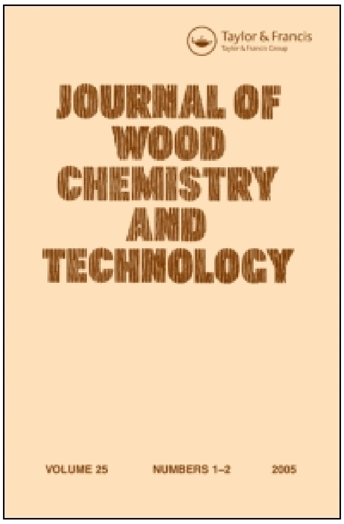

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Fullerton, Terry J. , Hemmingson, Jacqueline A. , Leary, Gordon J. and Wright, L. James(1982) 'Formation of 3-Guaiacylbenzanthrone by the Reaction of Reduced Forms of Anthraquinone with Quinone Methides', Journal of Wood Chemistry and Technology, 2: 1, 97 — 113

To link to this Article: DOI: 10.1080/02773818208085122

URL: http://dx.doi.org/10.1080/02773818208085122

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 2(1), 97-113 (1982)

FORMATION OF 3-GUAIACYLBENZANTHRONE BY THE REACTION OF REDUCED FORMS OF ANTHRAQUINONE WITH QUINONE METHIDES

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ABSTRACT

Anthrahydroquinone and anthrone readily react with stabilised quinone methides in alkaline solution to give 10-substituted oxanthrones and anthrones respectively. Similarly, reaction of a vinyl-substituted quinone methide gives the corresponding anthrone, both as the keto and enol adducts, and the substituted oxanthrone. Whilst both forms of the substituted anthrone can be partially converted to 3-arylbenzanthrones analogous to 3-guaiacylbenzanthrone formed during pulping, the oxanthrone adduct affords practically none of this product. This indicates that it is reduction of anthraquinone to its anthrone oxidation state which results in benzanthrone formation during pulping.

This paper was presented at the Ekman-Days 1981 International Symposium on Wood and Pulping Chemistry and is included in part in the proceedings.

INTRODUCTION

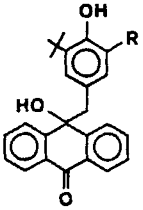
The ability of anthraquinone (AQ) to act as a catalyst for alkaline pulping processes is now generally accepted and the mechanism by which it operates is believed to be understood[1]. Although effective in catalytic amounts it is not a true catalyst since only a small proportion of the amount originally added is recoverable after pulping. The fate of the AQ has been investigated by ourselves[2,3] and others[4,5,6] and the isolation of trace amounts of 3-guaiacylbenzanthrone[3,7], 2-vanillylanthraquinone[3], benzanthrone[3] and 10-methyleneanthrone[8] from spent AQ pulping liquors indicates how some of the AQ is lost.

Since it is likely that the formation of these compounds will reduce the efficiency of the catalysts by depleting the amount of AQ available for pulping, a study of the mechanisms involved in these reactions was initiated. Such information should be most useful in the development of more stable and more effective catalysts with a greater potential for recovery or recycling.

RESULTS AND DISCUSSION

Reactions of Simple Quinone Methides

In view of the known reduction of AQ to anthrahydroquinone (AHQ) under pulping conditions the reaction of AHQ with t-butyl stabilised quinone methides in aqueous alkali was investigated initially. In each case the sole reaction product was the substituted oxanthrone 1.



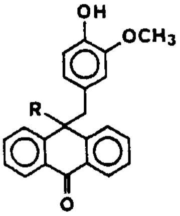
1a R = t-butyl
1b R = OCH_3

FIGURE 1 Substituted oxanthrones from t-butyl stabilised quinone methides.

The generality of this reaction has been confirmed by Dimmel et al.[9,10] using other quinone methides to give a series of similarly substituted compounds. The formation of these compounds by reaction of the quinone methide at the C-10 position of the AHQ rather than at oxygen is analogous to the reaction of phenols with quinone methides through the 4 position to give methylene bridged polymers, as found with the base catalysed condensation of vanillyl alcohol[11,12]. In contrast to the above results, refluxing AHQ with one equivalent or excess vanillyl alcohol in base gave the disubstituted anthrone 2 in 53% yield with none of the expected monosubstituted oxanthrone 3 being formed.

