and adsorbed on a short column of Florisil. Elution with hexane–benzene (1:1) gave an additional crop of **9a** (318 mg) recrystallized from methanol to provide **9a** (224 mg), mp 91–92 °C (27.8%).

Benzo[*c*]phenanthrene. (a) From 1,2-dihydro-BcP. Dehydrogenation of **9a** (230 mg, 1 mmol) was carried out with DDQ (227 mg, 1 mmol) in refluxing benzene (10 mL). Separation of the hydroquinone was almost instantaneous. After 10 min, the mixture was cooled, the hydroquinone was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in hexane–benzene (1:1) and filtered through a short column of Florisil eluted with the same solvent mixture. The product was crystallized from hexane–ethanol to provide BcP (139 mg, 61%): mp 66.5–67.5 °C (lit.[11] mp 68 °C); second crop 33 mg (14.5%), mp 64–66 °C.

(b) From 7. To a stirred solution of **7** (497 mg, 2 mmol) in methanol (50 ml) was added $NaBH_4$ (152 mg, 4 mmol) in portions over 25 min. The usual workup gave 4-hydroxy-1,2,3,4,5,6-hexahydrobenzo[c]phenanthrene (**10**) (497 mg, mp 139.5–140 °C). A mixture of **10** (250 mg) and 10% Pd–C catalyst was heated in an oil bath at 285 °C for 1 h. The usual workup and filtration through a short column of Florisil gave an oil (200 mg) which crystallized from hexane–ethanol to afford pure BcP (129 mg): mp 67–67.5 °C; second crop (29 mg), mp 66–67 °C (69% yield).

4-Hydroxybenzo[*c*]phenanthrene Acetate (11a). A solution of **8** (246 mg, 1 mmol), *p*-tosic acid (20 mg) in 12.5 mL of isopropenyl acetate, and 2.5 mL of acetic anhydride was heated at reflux for 16 h. The solution was cooled and stirred with ice–water for 30 min, and the mixture was extracted twice with ether. Conventional workup gave a residue which was dissolved in minimal benzene, adsorbed on 6 g of Florisil, and eluted with benzene to afford the enol acetate **9b** (228 mg, 100%) as yellow crystals.

The enol acetate was heated at reflux with DDQ (227 mg, 1 mmol) in 10 mL of anhydrous benzene for 15 min. The mixture was cooled, and the hydroquinone was filtered and washed with benzene. The filtrate was concentrated and chromatographed on a column of 6 g of Florisil. Elution with benzene afforded a crystalline residue of **11a** (208 mg). Recrystallization from methanol gave pure **11a** (137 mg, 47.9%), mp 126–127 °C, and a second crop of 49 mg (17%), mp 124–126.5 °C: NMR δ 9.18 and 9.02 (apparent d, 2, H_1 and H_{12}), 7.20–8.07 (m, 9, aryl), 2.48 (s, 3, CH_3).

(11) Cook, J. W. *J. Chem. Soc.* **1931**, 2524.

4-Hydroxybenzo[*c*]phenanthrene (11b). A solution of **11a** (100 mg) in 20 mL of methanol and 0.4 mL of concentrated HCl was allowed to stand for 24 h at room temperature under argon. The usual workup gave a tan, crystalline residue which was dissolved in a small amount of benzene and passed through a short column of Florisil eluted with benzene. The crystalline product (87 mg) was recrystallized from hexane to afford **11b** (71 mg, 82.7%), mp 112.5–113 °C (lit.[8] mp 110–111 °C); a second crop (5 mg, 5.8%) melted at 111–112 °C.

3-Oxo-1,2,3,4-tetrahydrobenzo[*c*]phenanthrene (12). To a solution of **9a** (430 mg, 1.87 mmol) in CH_2Cl_2 (43 mL) were added *m*-chloroperoxybenzoic acid (430 mg, 2.39 mmol) and a solution of 430 mg of $NaHCO_3$ in 20 mL of water. The mixture was stirred for 4 h, and then the organic layer was separated, washed with 5% Na_2CO_3 solution, and dried. Evaporation of the solvent under reduced pressure, avoiding heating, gave the crude epoxide which was dissolved in anhydrous tetrahydrofuran (40 mL) and diluted with 20 mL of anhydrous ether. To this solution was added 0.8 mL of BF_3 etherate. After 2 min, the reaction was quenched and worked up in the usual manner to furnish an oily residue. Crystallization from ether gave **12** (343 mg), mp 106–112 °C. Recrystallization from methanol afforded pure **12** (212 mg, 46%): mp 115–117 °C; NMR δ 7.28–8.54 (m, 8, aryl), 3.91 (t, 2, H_1), 3.8 (s, 2, H_4), 2.48 (t, 2, H_2).

3-Hydroxybenzo[*c*]phenanthrene Acetate (13a). Reaction of **12** (209 mg, 0.85 mmol) with isopropenyl acetate (10 mL), acetic anhydride (2 mL), and *p*-tosic acid (20 mg) was carried out by the procedure for the analogous reaction of **8** to afford the corresponding enol acetate. The latter (241 mg, 0.84 mmol) was dissolved in 10 mL of dry benzene, DDQ (191 mg, 0.84 mmol) was added, and the solution was heated to reflux for 15 min under argon. The usual workup gave 236 mg of an oil which crystallized from ether–hexane to give **13a** (178 mg, 73%), mp 126.5–127.5 °C, and 8 mg (3.3%), mp 124–125 °C; recrystallization from methanol raised the melting point to 127–128 °C: NMR δ 7.31–9.20 (m, 11), 2.37 (s, 3, CH_3).

3-Hydroxybenzo[*c*]phenanthrene (13b). Treatment of **13a** (100 mg) in 20 mL of methanol with 0.4 mL of concentrated HCl for 24 h, following the usual workup, gave **13b** (86 mg). Recrystallization from ether–hexane furnished **13b** (66 mg, 77%), mp 113–114 °C, and 12 mg (14%), mp 112–114 °C (lit.[8] mp 112–113 °C).

Acknowledgment. This research was supported by a grant (CA 11968) from the National Cancer Institute, USPHS.

Regioselective Alkylation of Anthrahydroquinone and Anthrone in Water with Quinonemethides and Other Alkylating Agents

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Anthrahydroquinone (AHQ) and anthrone are alkylated in the C_{10} position by quinonemethides, generated in situ from *p*-acetoxybenzyl chlorides, to give adducts **13–15, 24, 25, 28, 29,** and **32.** Aqueous alkylations of AHQ with methyl vinyl ketone, cinnamaldehyde, and benzyl chloride also produces C_{10}-substituted 10-hydroxyanthrones. Simple ketones and aldehydes do not, however, alkylate AHQ in aqueous alkali.

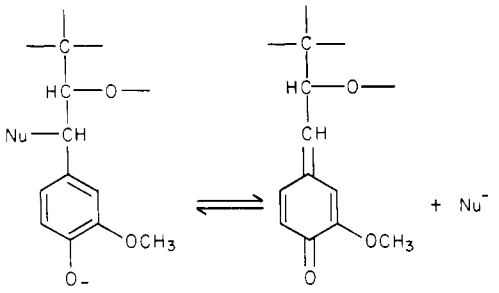
A critical step in the making of paper from wood by an alkaline pulping process is the efficient removal of one wood component, lignin, without destroying too much of the valuable component, cellulose.[1] Addition of catalytic amounts of anthraquinone (AQ) to alkaline pulping systems causes an acceleration in the rate at which lignin is removed, while increasing the yield of pulp.[2] Considerable interest has developed in the mechanism of how AQ achieves this desirable selectivity.

