37 (ddd, 1 H, J = 8, 5, 3.5 Hz), 4.70 (d, 1 H, J = 5 Hz), 7.56 (d, 1 H, J = 7 Hz), 7.61 (t, 2 H, J = 7 Hz), 7.73 (m, 3 H), and 8.34 ppm (dd, 2 H, J = 8, 1.5 Hz); ^{13}C NMR δ 17.83, 38.97, 43.17, 115.20, 116.95, 128.29, 128.40, 128.47, 129.37, 132.91, 133.11, 133.62, 133.72, 137.54, 137.78, and 183.25 ppm; MS (CI) 273 (P + H, 12), 246 (14), 196 (15), 195 (100), 194 (79), 193 (31), 165 (19), 79 (77); IR (KBr) 3017 (s), 2980 (m), 2401 (m), 1670 (m), 1600 (m), 1512 (w), 1425 (m), 1200 (br, s), 927 (m) cm^{-1}; MS (CI) calcd for $C_{18}H_{13}N_2O$ (P + H) 273.1028, found 273.1011.

Methyl 9,10-Dihydro-9-hydroxy-9,10-ethanoanthracene-11-carboxylate (18). The addition of 0.10 mL of isopropylamine (1.17 mmol) to a mixture of anthrone (677 mg, 3.49 mmol) and methyl acrylate (0.31 mL, 3.45 mmol) in 10 mL of THF caused the clear colorless solution to turn yellow. After 16 h at ambient temperature, volatiles were removed in vacuo (foaming) to give 925 mg (95%) of essentially pure 18 as an off-white solid: mp 102–103 °C; ^1H NMR δ 2.20 (m, 2 H), 2.86 (dd, 1 H, J = 9, 7 Hz), 3.57 (s, 3 H), 4.28 (app t, 1 H, J = 3 Hz), 5.17 (s, 1 H), 7.14 (m, 2 H), 7.20 (m, 2 H), 7.26 (d, 2 H, J = 7 Hz), 7.53 (d, 1 H, J = 7.5 Hz), and 7.64 ppm (d, 1 H, J = 7.5 Hz); ^{13}C NMR δ 32.21, 42.67, 48.07, 52.22, 120.32, 120.88, 122.78, 122.88, 125.78, 125.87, 126.26, 126.33, 141.67, and 141.74 ppm; MS (CI) 281 (P + H, 16), 280 (8), 249 (18), 223 (10), 196 (15), 195 (100), 194 (54), 87 (29); IR (KBr) 3037 (m), 3024 (vs), 2983 (m), 1715 (w), 1527 (m), 1430 (m), 1217 (br, vs) cm^{-1}; MS (CI) calcd for $C_{18}H_{16}O_3$ (P + H) 280.1099, found 280.1072.

10-(2-(Methoxycarbonyl)ethyl)-9(10*H*)-anthracenone (19). To a solution of NaOMe prepared by adding 10 mg of Na to 7 mL of MeOH was added 980 mg (3.50 mmol) of cycloadduct 18 dissolved in 7 mL of THF. The bright orange solution was stirred for 3 h and then poured into 30 mL of 5% aqueous acetic acid. The mixture was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic phase was concentrated under vacuum, and the residue was chromatographed (silica gel, CH_2Cl_2) to give 897 mg (92%) of **19** as a colorless oil: ^1H NMR δ 1.84 (AA′ m, app t, 2 H, J = 8 Hz), 2.32 (m incl BB′, 2 H), 3.49 (s, 3 H), 4.40 (t, 1 H, J = 5 Hz), 7.44 (t, 2 H, J = 7 Hz), 7.48 (d, 2 H, J = 8 Hz), 7.59 (t, 2 H, J = 8 Hz), and 8.28 ppm (d, 2 H, J = 8 Hz); ^{13}C NMR δ 28.93, 36.11, 41.15, 51.52, 127.30, 127.47, 128.10, 133.05, 143.70, 173.18, and 184.23 ppm; MS (CI) 281 (P + H, 100), 280 (23), 250 (15), 249 (76), 231 (17), 207 (29), 193 (25); IR ($CHCl_3$) 3021 (s), 1760 (s), 1662 (s), 1605 (s), 1523 (m), 1319 (m), 1219 (br, s) cm^{-1}; MS (CI) calcd for $C_{18}H_{17}O_3$ (P + H) 281.1178, found 281.1201.