Because of the unusual p.m.r. spectrum of this compound, its structure was confirmed by an X-ray crystal structure analysis[13]. This verified that the strong shielding of the aromatic methoxyl protons upfield to $\delta 3.21$ and the large upfield shifts of the vanillyl aromatic protons to give first-order splitting patterns was due to the two vanillyl rings having a preferred orientation above and below the central anthrone ring.

With an excess of AHQ the monosubstituted anthrone 4 was the major product formed, together with small variable amounts



2 R = vanillyl
3 R = OH
4 R = H

FIGURE 2 Products from reaction of vanillyl alcohol with AHQ.

of the divanillyl adduct 2 and the oxanthrone 3. It is likely that the oxanthrone 3 is formed during work-up of the product, as 4 is readily oxidised to 3 on stirring in base in the presence of air. The analogous three products without the methoxyl substituent have also recently been reported by Dimmel[14].

The formation of the monosubstituted anthrone 4 may occur by reduction of the substituted oxanthrone 3 by AHQ. The ready reversibility of the oxanthrone formation then provides a source of quinone methide for this product to react with to give the disubstituted anthrone. Alternatively, it is possible that the AHQ is reduced to anthrone prior to substitution as anthrone is obtained from the diacetate of AHQ in refluxing base and from AQ-glucose under pulping conditions. The significance of this reduction to anthrone-derived compounds at elevated temperatures to AQ pulping will be discussed later in the paper.

Reaction of Vinylogous Quinone Methides

As with the simple quinone methides, AHQ reacted cleanly with the vinylogous quinone methide 5 under mild conditions to give the allyl substituted oxanthrone 6 as shown in figure 3.

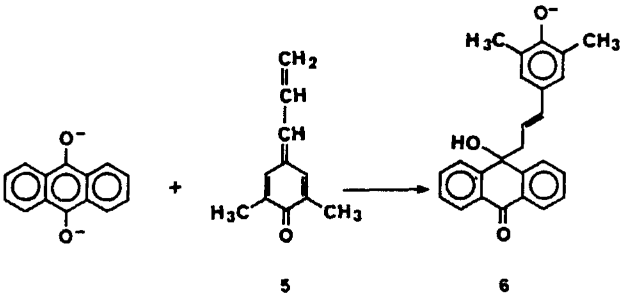
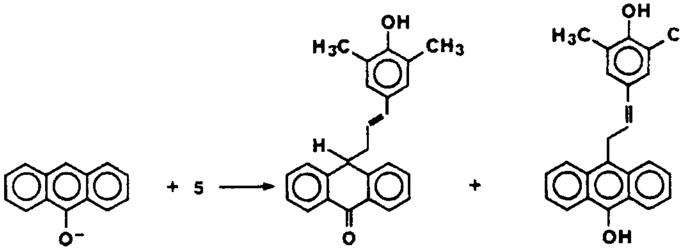


FIGURE 3 Reaction of vinylogous quinone methide with AHQ.

The product was unstable and partially decomposed on storage or attempted purification by chromatography. This compound was of interest, as a compound of this type with a vinyl-guaiacyl substituent derived from the extended quinone methide of coniferyl alcohol, was believed to be the precursor of 3-guaiacylbenzanthrone and benzanthrone, both of which had been previously isolated from AQ spent liquors[3]. However when this compound was heated under nitrogen in base for 1 hour at 80°C no benzanthrone-type compounds were obtained. The only identifiable products were 3,5-dimethyl-4-hydroxycinnamyl alcohol and AQ, indicating that the formation of the substituted oxanthrone is readily reversible. On prolonged heating (24 hr reflux) trace amounts (about 1%) of the 3-substituted benzanthrone together with polymeric material and AQ were obtained.

Anthrone-derived Products

In view of these results the alternative possibility that the benzanthrone and 3-guaiacylbenzanthrone were being formed from a substituted anthrone was investigated as it had previously been found that the yields of these two compounds were substantially higher from a soda-anthrone cook than from a



7 8

FIGURE 4 Reaction of vinylogous quinone methide with anthranol anion.

soda-AQ cook. As expected, reaction of anthrone with the 2,6-dimethyl- substituted vinylogous quinone methide 5 in base at room temperature gave the 10-substituted anthrone 7 and in addition the 10-substituted anthranol isomer 8 as shown in figure 4.

The reaction of the anthranol anion with the γ-position of the extended quinone methide once again occurs at the C-10 position leading to the formation of the isomers 7 and 8.

