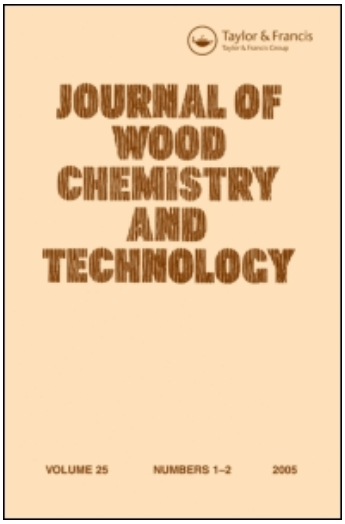


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

The Alkaline Reactions of Some Simple Quinonemethide-Anthrahydroquinone Adducts

Donald R. Dimmel[a]; Donaline Shepard[a]
[a] The Institute of Paper Chemistry, Appleton, Wisconsin

To cite this Article Dimmel, Donald R. and Shepard, Donaline(1982) 'The Alkaline Reactions of Some Simple Quinonemethide-Anthrahydroquinone Adducts', Journal of Wood Chemistry and Technology, 2: 1, 73 — 95
To link to this Article: DOI: 10.1080/02773818208085121
URL: http://dx.doi.org/10.1080/02773818208085121

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 2(1), 73-95 (1982)

THE ALKALINE REACTIONS OF SOME SIMPLE QUINONEMETHIDE-ANTHRAHYDROQUINONE ADDUCTS

Donald R. Dimmel and Donaline Shepard
The Institute of Paper Chemistry
Appleton, Wisconsin 54912

ABSTRACT

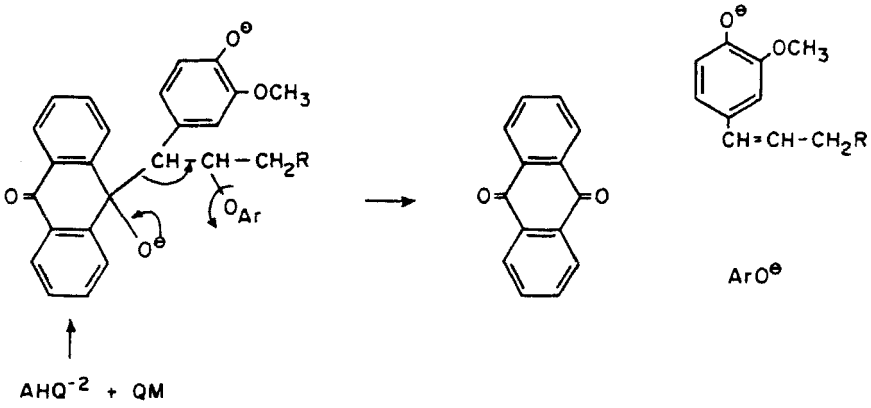
The rapid delignification rates associated with anthraquinone-alkaline pulping could be due to the formation and reactions of lignin quinonemethide-anthrahydroquinone (QM-AHQ) adducts. The chemistry of some simple QM-AHQ adducts is examined here. Upon heating in aqueous alkali, the QM-AHQ adducts fragment to QMs and AHQ. At 100° the adducts are reduced by AHQ dianion to afford QM-anthrone adducts and anthraquinone. At typical pulping temperatures (173°), the adducts are extensively, but not completely, decomposed, releasing AHQ and/or anthraquinone.

INTRODUCTION

Quinonemethides (QMs) are considered to be the focal point in two reactions which are important to the removal of lignin from wood during pulping, namely lignin fragmentation and condensation reactions.[1] Anthrahydroquinone (AHQ) has been shown to react with simple quinonemethides to give 1:1 addition products, referred to as QM-AHQ adducts.[2-4] Adducts containing β-aryl ether linkages decompose in warm alkali to give principally anthraquinone (AQ) and two phenolic products (Scheme I).[3,4] A fragmentation reaction of this type can partially explain the rapid delignification rates that are known to occur with anthraquinone pulping.