10,10-Bis(2-(methoxycarbonyl)ethyl)-9(10*H*)-anthracenone (20). A solution of NaOMe was prepared by adding 20 mg of Na to 10 mL of MeOH. To this was added 700 mg (3.61 mmol) of anthrone and 1.5 mL of methyl acrylate (16.7 mmol) in 10 mL of THF. The bright orange solution was stirred for 3 h and then poured into 60 mL of 0.05 M HCl. Extraction (2 × 60 mL) and concentration as above gave a solid residue, which was recrystallized from methanol to afford 1.28 g (97%) of colorless solid: mp 119.5–120 °C (lit.[33] mp 114–115.5 °C); ^1H NMR δ 1.58 (AA′ m, 4 H), 2.61 (BB′ m, 4 H), 3.44 (s, 6 H), 7.49 (dt, 2 H, J = 8, 1 Hz), 7.65 (d, 2 H, J = 8 Hz), 7.70 (dt, 2 H, J = 8, 1 Hz), and 8.40 ppm (dd, 2 H, J = 8, 1 Hz); ^{13}C NMR δ 29.13, 39.77, 51.51, 125.87, 127.51, 127.73, 132.63, 134.33, 144.83, and 173.15 ppm; MS (CI) 367 (P + H, 48), 335 (22), 303 (44), 280 (23), 279 (100), 219 (30); IR ($CHCl_3$) 3026 (vs), 2961 (s), 1730 (vs), 1660 (s), 1607 (s), 1441 (m), 1329 (m), 1215 (br, s) cm^{-1}; MS (CI) calcd for $C_{22}H_{23}O_5$ (P + H) 367.1546, found 367.1546.

9-Hydroxy-9,10,11,15-tetrahydro-9,10[3′,4′]-furanoanthracen-14(12*H*)-one (22). An orange solution of anthrone (460 mg, 2.67 mmol), 2-butenolide (200 mg, 2.38 mmol), and 0.50 mL (5.85 mmol) of isopropylamine in 15 mL of THF stood for 40 h before vacuum removal of volatiles. The solid residue was recrystallized from $CHCl_3$ to give 574 mg (87%) of a colorless solid: mp 228.5–229 °C; ^1H NMR (pyridine-d_5) δ 3.13 (m, 1 H), 3.37 (d, 1 H, J = 10.5 Hz), 3.81 (dd, 1 H, J = 9.5, 4 Hz), 4.25 (app t, 1 H, J = 9.5 Hz), 4.27 (d, 1 H, J = 2 Hz), 4.94 (br s, 1 H), 7.21 (m, 3 H), 7.31 (t, 1 H, J = 7.5 Hz), 7.40 (d, 2 H, J = 7.5 Hz), 8.06 (d, 1 H, J = 7 Hz), and 8.09 ppm (d, 1 H, J = 7 Hz); ^{13}C NMR (Me_2SO-d_6) δ 41.02, 45.22, 50.07, 68.80, 76.17, 120.47, 120.83, 122.99, 125.01, 125.54, 125.91, 125.96, 126.09, 137.58, 141.36, 142.19, 144.63, and 174.16 ppm; MS 278 (P, 0.1), 195 (15), 194 (100), 165 (43); IR (KBr) 3495 (vs), 3057 (m), 3039 (m), 3022 (m), 3001 (w), 2968 (m), 2944 (m), 2919 (m), 1752 (vs), 1459 (s), 1362 (s), 1269 (s), 1173 (s), 1007 (s) cm^{-1}; MS (CI) calcd for $C_{18}H_{15}O_3$ (P + H) 279.1021, found 279.0994.

10-(4-(3,4-Dihydro-2-oxofuran-4-yl))-9(10*H*)-anthracenone (23). A pale yellow solution of anthrone (374 mg, 1.93 mmol), 2-butenolide (163 mg, 1.94 mmol), and 0.10 mL of isopropylamine (1.17 mmol) in a solvent composed of 8 mL of methanol and 8 mL of THF was allowed to stand for 95 h. Vacuum removal of volatiles followed by chromatography (silica gel, CH_2Cl_2) gave 435 mg (81%) of a pale yellow solid: mp 154–158 °C; ^1H NMR δ 2.34 (m, 2 H), 2.81 (m, 1 H), 3.99 (d, 2 H, J = 8 Hz), 4.24 (d, 1 H, J = 6.5 Hz), 7.40 (d, 1 H, J = 7 Hz), 7.42 (d, 1 H, J = 8 Hz), 7.51, (t, 2 H, J = 7.5 Hz), 7.60 (t, 2 H, J = 7.5 Hz), and 8.26 ppm (app t, 2 H, J = 7 Hz); ^{13}C NMR (75 MHz) δ 30.18, 42.42, 43.97, 67.66, 124.07, 125.41, 125.49, 125.59, 125.69, 125.78, 130.15, 130.43, 130.56, 137.39, 138.52, 139.09, 172.83, and 181.94 ppm; MS 194 (20), 193 (100), 165 (20); IR (KBr) 3067 (m), 3004 (m), 2947 (m), 2920 (m), 2893 (m), 1770 (vs), 1661 (vs), 1599 (s), 1461 (m), 1322 (s), 1178 (s), 1015 (s) cm^{-1}; MS (CI) calcd for $C_{18}H_{14}O_3$ 278.0943, found 278.0934.