3-Arylbenzanthrones

Refluxing the anthrone adduct 7 or the anthranol adduct 8 in base for 1.5 hours gave a low yield (2-5%) of the 3-(3,5-dimethyl- 4-hydroxyphenyl)-benzanthrone analogous to 3-guaiacylbenzanthrone. This yield increased to about 10% on refluxing for 24 hours and the reaction mixture still contained unreacted adduct together with polymer. The recovery of unreacted starting material highlights the much greater stability of these compounds compared with that of the corresponding substituted oxanthrones.

Further evidence for the intermediacy of substituted anthrones in the formation of the benzanthrones was obtained from sealed tube experiments in which solutions of anthrone and oxanthrone in base were heated with coniferyl acetate at 150°C. As shown in Table 1 the yields of 3-guaiacylbenzanthrone were much higher with anthrone, and only trace amounts of unsubstituted benzanthrone were obtained from oxanthrone whereas substantial amounts were produced in the anthrone reaction.

It is also of interest that at 100°C, even with anthrone, very little 3-guaiacylbenzanthrone and no benzanthrone was formed. Attempts to obtain benzanthrone from 3-guaiacyl-

TABLE 1

Analysis of Sealed Tube Reaction Products and Liquor Extracts

Sample	3-GBA[a]		Benzanthrone	
	Moles/ litre $x10^{-4}$	Yield %	Moles/ litre $x10^{-5}$	Yield %
anthrone/coniferyl acetate/100°C	0.23	0.09	0	0
anthrone/coniferyl acetate/150°C	10.0	3.9	2.5	0.10
oxanthrone/coniferyl acetate/150°C	6.0	2.3	0.3	0.01
soda-AQ extract[b]	10.7	4.2	7.1	0.28
soda-anthrone extract[b]	17.9	7.0	17.4	0.68

a 3-guaiacylbenzanthrone
b Converted to concentrations equivalent to sealed tubes.

benzanthrone by heating it under pulping conditions were also unsuccessful.

Mechanism of Formation

On the basis of these results it appears that 3-guaiacylbenzanthrone is formed from the substituted anthrone. As shown in Figure 5 the reaction is believed to proceed by initial isomerisation of this adduct to the anthranol form and cyclisation analogous to that proposed by Aminoff *et al*[15] for the dimerisation of coniferyl alcohol, this is then followed by dehydrogenation to give the observed product. In support of this mechanism the substituted anthrone has recently been isolated from the reaction of acetylated milled wood lignin with AHQ at 10°C[16]. Furthermore current work in progress, to be published separately, has shown that the 3,5-dimethyl analogue of the product of step 1 (Fig. 5), protonated on the anthranol moiety, can be synthesised from anthrone 7 or anthranol 8 and that these quinone methides, when added to

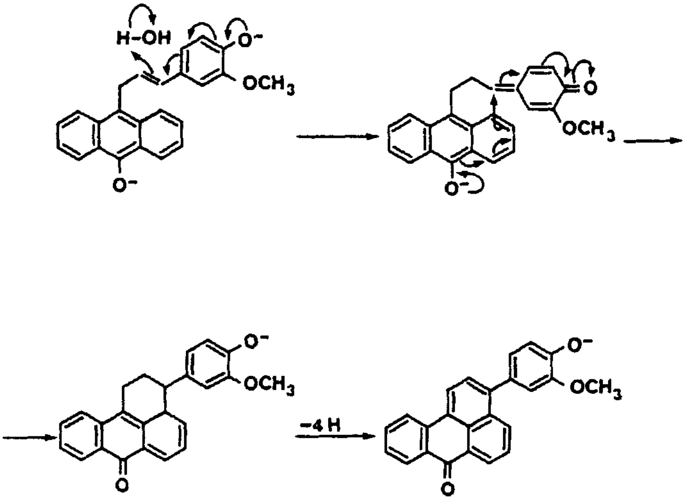


FIGURE 5 Mechanism of 3-guaiacylbenzanthrone formation.

oxygen-free base and refluxed give the benzanthrone in good yield.