(1) J. P. Casey, "Pulp and Paper Chemistry and Chemical Technology", 3rd ed., Vol. I, Wiley-Interscience, New York, 1980.

(2) H. H. Holton, *Pulp Paper Can.*, **78**, T218 (1977).

0022-3263/82/1947-0022$01.25/0

During typical alkaline pulping reactions, performed at 170 °C in water, some units of the lignin polymer are believed to form quinonemethides.[3] These lignin quinonemethides (QMs) should be very short lived, due to reactions with nucleophiles in the medium (eq 1); however, they are still considered to be key intermediates in most lignin reactions.[1,3]



(1)

The reactions of anthrone and anthrahydroquinone dianion (AHQ^{2-}), the reduced ionized form of AQ, with several substrates, including some QMs, is the subject of this report. The work was initiated in an attempt to understand the chemistry of alkaline pulping systems containing anthraquinone; the findings, however, may have implications in several other areas of organic chemistry.

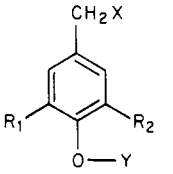
Results and Discussion

Quinonemethides. Quinonemethides, even at room temperature, are quite reactive species and are, therefore, generated in situ. The most ideal QM precursor would be a *p*-hydroxybenzyl chloride, which when treated with base would liberate a QM. However, these compounds are also not very stable. For example, *p*-acetoxybenzyl chloride (**1**),[4] upon treatment with acidic methanol, gave ether **4** rather than the desired transesterification product **5**. The reaction was followed by ^1H NMR and gave no evidence of **5** or an intermediate methoxy acetate **6**; presumedly the hydrolysis of **1** was rapidly followed by dehydrohalogenation to give a quinonemethide (**9**) and the latter was rapidly captured by solvent.

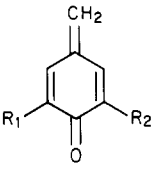
Treatment of **3**[4] with pyridine gave a salt **12**. The salt could be recrystallized from warm water but was unstable in either refluxing methanol or aqueous hydroxide, giving rise to **7** and **8**, respectively. Consequently, the salt looked to be an ideal candidate for generating a quinonemethide without the interference of a nucleophilic base in the system. Other potential QM precursors were **1–3**.

Anthrahydroquinone Dianion. Both AHQ and AHQ^{2-} are rapidly oxidized by air to AQ, and consequently their preparation and handling was done in a pure nitrogen atmosphere. The dianion, which is deep red in color, was made by treating AQ with sodium dithionite in aqueous alkali.[5] Acidification of the solution gave AHQ, a light-green, water-insoluble solid. The excess dithionite and inorganic salts were washed away by repeated filtrations under nitrogen. Addition of alkali regenerated the red colored AHQ^{2-}. Anhydrous AHQ was obtained by vacuum evaporation of the washed AHQ.

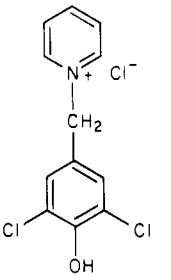
QM + AHQ^{2-} Reactions. In an attempt to avoid complications due to competing nucleophiles, we first examined the reaction of pyridine salt **12** with anhydrous AHQ in the presence of dioxane and a trace of pyridine.



1, X = Cl; Y = Ac; $R_1 = R_2$ = H
2, X = Cl; Y = Ac; R_1 = H; R_2 = OMe
3, X = Cl; Y = H; $R_1 = R_2$ = Cl
4, X = OMe; Y = H; $R_1 = R_2$ = H
5, X = Cl; Y = H; $R_1 = R_2$ = H
6, X = OMe; Y = Ac; $R_1 = R_2$ = H
7, X = OMe; Y = H; $R_1 = R_2$ = Cl
8, X = OH; Y = H; $R_1 = R_2$ = Cl
19, X = OH; Y = H; $R_1 = R_2$ = H
20, X = OH; Y = H; R_1 = H; R_2 = OMe



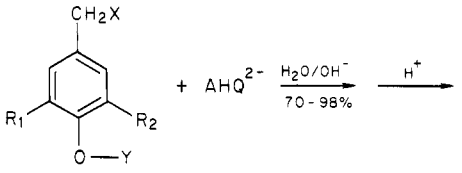
9, $R_1 = R_2$ = H
10, R_1 = H; R_2 = OMe
11, $R_1 = R_2$ = Cl

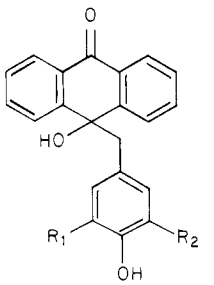


12

Workup of the reaction provided only recovered salt **12** and AQ (from AHQ and air). The lack of reaction may have been due to the insolubility of salt **12** in dioxane, the inability of the salt to enter into an equilibrium which generates QM (and pyridine hydrochloride), or to a low reactivity of nonionic AHQ. Interestingly, the salt **12**, when added to an aqueous solution of AHQ^{2-}, rapidly discharged the red color. A product was isolated in good yield, which was not the salt's hydrolysis product **8** but, when subjected to gas chromatography, gave rise to **8** and AQ.

This observation led us to examine the reactions of chloro acetate **1** and **2** with AHQ^{2-}. The reactions were conducted in aqueous alkali, where the chloro acetates would be expected to hydrolyze to quinonemethides **9** and **10**, respectively. Surprisingly, high yields of 1:1 addition products of QM, and AHQ, and henceforth referred to as QM·AHQ adducts, were isolated. The equation describing these reactions is given by eq 2; the starting materials were **1–3** and **12**.





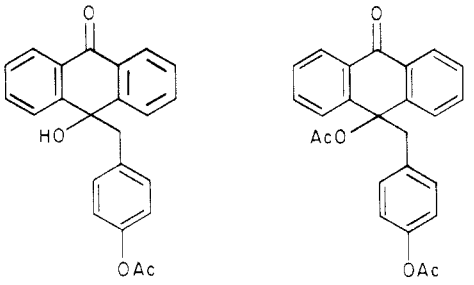
(2)

13, $R_1 = R_2$ = H
14, R_1 = H; R_2 = OMe
15, $R_1 = R_2$ = Cl

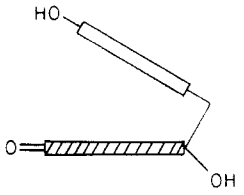
Structure Proof of QM·AHQ Adducts. The proof of structures for adducts **13–15** was based on elemental analysis and spectral data for the three compounds and

(3) J. Martin in "Lignins", K. V. Sarkanen and C. H. Ludwig, Ed., Wiley-Interscience, New York, 1971, Chapter 16.
(4) L. D. Taylor, J. M. Grasshoff, and M. Pluhar, *J. Org. Chem.*, 43, 1197 (1978).
(5) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed., Wiley-Interscience, New York, 1966, p 551.

two derivatives of adduct **13**. The infrared spectra, for example, clearly indicated the presence of hydroxyl and diaryl ketone functional groups. Acylation of **13** under mild conditions gave a monoacetate (**16**); more strenuous conditions gave a diacetate (**17**).