2-Methyl-3a,4,9,9a-tetrahydro-4,5,12-trihydroxy-4,9-[1′,2′]-benzeno-1*H*-benz[*f*]isoindole-1,3(2*H*)-dione (27). A pale yellow solution of dithranol (95 mg, 0.42 mmol) and NMM (47 mg, 0.42 mmol) in 8 mL of THF was stirred at room temperature for 4 days. The solvent was then vacuum evaporated, and the residue was recrystallized from $CHCl_3$ to yield 140 mg (99%) of colorless solid: mp 221–223 °C dec; ^1H NMR (acetone-d_6) δ 2.47 (s, 3 H), 3.30 (dd, 1 H, J = 9, 3.5 Hz), 3.49 (d, 1 H, J = 9 Hz), 4.58 (d, 1 H, J = 3.5 Hz), 6.66 (app t, 2 H, J = 7.5 Hz), 6.78 (d, 1 H, J = 7 Hz), 6.99 (m, 2 H), 7.06 (m, 1 H), and 9.50 ppm (br s); ^{13}C NMR δ 25.59, 44.59, 47.01, 51.65, 68.00, 115.84, 116.07, 116.15, 117.12, 122.18, 124.17, 128.77, 128.98, 137.97, 140.51, 152.60,

(33) Meek, J. S.; Evans, W. B.; Godefroi, V.; Benson, W. R.; Wilcox, M. F.; Clark, W. G.; Tiedeman, T. *J. Org. Chem.* **1961**, *26*, 4281.

152.98, 176.10, and 176.83 ppm; MS (CI): 339 (P + H, 3.7), 338 (13.5), 255 (18), 228 (14), 227 (90), 226 (23), 112 (100); IR ($CHCl_3$): 3380 (br, m), 3022 (vs), 2985 (s), 2890 (w), 2404 (m), 1692 (s), 1597 (m), 1435 (m), 1209 (br, s), 1048 (m) cm^{-1}; MS (CI) calcd for $C_{19}H_{16}NO_5$ (P + H): 338.1029. Found: 338.1034.

1,8-Dihydroxy-10-(1-methyl-2,5-dioxopyrrolidin-3-yl)-9-(10*H*)-anthracenone (28). A brown color developed immediately when triethylamine (1.0 mL, 7.2 mmol) was added to a pale yellow solution of dithranol (151 mg, 0.668 mmol) and NMM (75 mg, 0.68 mmol) in 7 mL of THF. After 0.5 h the volatiles were vacuum evaporated, and the residue was purified by chromatography (silica gel, CH_2Cl_2) to give 219 mg (97%) of a pale yellow solid: mp 235–237 °C; ^1H NMR δ 2.01 (dd, 1 H, J = 18.5, 5 Hz), 2.33 (dd, 1 H, J = 18.5, 9 Hz), 2.89 (s, 3 H), 3.33 (m, 1 H), 5.10 (d, 1 H, J = 3 Hz), 6.83 (d, 1 H, J = 7.5 Hz), 6.96 (m, 2 H), 7.03 (d, 1 H, J = 7.5 Hz), 7.42 (t, 1 H, J = 8 Hz), and 7.56 ppm (t, 1 H, J = 8 Hz); ^{13}C NMR δ 24.85, 29.21, 41.91, 51.30, 116.91, 117.85, 118.64, 118.74, 136.65, 137.22, 139.71, 144.03, 162.94, 163.16, 175.00, 177.41, and 193.15 ppm; MS (CI) 338 (P, 79), 255 (11), 241 (12), 227 (44), 226 (20), 225 (41), 114 (100), 112 (31); IR ($CHCl_3$) 3030 (vs), 1707 (vs), 1638 (m), 1619 (m), 1609 (s), 1453 (m), 1285 (m), 1220 (br, s) cm^{-1}; MS (CI) calcd for $C_{19}H_{16}NO_5$ (P + H): 338.1029. Found: 338.1050.