CONCLUSIONS

It now appears most likely that the reason for AQ's effectiveness as a pulping catalyst is related to its ability, in the reduced AHQ form, to react with lignin-derived quinone methides formed during pulping. In considering why the AQ is only partially recoverable after pulping it has been found that, whereas the formation of substituted oxanthrones is readily reversible with both short and vinyl-substituted quinone methides, the substituted anthrones are more stable and more likely to lead to irreversible condensation of the AQ with lignin fragments. An example of this is the reaction of the extended quinone methide of coniferyl alcohol leading to 3-guaiacylbenzanthrone formation. In this case the much higher yields from the substituted anthrone than from the substituted oxanthrone model compounds strongly suggest that the reaction proceeds via the substituted anthrone intermediate. The small amount of 3-arylbenzanthrone that is formed from the substituted oxanthrone may be rationalised as a partial dissociation to AHQ which can then give rise to the substituted anthrone.

Modification of the pulping conditions and catalyst design to minimise these secondary reactions should lead to the development of more efficient catalysts with a greater potential for recovery and recycling.

EXPERIMENTAL

Reaction of AHQ with 2-t-Butyl-6-methoxy-4-methylene-cyclohexa-2,5-dienone

2-t-Butyl-4-methyl-6-methoxyphenol (0.23 g) in benzene (10 ml) was oxidised to the quinone methide by briefly shaking this solution with a solution of potassium ferricyanide (0.79g) in aqueous sodium hydroxide (0.1 g in 10 ml H_2O). This benzene solution of the quinone methide was then added under nitrogen to a cooled solution of AHQ in 1N NaOH (20 ml), previously formed by refluxing AQ (0.50 g) with glucose (1.08 g) in the aqueous alkaline solution. The two phase mixture was stirred at 20°C for 10 minutes and then refluxed for 15 minutes. The product was then poured into water and extracted with chloroform to give the product as and oil (0.23 g) which was a one to one mixture of the substituted oxanthrone <u>1b</u> (10-hydroxy-10-(3-t-butyl-4-hydroxy-5-methoxybenzyl)-9-(10H)-anthracenone) and unoxidised phenol.

The product was purified by prep. t.l.c. in chloroform: ethyl acetate (9:1) R_f 0.6 and isolated as a crystalline solid. Recrystallisation from toluene-n-hexane gave colourless crystals m.p. 179-180°C.

High resolution m.s. M^+ 402.1791 $C_{26}H_{26}O_4$ requires 402. 1829. M.s. (200°C) m/e (%) 402 (M^+) (1), 385 (M^+) (100), 210(63), 193(62). P.m.r. δ ($CDCl_3$) 1.06 (9,s,t-butyl), 2.85 (1,s, exchanged with D_2O, tert OH), 3.10 (2,s,$ArCH_2$) 3.35 (3,s,$ArOCH_3$), 5.36 (1,d,$J_{2,6}$ = 2Hz, H_2 of benzyl substituent), 5.44 (1,d,$J_{2,6}$ = 2Hz, H_6 of benzyl substituent), 5.65 (1,s, exchanged with D_2O, phenolic OH), 7.34-8.02 (8, m, oxanthrone protons).

Reaction of AHQ with 2,6-Di-t-butyl-4-methylenecyclohexa-2,5-dienone

A solution of the dianion of AHQ was prepared by refluxing AQ (0.50 g) with glucose (1.08 g) in 1N sodium hydroxide solution (20 ml) with stirring under nitrogen. The resultant red solution was cooled to 40°C and a solution of 2,6-di-t-butyl-4-methylenecyclohexa-2,5-dienone in benzene was added. This quinone methide was previously prepared by shaking a benzene solution (10 ml) of 2,6-di-t-butyl-4-methylphenol (BHT) (1.58 g) with potassium ferricyanide (4.75 g) in aqueous sodium hydroxide solution (0.1g NaOH in 10 ml H_2O).

The two phase mixture of AHQ and the quinone methide were then refluxed for 60 minutes. The product was cooled, acidified and extracted with chloroform, dried over magnesium sulphate, filtered and concentrated to dryness and unreacted BHT removed by washing with n-hexane to give 0.50 g of crude product containing 53% by p.m.r. of 10-hydroxy-10- (3,5-di-t-butyl-4-hydroxybenzyl)-9(10H)-anthracenone (26% yield).