16 **17**



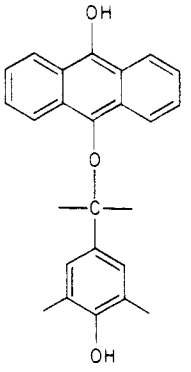
18

A detailed analysis of the ^1H and ^{13}C NMR spectra[6] of the adducts and the two acetate derivatives strongly indicated that the structure of the adducts was that of a 10-benzyl-10-hydroxyanthrone. Run in Me_2SO as the solvent,[7] the adduct ^1H NMR spectra displayed hydroxyl signals at δ 8.5–9.7 (phenolic) and δ 6.4–6.5 (dibenzylic), both of which exchange with addition of D_2O. The ^{13}C NMR spectra show only two aliphatic signals, a singlet at about 73 ppm and a triplet at about 55 ppm. The spectral evidence suggests that the adducts exist at least partially in folded over conformations, such as **18**.

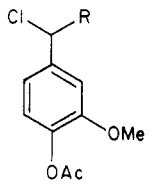
Other QM·AHQ Reactions. An interesting feature of the adduct formation reactions was that yields were so high, considering the side reactions that are available to the *p*-hydroxy- or *p*-acetoxybenzyl chlorides and proposed quinonemethide components. All of these would be expected to hydrolyze rapidly in an aqueous alkaline medium to give *p*-hydroxybenzyl alcohols.[8-10] As an example, the half-life of a simple substituted quinonemethide in neutral methanol at 25 °C is reported[8] to be 17 s. Apparently, the reactions between AHQ^{2-} and simple QMs are very fast.

Adduct formation was poor when benzyl alcohols were used as precursors of quinonemethides. Both *p*-hydroxybenzyl alcohol (**19**) and vanillyl alcohol (**20**) produced adducts (**13** and **14**) when reacted with AHQ^{2-} at 60 °C, but the yields were only about 2%; the major products were phenolic condensation products.[11] The poor yields in these cases could be due to: (a) poor QM generation, since in basic media chloride ion is a better leaving group than hydroxide ion, (b) a greater reactivity between the QMs and phenolate ions in solution, as compared to AHQ^{2-}, and (c) instability of the adducts, which allows the more stable condensation products to build. Concerning this latter point, evidence exists that the adducts enter into an equilibrium with their constituent parts, AHQ and QM, at temperatures of 60 °C and above.[11]

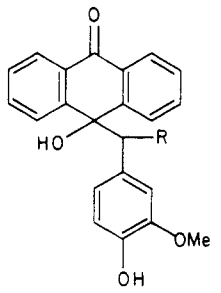
The three adducts discussed so far are all C_{10} alkylated anthrone derivatives. The dianion of AHQ has several resonance forms; why didn't alkylation occur at one of these other sites? Could conditions be set up to promote O-alkylation to give an adduct such as **21**? The reaction of chloro acetate **1** with AHQ^{2-} has been done in several different ways, such as a solvent system of 50% aqueous dioxane and reaction times of 1 min, and only adduct **13** was obtained (yields > 90%).



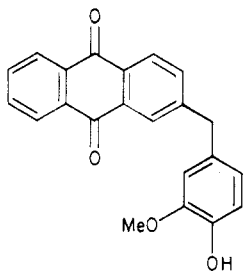
21



22, R = Me
23, R = Et



24, R = Me
25, R = Et



26

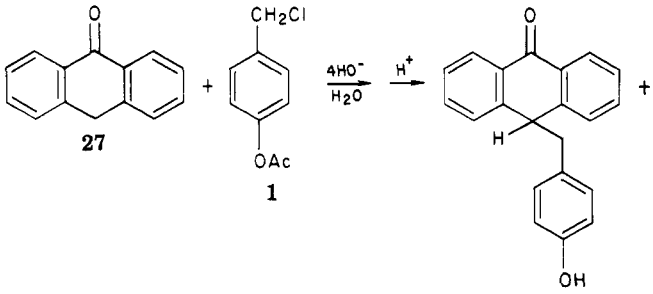
The reactions of somewhat hindered chloro acetates **22** and **23** with AHQ^{2-} gave adducts **24** (18%) and **25** (25%), respectively. The low yields appeared to be due to competing reactions which generate phenolic styrenes and polymers thereof. There was no indication of O-alkylated products, such as **21**, in the NMR spectra of the crude product mixtures. Consequently, even somewhat hindered alkylating agents still gave C_{10} alkylation. Crude calculations, based on bond strength and resonance energy data, indicate that a C_{10}-alkylated product should be about 23 kcal/mol more stable than an O-alkylated AHQ derivative.

Alkylation of AHQ^{2-} at one of the two side rings should have a higher activation energy than alkylation at C_{10} since some aromaticity must be lost during the process. However, if the alkylation reactions are reversible, side-ring alkylation may occur under more strenuous conditions, giving rise to a more stable type of product. This fact may account for the appearance of 2-vanillylanthraquinone (**26**) in wood pulping liquors[12] and alkaline vanillyl alcohol cooks done at 173 °C in the presence of AQ.[11]

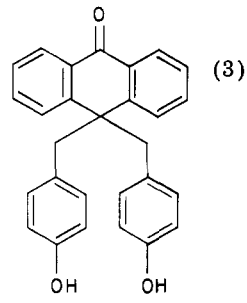
Anthrone and Quinonemethide Reactions. Alkylation of anthrone (**27**) with chloro acetate **1** in aqueous dioxane containing sodium hydroxide gave a mixture of mono- and dialkylated products **28** and **29** (eq 3). Even though a 1:1 ratio of reactants was used, more dialkylated product was formed than monoalkylated product. Apparently, the monoalkylated material is more reactive toward the alkylating agent than is anthrone. Treating an-

(6) D. R. Dimmel, accompanying article in this issue.
(7) R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds," 3rd ed., Wiley, New York, 1974, p 175.
(8) L. J. Filar, and S. Winstein, *Tetradhedron Lett.*, 9 (1960).
(9) G. Leary and W. Thomas, *Tetrahedron Lett.*, 3631 (1975).
(10) G. Leary, I. J. Miller, W. Thomas, and A. D. Woolhouse, *J. Chem. Soc., Perkin Trans. 2*, 1737 (1977).
(11) D. R. Dimmel and D. Shepard, *J. Wood. Chem. Technol.*, submitted for publication.
(12) T. J. Fullerton and B. I. Fleming, *Sven. Papperstidn.*, **83**, 396 (1980).

throne with 2 equiv of 1 gave **29** in high yield.