Preparation of 28-*d*. Dithranol-d_4 (**24-*d***) was prepared by treating a solution of dithranol (304 mg, 1.35 mmol) in 4 mL of THF with 4 mL of D_2O (99.5+ %, 221 mmol), followed by 1 mL of Et_3N. This deep red-brown mixture was stirred for 15 min, and then volatiles were removed under vacuum. A ca. 10-mg sample was taken for ^1H NMR analysis. By integration it was found to contain ≥98% D at each of the C-10 and hydroxylic oxygens. This product was taken up in 12 mL of THF and 148 mg (1.33 mmol) of NMM was added. The clear tan solution was treated with 0.2 mL of Et_3N, which caused a dark brown color to form. Volatiles were vacuum evaporated after 12 min (aliquot) and 1 h (bulk), and the residues were found to have identical NMR spectra.

Deuterium content of **28-*d*** was measured by integration of the ^1H NMR spectrum, as follows. Identification of proton position is based on J values, as reported above for **28**. For **28-*d***, the absorptions centered at ca. 2.0 and 3.3 each had total integrals which were $^1/_3$ that of the NMe integral at 2.89 ppm, indicating that no deuterium had been incorporated into the cis (to anthracene) and methine positions of the succinimide ring. The dd at 2.33 integrated for 0.22 H, and retained its sharp structure, suggesting that it arises from completely undeuterated (succinimide ring) material. The 2.0 dd retained its downfield pair in equal magnitude (0.11 H), while the upfield pair (0.11 H inferred) fell under a new absorption, the m attributed to (C*H*D, 0.78 H).

10-(1,2-Dicyanoethyl)-1,8-dihydroxy-9(10*H*)-anthracenone (29). A clear yellow solution of dithranol (231 mg, 1.02 mmol) and fumaronitrile (81 mg, 1.04 mmol) in 10 mL of THF was treated with 0.10 mL of Et_3N, which caused the mixture to turn dark brown. After 7 h the volatiles were removed, and the residue was chromatographed as above to yield 312 mg (98%) of a yellow solid: mp 226–228 °C; ^1H NMR δ 2.52 (m, 2 H), 3.28 (m, 1 H), 4.56 (d, 1 H, J = 4.5 Hz), 6.99 (d, 1 H, J = 7.5 Hz), 7.09 (m, 3 H), 7.60 (ca. t, 2 H, J = 8 Hz), 12.03 (s, 1 H), and 12.06 ppm (s, 1 H); ^{13}C NMR (75 MHz) δ 15.94, 37.44, 41.14, 116.34, 116.43, 116.51, 116.88, 117.01, 117.14, 119.23, 134.33, and 134.66 ppm; MS 304 (P, 8), 226 (20), 225 (100), 197 (23); IR (KBr) 3065 (m), 2980 (m), 2945 (m), 2252 (m), 1605 (vs), 1487 (s), 1450 (vs), 1425 (s), 1375 (s), 1270 (s), 1225 (s), 1178 (s), 1160 (s) cm^{-1}; MS calcd for $C_{18}H_{12}N_2O_3$ 304.0857, found 304.0847.

1,8-Dihydroxy-10-(1,2-bis(methoxycarbonyl)ethyl)-9-(10*H*)-anthracenone (30). A dark orange brown solution of dithranol (235 mg, 1.04 mmol), dimethyl fumarate (150 mg, 1.04 mmol), and 0.10 mL of Et_3N in 10 mL of THF was allowed to stand for 8 h. The usual removal of solvent and chromatography gave 304 mg (79%) of a pale yellow solid: mp 137–138 °C; ^1H NMR δ 1.96 (dd, 1 H, J = 17, 4 Hz), 2.26 (dd, 1 H, J = 17, 10.5 Hz), 3.35 (m, 1 H), 3.54 (s, 3 H), 3.73 (s, 3 H), 4.78 (d, 1 H, J = 4 Hz), 6.66 (d, 1 H, J = 7.5 Hz), 6.94 (m, 2 H), 7.01 (d, 1 H, J = 7.5 Hz), 7.44 (t, 1 H, J = 8 Hz), 7.52 (t, 1 H, J = 7.5 Hz), 12.07 (s, 1 H), and 12.11 ppm (s, 1 H); ^{13}C NMR (75 MHz) δ 28.03, 41.53, 41.65, 49.58, 49.70, 113.43, 113.54, 114.44, 114.82, 116.25, 116.80, 133.96, 134.33, 139.15, 141.13, 160.14, 160.51, 169.35, 169.72, and 190.78 ppm; MS 370 (P, 7), 279 (21), 225 (100), 197 (30), 151 (12); IR ($CHCl_3$) 3027 (m), 2960 (m), 1755 (s), 1603 (s), 1560 (m), 1477 (s), 1200 (br, s) cm^{-1}; MS calcd for $C_{19}H_{15}O_6$ (P–OMe) 339.0869, found 339.0840.