Another way that AHQ can influence delignification rates is by retarding lignin condensation reactions. We have observed that AHQ is capable of suppressing the condensation reactions of a

Scheme I



simple lignin model, vanillyl alcohol.[5] This model contains no β-carbons, but is capable of forming quinonemethides.

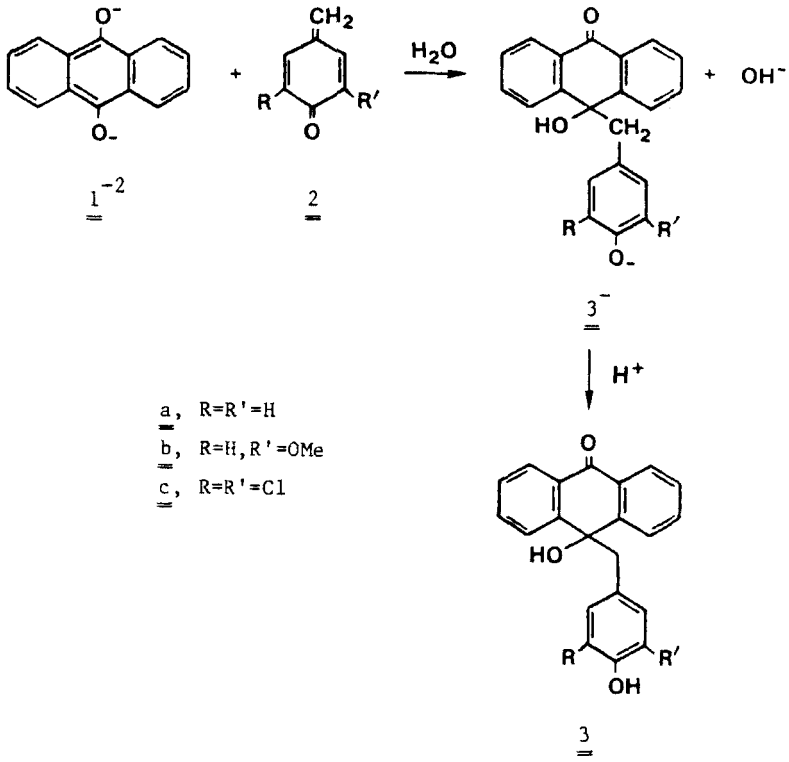
This report concerns the aqueous alkaline reactions of some simple QM-AHQ adducts which do not contain β-aryl ether linkages. The adducts show a different chemical behavior depending upon the heat applied. The results provide some insights into possible reactions which could be occurring during alkaline pulping with AQ.

RESULTS AND DISCUSSION

Reactions of Adducts at Low Temperatures

The adducts used in this study were prepared by the reaction of anthrahydroquinone dianion ($\underline{1}^{-2}$) with quinonemethides which were generated *in situ* in aqueous alkali at 60° (eq. 1).[2] The reactions were done in a nitrogen atmosphere in order to avoid the rapid air oxidation of AHQ forms to AQ.

Adducts 3a-c, were each placed in aqueous alkali and stirred at room temperature for 24-hours in open-air flasks. Acidification led to nearly complete recovery of the adduct in each case. However, noticeable changes occurred when solutions of 3a and 3b were warmed past 60°. Adduct 3c was recovered unchanged after



1^{-2} 2 3^{-} (1)

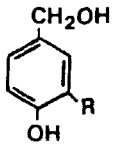
a, R=R'=H
b, R=H, R'=OMe
c, R=R'=Cl

3

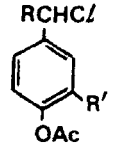
heating in alkali; presumably, the low reactivity here is due to a very low solubility of 3c in aqueous alkali.

Several color changes occurred when heating either 3a or 3b in alkali. If the initial heating was done in a nitrogen atmosphere, the solutions took on a strong red color which is indicative of AHQ^{-2}. Upon exposure of the hot solutions to air the solutions turned orange and gradually light yellow in color. The product consisted of a mixture of AQ and condensation materials, similar to those that occurred when either p-hydroxybenzyl alcohol (4) or vanillyl alcohol (5) was heated under comparable conditions in aqueous alkali.