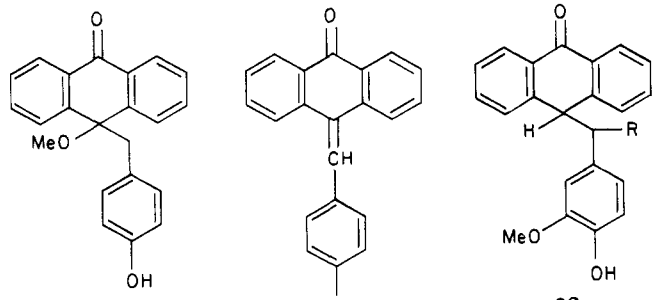


27 1 28



29 (3)

Two other compounds also isolated from the reaction outlined by eq 3 were anthraquinone and methoxy adduct **30**. The production of AQ was a result of the workup procedure employed. The alkaline solution was exposed to air at the end of the reaction period to precipitate the anthrone as AQ; filtration and acidification afforded the products. No AQ was produced if the workup was done in a pure nitrogen atmosphere. There is ample literature supporting the autoxidation of anthrone in an alkaline medium to give AQ.[13]

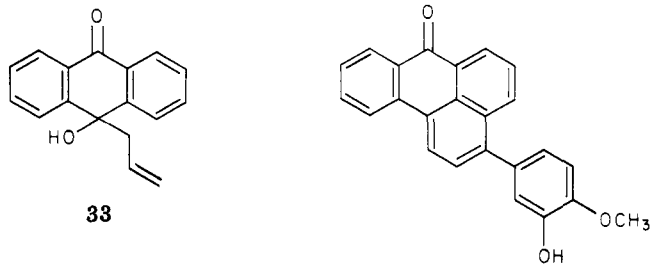


30 31 32

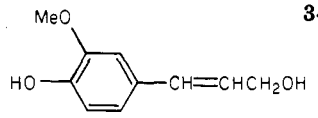
The methoxy adduct **30** was assumed to arise from an autoxidation of **28** before or during attempted methanol recrystallization of the product mixture. Adduct **13** is not a source of **30** since recrystallization of **13** from methanol gave no methanol incorporation. Quinonemethide **31** is also not a logical precursor of **30** since methanol would be expected to add to the methine carbon. Compound **31** was produced from adduct **13** by dehydration with an acid catalyst; it showed no unusual upfield shifts in its NMR spectrum and was surprisingly stable to nucleophiles—it was recrystallized from Me_2SO/water.

All indications are that monoalkylated anthrone adduct **28** is a sensitive compound. It was isolated in poor yield after several column chromatographies. It decomposed on attempted derivatization with dimethyl sulfate in alkaline THF. In contrast, alkylation of anthrone with a slightly bulkier reagent **22** afforded a monoalkylated product **32** (R = Me) which was easy to handle. Treating anthrone with 2 equiv of **21** still yields only monoalkylated product. Apparently the formation of dialkylated product is inhibited for steric reasons.

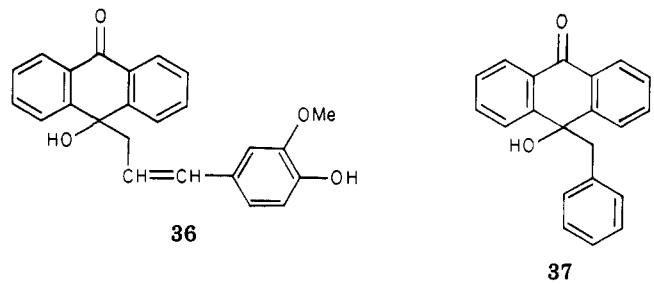
Other Reactions of AHQ^{2-}. Deshpande[14] reported in 1978 that AHQ^{2-} reacts with allyl bromide to give a C-alkylated product **33**. Recently, Fullerton and Ahern[15] have reported that **34**, which has been isolated from pulping liquors,[15,16] can be obtained from the reaction of coniferyl alcohol **35** with AQ/glucose; presumably, the C-alkylated derivative **36** is an intermediate in this reaction. We have alkylated AHQ^{2-} with benzyl chloride and obtained a 60% yield of C-alkylated product **37**.



33 34



35



36 37

In the pulping of wood a great variety of different organic compounds can be generated, i.e., aromatic ketones and cinnamaldehyde structures from lignin, aliphatic ketones from carbohydrates, etc. Gratzl and co-workers have proposed that AHQ^{2-} may add to lignin carbonyl groups and subsequently cause the fragmentation of lignin.[17] It is important to establish what kind of substrates could interact with AHQ dianion, from the points of view of defining potential pathways by which AQ is lost during pulping and of defining the synthetic utility of AHQ alkylations.

The addition of AHQ^{2-} to a QM is formally a Michael reaction. Other Michael acceptors, which were examined, were methyl vinyl ketone (**38**) and cinnamaldehyde (**39**); adducts **40** (54%) and **41** (40%) were obtained, respectively. On the basis of spectral evidence,[6] the methyl vinyl ketone adduct exists as an open structure (**40A**), while the cinnamaldehyde adduct exists as a mixture of stereoisomers having a closed structure (**41B**).

No trace of adducts was observed when AHQ^{2-} was reacted with either acetone (CH_3COCH_3), benzaldehyde (PhCHO), acetovanillone (4-OH-3-OMe-$PhCOCH_3$), ben-

(13) G. A. Russell et al. and Hawthorne et al. in "Oxidation of Organic Compounds", Vol. 1, American Chemical Society, Washington, DC, 1968, Adv. Chem. Ser. No. 75, pp 184, 203–215.

(14) R. J. Deshpande, *Indian J. Chem.*, **16B**, 389 (1978).

(15) T. J. Fullerton and S. P. Ahern, *J. Chem. Soc., Chem. Commun.*, 457 (1979).

(16) D. W. Cameron and E. L. Samuel, *Tetrahedron Lett.*, 3035 (1979).

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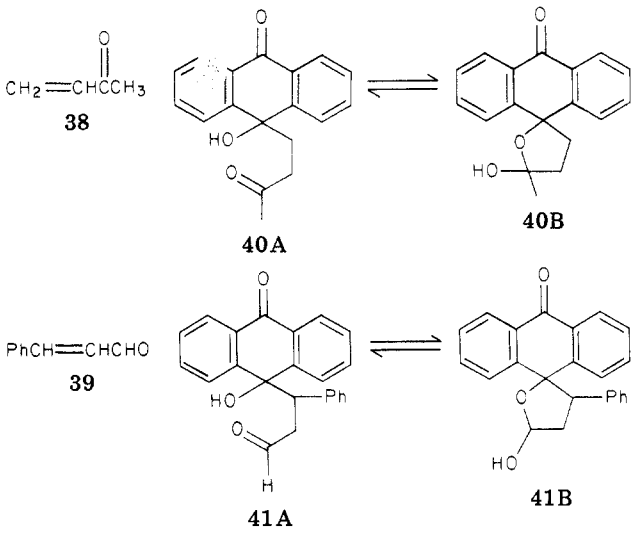


zophenone (PhCOPh), anthrone (**27**), or ferulic acid (4-OH-3-OMe-PhCH=CHCO$_2$H). In fact no reactions of any type were observed in these cases. Consequently, alkylation of AHQ^{2-} under these conditions by a simple ketone or aldehyde does not lead to a stable product. However, the treatment of tetrahydroanthraquinone with D-[1-^{14}C]glucose, a "simple" aldehyde, at 180 °C under slightly alkaline conditions gives a 20% yield of 10-[*methyl*-^{14}C]-anthrone.[18]