1,8-Dihydroxy-10-(2-(methoxycarbonyl)ethyl)-9(10*H*)-anthracenone (31). Isopropylamine (0.10 mL, 1.17 mmol) was added to a pale yellow solution of dithranol (134 mg, 0.60 mmol) and 0.055 mL of methyl acrylate (0.61 mmol) in 5 mL of THF, whereupon the solution became bright red-orange, changing to brown in a short time. After 1 h the solvent was removed, and the residue was chromatographed as above to give 156 mg (84%) of pale yellow solid: mp 162.5–164 °C; ^1H NMR δ 1.96 (AA′ m, ca. t, 2 H, J = 8 Hz), 2.24 (m, 2 H), 3.56 (s, 3 H), 4.34 (t, 1 H, J = 5.5 Hz), 6.92 (d, 4 H, J = 8 Hz), 7.51 (t, 2 H, J = 8 Hz), and 12.20 ppm (s, 2 H); ^{13}C NMR δ 29.13, 37.75, 41.84, 51.64, 116.18, 118.89, 136.54, 141.07, 145.52, 162.87, and 193.46 ppm; MS 312 (P, 48), 281 (19), 280 (25), 238 (99), 225 (100), 197 (54), 151 (24); MS (CI) calcd for $C_{18}H_{16}O_5$ 312.0997, found 312.0985.

1,8-Dihydroxy-10-(3,4-dihydro-2-oxofuran-4-yl)-9(10*H*)-anthracenone (32). A solution of dithranol (224 mg, 0.99 mmol), butenolide (83 mg, 0.99 mmol), and 0.10 mL of isopropylamine in 10 mL of THF was vacuum evaporated after standing for 5 h. The usual chromatography afforded 279 mg (91%) of a pale yellow solid: mp 224–226 °C; ^1H NMR δ 2.36 (m, 2 H), 2.73 (m, 1 H), 4.01 (m, 2 H), 4.11 (d, 1 H, J = 7 Hz), 6.83 (d, 1 H, J = 7.5 Hz), 6.86 (d, 1 H, J = 7.5 Hz), 6.98 (m, 2 H), 7.50 (m, 2 H), and 12.00 ppm (s, 2 H); ^{13}C NMR (75 MHz) δ 30.33, 43.27, 44.35, 67.71, 115.01, 115.17, 116.39, 116.52, 133.96, 134.10, 139.98, 140.64, 160.73, 160.91, 172.67, and 190.56 ppm; MS 310 (P, 5), 226 (24), 225 (100), 197 (26), 151 (10); IR (KBr) 3018 (w), 3000 (m), 2982 (w), 2904 (m), 1778 (vs), 1602 (vs), 1574 (m), 1480 (s), 1449 (s), 1282 (s), 1231 (s), 1030 (m) cm^{-1}; MS calcd for $C_{18}H_{14}O_5$ 310.0841, found 310.0827.

Acknowledgment. Support by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. **4**, 118494-67-0; **5a**, 125353-69-7; **9**, 118494-66-9; **9-*d***, 125249-97-0; **9-*d*** (deuterated), 125280-83-3; **10**, 125249-98-1; **10-*d***, 125250-05-7; *trans*-**10-*d***, 125250-13-7; *cis*-**10-*d***, 125250-14-8; **11**, 3073-99-2; *endo*-**12**, 125353-70-0; *exo*-**12**, 118494-69-2; **13**, 125249-99-2; **14**, 125250-00-2; **15**, 125250-01-3; **16**, 125250-02-4; **17**, 125250-03-5; **18**, 125280-81-1; **19**, 125250-04-6; **20**, 100434-12-6; **22**, 125250-06-8; **23**, 125250-07-9; **24-*d***, 125250-12-6; **27**, 93960-74-8; **28**, 125250-08-0; **28-*d***, 125280-82-2; **29**, 125250-09-1; **30**, 83201-02-9; **31**, 125250-10-4; **32**, 125250-11-5; NMM, 930-88-1; (*E*)-MeOCOCH=CHCO$_2$Me, 624-49-7; H$_2$C=CHCO$_2$Me, 96-33-3; fumaronitrile, 764-42-1; anthrone, 90-44-8; dithranol, 1143-38-0; maleonitrile, 109-77-3; 2-butenolide, 497-23-4.

Supplementary Material Available: ^1H NMR spectra of **4** and **5a**/**5b** and ^{13}C NMR spectra of **9**, **10**, **13–20**, **22**, **23**, **27–32** (21 pages). Ordering information is given on any current masthead page.