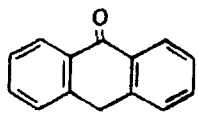
Apparently deprotonation of the adducts gives ions 3^{-} which, at temperatures above 60°, enter into an equilibrium with AHQ^{-2} and



4, R=H
5, R=OMe



6, R=R'=H
7, R=H,R'=OMe
8, R=Me,R'=OMe



9

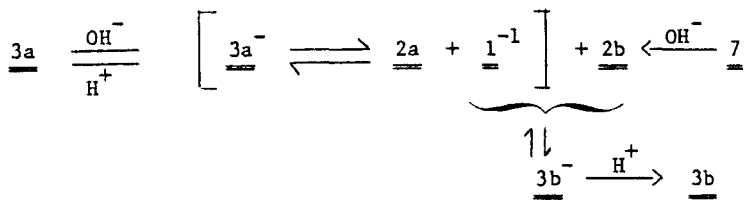
the corresponding QM. In other words, the reaction described by equation 1 is reversible at elevated temperatures. When air is present, the equilibrium is shifted since AHQ^{-2} will be converted to AQ. The liberated quinonemethides are converted by the alkali to the phenolate ions of 4 or 5, and eventually phenolic condensation products are formed.

The crossover[6] experiment outlined by equation 2 further verified the instability of the adducts at elevated temperatures. Here, adduct 3a was mixed with chloroacetate 7 and heated at 100°, in alkali, under nitrogen, to afford adduct 3b, along with condensation products and relatively large amounts of recovered 3a. The ratio of 3a to 3b was about 6:1. The expected ratio of 1:1 was not obtained, probably because the production of intermediate QM 2b did not coincide with the establishment of the equilibrium shown in the brackets. The condensation products were a mixture of components derived from quinonemethides 2a and 2b, with the latter predominating.

In summary, the air studies at 60-90° and the crossover experiment clearly demonstrate that QM-AHQ adducts enter into an equilibrium with their component parts, AHQ^{-2} and QMs, at temperatures above about 60°.

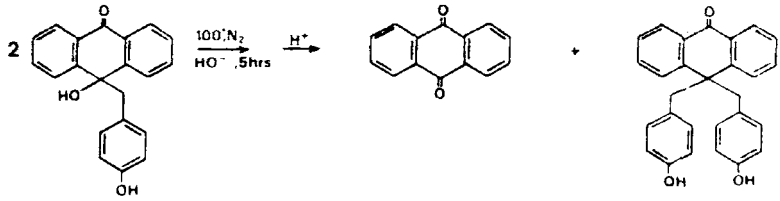
Anaerobic Reactions of Adduct 3a at 100°

Heating adduct 3a for several hours at 100°, under nitrogen, gave a 100% yield of AQ and a 93% yield of a $(QM)_2$-AHQ adduct 10.



(2)

The yield calculations were based on the stoichiometry indicated by equation 3. The structural proof of 10 was provided by elemental analysis, extensive spectral analysis and synthesis, from anthrone (9).[2,7] A small amount of 10 was observed in the cooks done at 60-90° which began under nitrogen before being exposed to air; the material was not characterized there because of interfering condensation products.