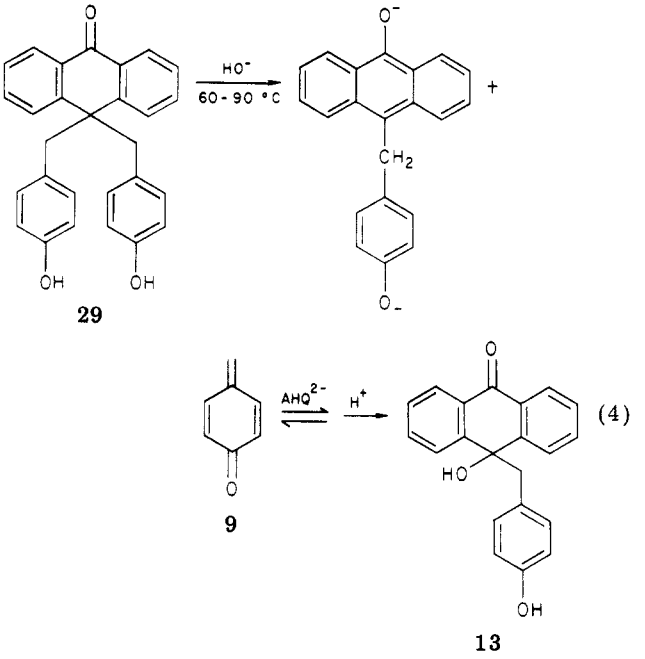
The alkylation of AHQ or anthrone anions by *p*-acetoxybenzyl chlorides was quite efficient. In light of the fact that benzyl chloride also alkylates AHQ dianion, what is the probability that the *p*-acetoxybenzyl chlorides are reacting as benzyl chlorides (S_N2 mechanism) rather than quinonemethides? Taylor claims that *p*-acetoxybenzyl chloride (**1**) reacts with heteroatom nucleophiles via a quinonemethide; this conclusion was reached by comparing the reactivity differences of **1** and *m*-acetoxybenzyl chloride, a compound which can not form a QM. We experienced considerable difficulty in preparing *m*-acetoxybenzyl chloride and, thus, were not able to make a similar comparison study.

Heating adducts of AHQ which have attached *p*-hydroxybenzyl groups above 60 °C in an alkaline medium leads to the production of AHQ dianion.[11] However, the simple benzyl adduct is stable to these conditions. Therefore, it was possible to demonstrate that quinonemethides, generated by adduct decomposition, could alkylate AHQ^{2-}; this is shown by the reaction outlined in eq 4, in which adduct **13** was formed by heating **29** in base at 100 °C in the presence of AHQ^{2-}.

Supporting evidence for the production of QM·AHQ adducts from QMs comes from the recent work of Landucci[19] and Fullerton.[20] Landucci generated ligninlike quinonemethides in solution and observed their UV spectra prior to reaction with AHQ^{2-} to give adducts. Fullerton and co-workers obtained adducts from the reaction of AHQ^{2-} with *tert*-butyl-stabilized QMs.

Conclusions

Anthrahydroquinone and anthrone readily undergo reactions with conjugated ketones and aldehydes, of which quinonemethides are an example, to give addition products at the C_{10} position. Simple nonconjugated carbonyl electrophiles do not give stable addition products with AHQ^{2-}.



Mechanisms involving adduct intermediates of lignin quinonemethides and AHQ have been put forth to explain how AHQ promotes lignin fragmentation reactions.[11,17,19,21,22]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 700 infrared spectrometer and standardized with polystyrene. The ultraviolet spectra were obtained with a Perkin-Elmer 576 ST spectrometer. A JEOL FX 100 spectrometer was used to obtain the NMR spectra. The NMR data for many of the compounds are reported in the accompanying paper[6] and will not be discussed here. The mass spectra were obtained with a Hewlett-Packard Model 5985 GC-MS spectrometer. Detailed analysis of the mass spectra of the adducts will be treated elsewhere and not be repeated here.[11] Elemental analyses were performed by Micro-Tech Laboratories, Skokie, IL.

Anthrahydroquinone. Anthraquinone was stirred in an aqueous solution of 1 equiv of sodium dithionite and 4 equiv of sodium hydroxide under nitrogen at 60 °C for 45 min. The red-colored solution was cooled, acidified with concentrated hydrochloric acid, and filtered by forcing the water out of the flask through a gas dispersion tube with nitrogen pressure. The resulting light-green AHQ was washed 2–3 times by adding water to the flask, stirring briefly, and filtering, as above. (This washing procedure was not necessary to obtain high yields of adducts from AHQ but did simplify the oxidative workup procedure employed in the alkylations.)

Anhydrous AHQ was obtained by warming the flask containing the wet AHQ with a heat gun while applying a vacuum. The vacuum was broken by bleeding in nitrogen. Subsequent reactions employed the same flask. Aqueous AHQ^{2-}, which is deep red in color, was obtained by adding water containing 4 equiv of sodium hydroxide to the dry AHQ.

General Alkylation Procedure. The alkylating agent was added directly (no solvent) to an aqueous alkaline solution of 1.3 equiv of AHQ^{2-} or anthrone monoanion (prepared from anthrone and excess sodium hydroxide), and the mixture was stirred for 1–3 h at 60 °C under nitrogen and cooled to room temperature. Stirring in air converted the excess AHQ^{2-} and anthrone to AQ,[11] which was then removed by filtration. The filtrate was acidified and the precipitated product collected (depending on its state) by filtration or ether extraction, followed by drying (Na_2SO_4) and

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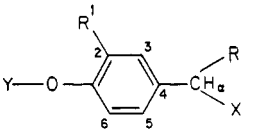
Table I. ^{1}H NMR Assignments and Elemental Analyses of Some Quinonemethide Precursors[a,b]



no.	solvent	X	Y	R	R^1	C-6	C-5	C-3	C-α	calcd (found)[e] % C	calcd (found)[e] % H
1	$CDCl_3$	Cl	$COCH_3$	H	H						
			2.27 (s)			7.05 (d)	7.38 (d)		4.51 (s)		
2	$CDCl_3$	Cl	$COCH_3$	H	OCH_3					55.94 (56.03)	5.13 (5.14)
			2.30 (s)		3.84 (s)	6.7-6.9 (m)			4.56 (s)		
4	$CDCl_3$	OCH_3	H	H	H						
		3.37 (s)	5.91 (s)			6.74 (d)	7.18 (d)		4.38 (s)		
	Me_2SO	OH	H	CH_3	OCH_3						
		4.94 (d)[c]	8.68 (s)	1.27 (d)	3.74 (s)	6.7-6.9 (m)			4.5 (d of q)[c]		
22	$CDCl_3$	Cl	$COCH_3$	CH_3	OCH_3					57.77 (58.18)	5.69 (5.87)
			2.25 (s)	1.80 (d)	3.79 (s)	7.07 (s)		7.22 (s)	5.23 (q)		
	$CDCl_3$	OH	H	CH_2CH_3	OCH_3						
		1.89 (s)	5.63 (s)	1.73 (m) 0.90 (t)	3.38 (s)	6.7-6.9 (m)			4.51 (t)		
23	$CDCl_3$	Cl	$COCH_3$	CH_2CH_3	OCH_3					59.38 (59.65)	6.19 (6.24)
			2.28 (s)	2.06 (p)[d] 1.00 (t)	3.81 (s)	6.9-7.0 (m)			4.74 (t)		

[a] Values are in δ units relative to Me_4Si = 0. [b] The coupling constants, J, were all in the 7-9 Hz range unless noted otherwise. [c] Doublet has J = 4 Hz. [d] p = pentet. [e] Analyses are only given for those compounds which have not been reported in the literature.

concentration. Product purification was generally accomplished by recrystallization.