The product was purified by prep. t.l.c. in benzene (R_f 0.15) and crystallised from toluene as needles m.p. 218-219°C.
High resolution m.s. M^+ 428.2318 $C_{29}H_{32}O_3$ requires 428.2349.
M.s. m/e (%) 428(M^+) (0.1), 369(2.5), 219(30.4), 210(100). P.m.r. δ ($CDCl_3$) 1.08 (18, s, t-butyl), 2.65 (1,s, exchanged with D_2O, tert hydroxyl), 3.13 (2,s,$ArCH_2$), 4.86 (1,s, exchanged with D_2O, phenolic OH), 5.68 (2,s,aromatic protons of benzyl substituent), 7.38-8.0 (8,m, oxanthrone protons).
$V_{c=o}$ 1656 cm^{-1} (KBr).

Reaction of AHQ with Vanillyl Alcohol (mole ratio 1:1)

A suspension of AHQ diacetate (0.51 g) in 1N sodium hydroxide (10 ml) was refluxed under nitrogen for 150 minutes to give a homogeneous red solution of the dianion of AHQ which was then cooled to 60°C and a solution of vanillyl alcohol (0.26 g) in 1N sodium hydroxide (3 ml) was added under nitrogen. This solution was then refluxed for 17 hours, cooled and the residual AQ extracted with chloroform. The aqueous layer was then neutralised with dilute hydrochloric acid, extracted with chloroform, dried over magnesium sulphate and concentrated to dryness to give 10,10-bis(4-hydroxy-3-methoxybenzyl)-9(10H)-anthracenone,2, as a light yellow oil (0.21 g, 53% yield) which was crystallised from toluene as light yellow needles m.p. 202-204°C.

M.s. (120°C) m/e (%) 466 (3) (M^+), 330 (100), 297 (2), 269 (2) 239 (2), 194 (67), 165 (7), 137 (58). High resolution m.s. M^+ 466.1779 $C_{30}H_{26}O_5$ requires 466.1820.
P.m.r. δ($CDCl_3$) 3.21 (6, s, aromatic methoxyls), 3.61 (4, s, benzylic protons), 5.39 (2, broad s, exchanged with D_2O, phenolic hydroxyls), 5.63 (2,d, $J_{2,6}$ = 2Hz, H_2 and H_2' of vanillyl groups), 5.92 (2, dxd, $J_{2,6}$ = 2Hz, $J_{5,6}$ = 8Hz, H_6 and H_6' of vanillyl groups), 6.35 (2, d, $J_{5,6}$ = 8Hz, H_5 and H_5 of vanillyl groups), 7.30-8.19 (8, m, anthrone protons). ^{13}C n.m.r. δ(DMSO) 48.58 (benzylic carbons), 49.78 (C_{10} of anthrone) 54.92 (aromatic methoxyls), 113.46, 114.49 (C_2 and C_5 carbons of vanillyl rings), 121.97 (C_6 of vanillyl ring), 126.23, 126.83, 128.96, 133.19 (anthrone CH carbons), 127.76, (C_1 of vanillyl rings), 132.32 (C_{8a}, C_{9a} anthrone carbons), 144.50 (C_{4a}, C_{10a} anthrone carbons), 146.25, 146.72 (O-substituted C_3 and C_4 of vanillyl rings).

Reaction of AHQ with Vanillyl Alcohol (mole ratio 3:1)

A suspension of 9,10-diacetoxyanthracene (6.0 g) in 1M sodium hydroxide (100 ml) was refluxed under oxygen free nitrogen for 150 minutes to give a red homogeneous solution of the anion of AHQ. Vanillyl alcohol (1.04 g) was added and the heating under reflux continued for 20 hr. The solution was cooled to room temperature and acidified by addition of solid ammonium chloride (20 g) followed by 3M hydrochloric acid. The solution was extracted with diethyl ether, dried over sodium sulphate and concentrated to dryness under reduced pressure. The resulting yellow oil was extracted again with diethyl ether (50 ml) and the small amount of insoluble AQ removed by filtration. Removal of the solvent under reduced pressure gave the product as a yellow oil (1.8 g) as a mixture of 10-vanillylanthrone, 4, (1.5 g, 67% yield based on vanillyl alcohol) and the disubstituted anthrone, 2, (0.3 g, 19% yield) with small variable amounts of 10-vanillyloxanthrone, 3, depending on the amount of exposure of the reaction mixture to oxygen prior to acidification.