4-Acetoxy-3-methoxybenzyl Chloride (2). The chloro acetate **2** was prepared (54.5% yield) from commerical vanillyl alcohol (Aldrich) according to the method of Taylor et al.[4] and recrystallized from hexane: mp 48–50 °C; IR (neat) 1790 cm^{-1} (carbonyl); NMR and elemental analysis (Table I).

Methanolysis of 4-Acetoxybenzyl Chloride (1). A solution of 1 g of the chloro acetate **1**[4] in 25 mL of anhydrous methanol, containing 1 drop of concentrated sulfuric acid, was stirred for 48 h at room temperature. The reaction mixture was poured into 150 mL of water and the water solution was extracted with ether (3 × 30 mL). The ether layer was separated and washed with water and dried over anhydrous Na_2SO_4, and the solvent was removed by evaporation in a nitrogen stream. The residue was a white crystalline material, mp 50–80 °C, showing no carbonyl absorption bands (IR) and a NMR spectrum ($CDCl_3$) showing the following: δ 2.18 (s, 1, ?), 3.37 (s, 3, OCH_3), 4.38 (s, 2, CH_2), 5.91 (s, 1, OH), 6.74 (d, 2, J = 8 Hz, 3,5-aryl protons), and 7.18 (d, 2, J = 8 Hz, 2,6-aryl protons).

This reaction was also performed in a NMR tube. The chloro acetate (90 mg) was weighed into the tube and a 1:4 mixture of Me_2SO-d_6 and methanol added. A small drop of concentrated H_2SO_4 was added, and spectra were recorded at 5, 15, 40, 60, and 128 min. The reaction, as described above, to give ether **4** was complete after about 60 min; the spectra showed no other signals than those due to either **1** or **4**.

(3,5-Dichloro-4-hydroxybenzyl)pyridinium Chloride (12). To a slurry of 5 g of 4-hydroxy-α,2,6-trichlorotoluene (**3**),[4] mp 86–88.5 °C, in 10 mL of ether was added dropwise with stirring 50 mL of pyridine. A precipitate formed immediately and additional ether was added to aid the stirring. After only a few minutes, the reaction mixture was emptied into 3 N HCl and extracted with ether. The ether extract was dried (Na_2SO_4) and concentrated to give 6.9 g (100%) of **12**: mp 130–135 °C dec (water); IR (mull) 2000–3700 cm^{-1} (phenolic and hydrated OH); ^{1}H NMR (Me_2SO-d_6) δ 5.84 (s, 2, CH_2), 7.78 (s, 2, aryl of chlorinated ring), 8.17 (t, 2, J = 7.5 Hz, pyr C-3 H), 8.62 (t, 1, J = 7.5 Hz, pyr C-4 H), 9.34 (d, 2, J = 7.5 Hz, pyr C-2 H), 10.60 (s, 1, OH), 3.4 (H_2O).

Anal. Calcd. for $C_{12}H_{10}Cl_3NO$: C, 49.65; H, 3.45; N, 4.83. Found: C, 44.51; H, 4.26; N, 4.28. Calcd. for $C_{12}H_{14}Cl_3NO_2$ (dihydrate): C, 44.17; H, 4.29; N, 4.29.

3,5-Dichloro-4-hydroxybenzyl Methyl Ether (7). The pyridine salt (**12**, 0.5 g) was dissolved in methanol (5 mL) and refluxed on a steam bath for 7 h. A small amount of white precipitate formed. The methanol solution was diluted with water and extracted with ether; the ether was dried (Na_2SO_4) and concentrated: ^{1}H NMR ($CDCl_3$) δ 3.36 (s, 3, CH_3), 4.33 (s, 2, CH_2), 5.91 (s, 1, OH), 7.25 (s, 2, aryl).

3,5-Dichloro-4-hydroxybenzyl Alcohol (8). A solution of 1.11 g of pyridine salt **12** in 55 mL of 1 N NaOH was stirred at 80 °C for 1 day, cooled, acidified, and extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated to afford alcohol **8**: ^{1}H NMR ($CDCl_3$) δ 3.2–4.7 (br signal, 2, OH), 4.51 (s, 2, CH_2), 7.20 (s, 2, aryl).

10-Hydroxy-10-(4-hydroxybenzyl)-9(10*H*)-anthracenone (13). The adduct **13** was prepared (85% yield) by the reaction of 4-(chloromethyl)phenyl acetate[4] with AHQ^{2-} according to the general procedure for AHQ reactions given above. The reaction was carried out in both water and 50% aqueous dioxane with reaction times varying from 1 min to 3 h. The same high yields (70–98%) were obtained in all cases. However, the yield of **13** was only about 2% (estimated by GC and NMR) when *p*-hydroxybenzyl alcohol (**19**) was reacted with AHQ^{2-} in the standard way. The properties of the adduct were as follows: mp 224–228 °C (methanol); IR (mull) 3100–3500 (OH), 1640 cm^{-1} (carbonyl); UV (ethanol) λ_{max} 277 (ε 12 300); ^{1}H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

10-Hydroxy-10-(4-hydroxy-3-methoxybenzyl)-9(10*H*)-anthracenone (14). This adduct was prepared in high yield (82%) from the alkylation of AHQ^{2-} with chloro acetate **2** and low yield (estimated to be about 2% based on NMR and GC analysis)[11] from the alkylation of AHQ^{2-} with vanillyl alcohol (**20**). The standard alkylation procedure was used in each case. The properties of adduct **14** were as follows: mp 161–165 °C (meth-

Table II. Elemental Analyses

	13	14	15	16	17	28	29	30	31	37	40A	41B
calcd % C	79.75	76.30	65.45	77.09	75.00	84.00	82.76	80.00	84.55	84.00	77.10	80.70
obsd % C	79.30	75.86	65.29	77.08	75.17	81.86	82.28	73.69	83.76	83.95	77.06	80.39
calcd % H	5.06	5.20	3.64	5.03	5.00	5.33	5.42	5.45	4.70	5.33	5.83	5.26
obsd % H	5.13	5.90	3.69	5.11	5.07	5.53	5.61	5.13	4.84	5.32	5.71	5.31

anol–water); IR (mull) 3100–3600 (OH), 1650 cm^{-1} (carbonyl); UV (ethanol) λ_{max} 272 (ϵ 12700); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

10-Hydroxy-10-(3,5-dichloro-4-hydroxybenzyl)-9(10*H*)-anthracenone (15). The adduct **15** was prepared from AHQ^{2-} and either the pyridine salt **12** or 4-(chloromethyl)-2,6-dichlorophenol[4] according to the general procedure given above. The crude product was obtained in 70% yield and was recrystallized from methanol/water: mp 198–208 °C; IR (mull) 3100–3700 (OH), 1640 cm^{-1} (carbonyl); UV (ethanol) λ_{max} 278 (ϵ 11900); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