The products were purified by prep. t.l.c. in chloroform. 10-(3-Methoxy-4-hydroxybenzyl)-9(10H)-anthracenone, 4 (R_f $CHCl_3$ 0.3). M.s. (120°C) m/e (%) 330(8) (M^+), 195(38), 194(100), 193(17), 165(37), 137(100), 122(19), 94(10), 82(5), 77(5). P.m.r. δ ($CDCl_3$) 3.09 (2,d,J = 5Hz, $ArCH_2$), 3.42 (3,s,$ArOCH_3$), 4.51 (1,t,J = 5Hz, C-10 proton), 5.38 (1,s, phenolic OH), 5.62 (1,d,$J_{2,6}$ = 2Hz,H_2 of vanillyl), 5.89 (1,dxd,$J_{2,6}$ = 2Hz, $J_{5,6}$ = 8Hz, H_6 of vanillyl), 6.50 (1,d,$J_{5,6}$ = 8Hz, H_5 of vanillyl), 7.22-8.20 (8,m, anthrone protons).

10-Hydroxy-10-(3-methoxy-4-hydroxybenzyl)-9(10H)- anthracenone, 3 (R_f $CHCl_3$ 0.2). M.s. (120°C) m/e (%) 346(3) (M^+), 210(44), 137(96). P.m.r. δ ($CDCl_3$) 3.05(2,s,$ArCH_2$), 3.30(3,s,$ArOCH_3$), 5.40 (2,m, phenolic OH and H_2 of vanillyl), 5.58 (1,dxd, $J_{2,6}$ = 2Hz, $J_{5,6}$ = 8Hz, H_6 of vanillyl), 6.30 (1,d,$J_{5,6}$ = 8Hz, H_5 of vanillyl), 7.22-8.1 (8,m, oxanthrone protons).

^{13}C n.m.r. δ(DMSO) 54.9 (benzylic carbon) 55.07 ($ArOCH_3$), 73.1 (C-10 of oxanthrone), 114.0, 114.4, (C-2 and 5 of vanillyl), 122.5 (C-6 of vanillyl) 125.3 (C-1 of vanillyl) 125.6, 126.8, 127.6, 133.4 (C-H carbons of oxanthrone), 131.0, 147.9 (quaternary carbons of oxanthrone), 144.9, 146.2 (C-O carbons of vanillyl).

Reaction of AHQ with 4-allylidene-2,6-dimethyl-cyclohexa-2,5-dienone

A solution of ionised AHQ was prepared by heating 9,10-diacetoxyanthracene (294 mg) in a nitrogen purged 0.7 N solution of sodium hydroxide in 30% t-butanol - water for 2 hr at 80°C.

A solution of 4-allyl-2,6-dimethylphenol (162 mg) in dichloromethane (100 ml) was shaken for 45 sec. with 50 ml of an aqueous solution of potassium ferricyanide (4 g) and potassium hydroxide (0.5 g) and the resulting solution of 4-allylidene- 2,6-dimethylcyclohexa-2,5-dienone was concentrated to ca. 20 ml.

The solution of quinone methide was added dropwise to the solution of AHQ at 30°C and the reaction mixture was stirred for 2 hr. The dichloromethane was removed by the nitrogen purge. The reaction mixture was then neutralised with ammonium chloride (5.5 g) and extracted twice with chloroform (100 ml). The chloroform solubles were concentrated to dryness at ca. 30°C.

The crude product, obtained in about 80% yield, was purified by preparative layer chromatography (p.l.c.) (ether : hexane 2:1), to give the oxanthrone adduct, 6, as a yellow gum in 30-40% yield.

High resolution m.s. M^+ 370.1593. $C_{25}H_{22}O_3$ requires 370.1569. M.s. (100°C) m/e (%) 370 (M^+) 0.5, 352 (2), 218 (3), 210 (56), 209 (38), 208 (56), 180 (44), 161 (100), 152 (38), 146 (18). P.m.r. δ ($CDCl_3$) 2.10 (6,s,Me), 2.70 (2,d,J = 6.8Hz,CH_2), 3.10 (1,br.s,OH), 4.86 (1,br.s,OH), 5.06-5.67 (1,m,CH), 5.79 (1,d,J = 15.6 Hz, CH), 6.64 (2,s,ArH), 7.24-8.20 (8,m,ArH).