10-Hydroxy-10-(4-acetoxybenzyl)-9(10*H*)-anthracenone (16). A mixture of 1.0 g of adduct **13**, 2 mL of acetic anhydride, and 0.5 mL of pyridine was stirred under nitrogen at room temperature for 24 h. The reaction mixture was diluted with water and extracted with ether. The ether extract was washed with saturated $NaHCO_3$ solution and then water, dried (Na_2SO_4), and concentrated to affford a colorless solid (**16**): mp 168–170 °C (toluene); IR (mull) 3400–3600 (OH), 1660, 1715 cm^{-1} (carbonyls); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

10-Acetoxy-10-(4-acetoxybenzyl)-9(10*H*)-anthracenone (17). A mixture of 0.8 g of adduct **13**, 2 mL of acetic anhydride, and 0.5 mL of pyridine was stirred under nitrogen at 95 °C for 24 h. After the mixture cooled, the reaction mixture and a little wash ether were emptied into dilute HCl. Agitation produced a precipitate (0.71 g, 68%) of **17**: mp 167–167 °C (toluene); IR (mull) 1660, 1740, 1760 cm^{-1} (carbonyl groups); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

1-Chloro-1-(4-acetoxy-3-methoxyphenyl)ethane (22). Chloroacylation[4] of α-methylvanillyl alcohol,[23] mp 91–93 °C, afforded after vacuum distillation a 79% yield of **22**: bp 124–127 °C (1 mm); IR (neat) 1760 cm^{-1} (carbonyl); elemental analysis and NMR (Table I).

1-Chloro-1-(4-acetoxy-3-methoxyphenyl)propane (23). First, 1-(4-hydroxy-3-methoxyphenyl)-1-propanol was prepared according to the method of Zentner[24] and recrystallized once from toluene and twice from chloroform, mp 78–79.5 °C. This material was then chloroacylated according to the procedure of Taylor et al.[4] and vacuum distilled to afford (65% yield) compound **23**: bp 125–126 °C (1 mm); IR (neat) 1760 cm^{-1} (carbonyl); elemental analysis and NMR (Table I).

10-Hydroxy-10-(4-hydroxy-3-methoxy-α-methylbenzyl)-9-(10*H*)-anthracenone (24). With the standard alkylation procedure, chloro acetate **22** and AHQ^{2-} afforded an 87% yield of a complex product mixture. The crude product was applied to a silica gel column (EM 60) and eluted with hexane, combinations of hexane and chloroform, pure chloroform, and finally methanol. The three chloroform fractions were combined and rechromatographed on a silica gel column (EM 60) and eluted with chloroform, combinations of chloroform and ether, pure ether, and finally methanol. The adduct (**24**) was obtained (10% yield) from the eight fractions which eluted with the 10% ether/chloroform solvent mixture: IR (neat) 3100–3700 (OH), 1660 cm^{-1} (carbonyl); ^1H and ^{13}C NMR;[6] mass spectrum.[11] A few minor impurities were noted in the spectra.

10-Hydroxy-10-(4-hydroxy-3-methoxy-α-ethylbenzyl)-9-(10*H*)-anthracenone (25). Anthrahydroquinone dianion was alkylated with chloro acetate **23** in the standard manner, as described above, using an ether extraction isolation procedure. The crude product was then placed in a few milliliters of ether. A small amount of insoluble yellow crystals of **25** was collected by filtration; ^1H and ^{13}C NMR;[6] mass spectrum.[11] A few minor impurities were noted in the spectra. The filtrate was chromatographed on a silica gel (EM 60) column, eluted with hexane, hexane/chloroform, chloroform, chloroform/ether, and ether. ^1H NMR spectra of the fractions resulting from this chromatography showed a mixture of products, one of which was the adduct (**25**). The yield of **25** was estimated to be 25%.

Alkylation of Anthrone (27) with *p*-Acetoxybenzyl Chloride (1). The disubstituted alkylation product, 10,10-bis-(4-hydroxybenzyl)-9(10*H*)-anthracenone (**29**), was prepared in good yield (98%) by reacting 1 equiv of anthrone (**27**) with 2 equiv of chloro acetate **1**, using the general alkylation procedure, 50% aqueous dioxane and 2 h at 95 °C. The product was recrystallized from methanol/water: mp 211–214 °C; IR (mull) 3100–1700 (OH), 1630 cm^{-1} (carbonyl); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

The monoalkylated product, 10-(4-hydroxybenzyl)-9(10*H*)-anthracenone (**28**), was prepared in the same manner as **29** above, using only 1 equiv of chloro acetate **1**. The crude product, isolated by chloroform extraction of the acidified reaction mixture, was a complex mixture of components, one of which was the dialkylated product **29**. The chloroform residue was worked up by a series of rather complicated recrystallizations involving several different types of solvents. Anthraquinone was isolated in several of the steps, indicating that the product mixture was probably decomposing. Briefly, the product was taken up in toluene; that which did not dissolve was largely AQ but contained some 10-methoxy-10-(4-hydroxybenzyl)-9(10*H*)-anthracenone (**30**). The latter was separated from the AQ by washing with ethanol, evaporation, and recrystallization from methanol: mp 132 °C dec; IR 2800–3500 (OH), 1650 cm^{-1} (carbonyl); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

The toluene-soluble material was concentrated to give a gummy solid and a filtrate. The gummy solid was a mixture of AQ and a material with a melting point of 170–173 °C (from MeOH), whose ^1H NMR spectrum changed upon standing; no structural assignment was made.

A ^1H NMR spectrum of the toluene filtrate (concentrated) indicated the presence of the desired alkylation product (**28**). This material was chromatographed on a silica gel (EM 60) column and eluted with hexane, hexane/chloroform, chloroform, and methanol. The desired product (**28**) was found in several fractions which eluted with 50% chloroform/hexane. Further attempts to purify the product by recrystallization from methanol/water were unsuccessful. The elemental analysis (Table II) of the chromatographed product indicated the sample was not completely pure; the NMR spectra[6] were, however, quite clean—the only significant impurity appeared to be water. The mass spectrum[11] also supported the proposed structure **28**.

Dehydration of Adduct 13 To Give 31. A mixture of 1.0 g of **13**, 0.6 g of *p*-toluenesulfonic acid, and 30 mL of toluene was refluxed for 2 h, cooled, and extracted with aqueous $NaHCO_3$. The separated toluene phase was dried (Na_2SO_4) and evaporated to give 0.9 g (95%) of orange solid (**31**): mp 139–141 °C (Me_2SO–water); IR (mull) 2600–3400 (hydrated ArOH), 1660 cm^{-1} (carbonyl); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II). Drying in an oven at 105 °C overnight changed the melting point to about 190 °C dec but did not have much effect on the spectral properties.

10-(4-Hydroxy-3-methoxy-α-methylbenzyl)-9(10*H*)-anthracenone (32). Anthrone (**27**; 3.0 g, 15.4 mmol) was stirred with chloro acetate **22** (3.9 g, 17 mmol) and NaOH (4.2 g) in 200 mL of 50% aqueous dioxane under nitrogen while the mixture was warmed from room temperature to 95 °C over 2 h. The reaction mixture was stirred 0.5 h longer at 95 °C and then cooled, stirred in air for 5 min, and filtered to remove AQ. The filtrate was diluted with water and acidified with concentrated hydrochloric acid. The crude product was separated from residual AQ by methanol washing. The residue from evaporation of the methanol was dissolved in ether, dried (Na_2SO_4), and evaporated.

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(24) T. G. Zentner, Doctoral Thesis, The Institute of Paper Chemistry, Appleton, WI, June 1952.

The resulting amber-colored viscous liquid was purified by column chromatography, using silica gel (EM 60) and eluting with hexane, chloroform–hexane mixtures, chloroform, and methanol. Fractions eluting with 50–70% chloroform–hexane contained **32**: IR (neat) 3150–3650 (OH), 1660 cm^{-1} (carbonyl); ^1H and ^{13}C NMR;[6] mass spectrum.[11] A few minor impurities were noted in the spectra. Attempts to recrystallize **32** failed. The estimated yield was 65%.

Methylation of Adducts. Adducts **13**, **14**, **28**, **29**, and **32** were methylated with dimethyl sulfate[25] and analyzed by GC/MS. The products were principally the dimethylated derivatives, contaminated by small amounts of decomposition byproducts resulting from the alkali and THF used in the derivatization procedure.[11] An exception was adduct **28**, which was nearly totally destroyed by the derivatization procedure. The mass spectra are discussed elsewhere.[11]

10-Hydroxy-10-benzyl-9(10*H*)-anthracenone (37). Benzyl chloride was reacted with AHQ^{2-} under the standard conditions; the product **37**, not being a phenol, was precipitated along with the AQ. The precipitate was washed several times with ether to solubilize **37** and leave behind AQ, which is relatively insoluble in ether. The combined ether washings were dried (Na_2SO_4) and evaporated to afford (59% yield) a pale-yellow solid (**37**), which turned pink upon standing in air: mp 144–146 °C, (hexane/toluene); IR (mull) 3200–3500 (OH), 1660 cm^{-1} (carbonyl); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

10-Hydroxy-10-(3-oxobutyl)-9(10*H*)-anthracenone (40A). A procedure identical with that used to prepare **37** was employed, the only exception was that the alkylating agent was methyl vinyl ketone (**38**). The crude product was purified by column chromatography, employing silica gel (EM 60) and eluting with hexane, 50:50 hexane–chloroform, chloroform, 50:50 chloroform–THF, and dioxane. The major portion of the product (54% yield) was eluted with the 50:50 chloroform–THF solvent mixture; **40A** was a colorless solid: mp 99–102 °C (methanol–water); IR (mull) 3150–3800 (OH), 1710, 1660 cm^{-1} (carbonyls); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

10-Hydroxy-10-(1-phenyl-3-oxopropyl)-9(10*H*)-anthracenone Hemiacetal (41B). Freshly distilled cinnamaldehyde (**39**) was reacted with AHQ^{2-} under the standard conditions. The workup, however, involved quenching the cool reaction mixture with dilute hydrochloric acid, under nitrogen, filtering in air, and separating the product from AQ by exhaustive extraction with ether, using a Soxhlet extractor. The ether solution was dried (Na_2SO_4) and evaporated to give **41B** in 38% yield: mp 201–205 °C (methanol); IR (mull) 3100–1800 (OH), 1660 cm^{-1} (carbonyl); ^1H and ^{13}C NMR;[6] mass spectrum;[11] elemental analysis (Table II).

Quinonemethide Transfer from 29 to AHQ^{2-}. A mixture of 1.5 g of 10,10-bis(4-hydroxybenzyl)-9(10*H*)-anthracenone (**29**) and 4 equiv of AHQ^{2-} was stirred at 60 °C for 4 h, cooled, exposed to air (until the red color disappeared), and filtered to remove the excess AQ. The filtrate was acidified and the precipitate collected by filtration. Analysis of the product mixture by ^1H NMR and GC/MS (after derivatization)[11] showed that the major components were starting material **29**, adduct **13**, and AQ; there was no evidence for the presence of monoalkylated anthrone adduct **28**.

Registry No. **1**, 39720-27-9; **2**, 60998-35-8; **3**, 45952-61-2; **4**, 5355-17-9; **7**, 79817-03-1; **8**, 22002-17-1; **12**, 79817-04-2; **13**, 79769-65-6; **14**, 79769-67-8; **15**, 79769-66-7; **16**, 79769-68-9; **17**, 79769-69-0; **19**, 623-05-2; **20**, 498-00-0; **22**, 79827-27-3; **23**, 79827-28-4; **24**, 79769-76-9; **25**, 79769-73-6; **27**, 90-44-8; **28**, 79769-71-4; **29**, 79769-72-5; **30**, 79769-70-3; **31**, 69544-83-8; **32** (R = Me), 79769-77-0; **37**, 78787-97-0; **38**, 78-94-4; **39**, 104-55-2; **40A**, 79769-74-7; **41B**, 79769-75-8; α-methylvanillyl alcohol, 2480-86-6; 1-(4-hydroxy-3-methoxyphenyl)-1-propanol, 6997-34-8; AHQ, 4981-66-2; AQ, 84-65-1; AHQ^{2-}, 35339-92-5.

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Spectral Evidence of π–π Sandwiching of Aromatic Rings in 10-Benzylanthrones

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A detailed analysis of the ^1H and ^{13}C NMR spectra of several 10-benzylanthrones has shown that the benzyl substituent lies, at least to some extent, over the plane of the anthrone ring. This intramolecular sandwiching of π systems also occurs with selected C_{10}-allyl, alkyl ketone, condensed ring structures. Supporting evidence for sandwiching comes from UV, mass spectral, and X-ray studies.

Alkylation of anthrone and anthrahydroquinone affords C_{10}-substituted anthrones.[1] The latter were characterized by elemental analysis, preparation of derivatives, and spectral means. A portion of the spectral characterization involved nuclear magnetic resonance (NMR). The NMR data is presented here as confirming structural data and as evidence of an unusual conformational preference for the C_{10} substituents.

Results and Discussion

^1H NMR. Table I and II present the ^1H NMR spectral data for some selected anthrone derivatives. In Me_2SO solvent C_{10}-hydroxyl protons appeared at δ 6.3–6.5, indicative of dibenzyl alcohol structures,[2] and phenolic hydroxyl protons came at δ 8.5–9.8; both types exchanged with D_2O addition.

The diacetate derivative of **1**, namely **5**, displayed both aliphatic and aromatic acetate signals; an infrared spectrum also supported this conclusion. The diacetate **5** was one of only a few compounds in which the C_1 and C_8 protons were observed (downfield doublet) separate from the other anthrone aromatic protons.

An interesting feature of the ^1H NMR spectra of 10-(*p*-hydroxybenzyl)anthrones was the peculiar upfield shifts observed for the C_{10}-aryl protons. Ordinarily, phenols show

(1) D. R. Dimmel and D. Shepard, accompanying article in this issue.

(2) R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 4th ed., Wiley, New York, 1974, pp 181–278.

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