Reaction of Anthrone with 4-allylidene-2,6-dimethylcyclohexa-2,5-dienone

A 0.7 N solution of sodium hydroxide in 30% t-butanol - water was purged with nitrogen for 2 hr. Solid anthrone (194 mg) was then added and 5 min. later, a solution of quinone methide (prepared as described above) was added slowly at 20°C and the reaction mixture was stirred for 1 hr. Workup was as described above for the oxanthrone adduct. The anthrone adduct, 7, was isolated as an orange gum and the anthranol adduct, 8, as a yellow solid.

Adduct 7:
High resolution m.s. M^+ 354.1639. $C_{25}H_{22}O_2$ requires 354.1620. M.s. (200°C) m/e (%) 354 (M^+) (0.7), 353 (2.5), 352 (10), 231 (8), 194 (88), 193 (35), 165 (37), 161 (100), 146 (14). P.m.r. δ ($CDCl_3$) 2.15 (6,s,Me), 2.72 (2,t,J = 5.8Hz CH_2), 4.35 (1,t,J = 5.8Hz,C_{10} proton), 4.80 (1,br.s,OH), 5.22-5.71 (1,m, vinyl CH), 5.84 (1,d, = 15.8Hz, vinyl CH), 6.68 (2,s,ArH of phenolic ring), 7.51 (6,m,ArH), 8.17-8.31 (2,m,C_1 and C_8ArH).
$\nu_{c=o}$ 1666 cm^{-1} (KBr),

Adduct 8:

High resolution m.s. M-2H$^+$ 352.1466. $C_{25}H_{20}O_2$ requires 352.1462. M.s. (200°C) m/e (%) 354 (M$^+$) (2), 353 (4), 352 (15), 231 (13), 207 (17), 194 (26), 193 (10), 165 (10), 161 (100), 145 (27). P.m.r. δ(CDCl$_3$) 2.10 (6,s,Me), 3.15 (2,d,6.8Hz,CH$_2$), 4.94 (2,br.s, OH), 4.97-5.83 (1,m,CH), 5.95 (1,d,J = 15.4Hz,CH), 6.57 (2,s,ArH), 7.42-7.86 (6,m,ArH), 8.32 (2,br.d,J = 7.2Hz,ArH).

Cyclisation of Adducts 7 and 8 and Isolation of 3-(3,5-dimethyl-4-hydroxy-phenyl)benzanthrone

Cyclisation experiments were carried out in the same reaction medium as was used for preparing the adducts. Product workup was also as described above. In both cases the benzanthrone product was isolated and purified by p.l.c. (ether:hexane 3:2). It was obtained as an orange solid, contaminated with small amounts of 3,5-dimethyl-4-hydroxy- benzaldehyde, with which it co-chromatographed.

High resolution m.s. M$^+$ 350.1334. $C_{25}H_{18}O_2$ requires 350.1307. M.s. (200°C) m/e (%) 350 (M$^+$) (100), 335 (15), 320 (10), 207 (60). P.m.r. δ(CDCl$_3$) 2.36 (6,s,Me), 4.78 (1,br,s,OH), 7.15 (2,s,ArH), 7.54-7.83 (4,m,ArH), 8.34-8.59 (4,m,ArH), 8.81 (1,dd,J = 1.3Hz, J = 7.3 Hz,C$_6$ArH).

vis. λ max 426 (EtOH).

Decomposition products of the adducts were identified from uv, mass and n.m.r. spectral data.

Sealed Tube Reactions

Mixtures of coniferyl acetate (56 mg) and anthrone (50 mg) or oxanthrone (53 mg)[12] in 1N NaOH (10 ml) were degassed and sealed under argon. The tubes were then heated at 100°C or 150°C for 1 hr. The resultant mixtures were neutralised with CO$_2$, chloroform extracted (4 x 20 ml), dried over magnesium sulphate, filtered and made up to 100 ml.

The extracts were analysed by quantitative t.l.c. using *in situ* fluorescence photometry. For the 3-guaiacylbenzanthrone analyses 23 µl of each extract and of three standards were applied to a precoated silica gel 60 F-254 t.l.c. plate (Merck) and the plate was developed in chloroform. The intensity of each of the 3-guaiacylbenzanthrone spots (R_f 0.35) was then measured using a scanning densitometer with 366 nm irradiation and 490 nm secondary interference line filters. For the benzanthrone analyses the plate was developed twice in toluene and the fluorescene intensity of the benzanthrone spot (R_f 0.30) measured with 366 nm irradiation and a 400-600 bandpass filter. The results obtained are summarized in Table 1.

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