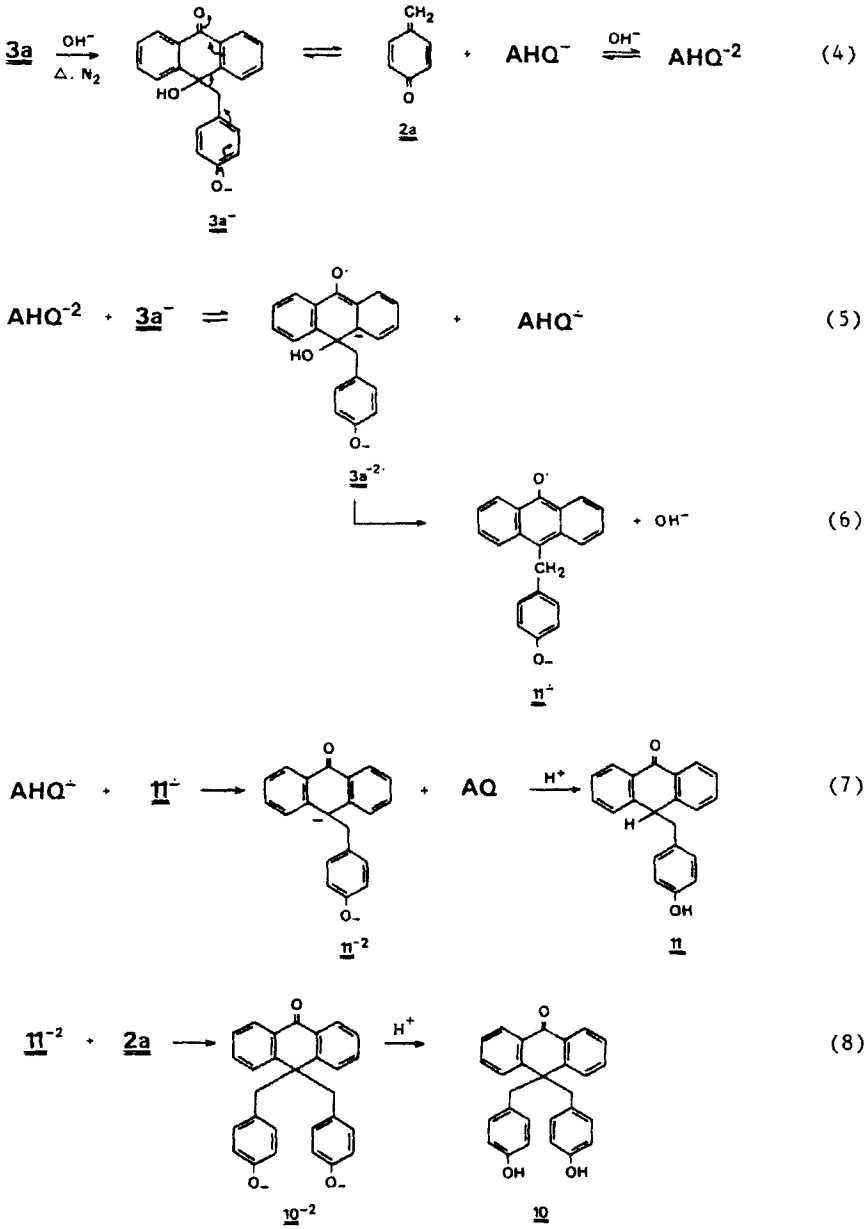
(3)

3a 10

A possible mechanism for the formation of 10 from 3a, which is essentially a *reduction* process, is shown in Scheme II. The sum of equations 4-8 equals equation 3. The scheme predicts that the dianion of 10-(4'-hydroxybenzyl)-9(10H)-anthracenone (11) should be an intermediate in this transformation. Compound 11 has been previously prepared, with much difficulty, by alkylating anthrone with one equivalent of p-acetoxybenzyl chloride (6).[2]

We sought to show the existence of 11 during the conversion of 3a to 10 by withdrawing aliquots at various time intervals, methylating the resulting samples and analyzing by GC-MS.[7] Compound 11 was not observed in any of the samples. This was puzzling until it was demonstrated that an authentic sample of 11 decomposed during methylation. Qualitatively, we observed that the con-

Scheme II



centration of 3a decreased and 10 increased as the 100° anaerobic reaction proceeded, but the latter increased at a slower rate than the former decreased. Presumably, the difference is due to the production of 11.

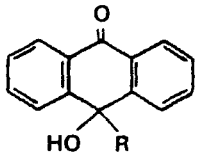
Heating 3a in the presence of eight equivalents of AHQ^{-2}, however, produced reasonable amounts of 11, as determined by NMR. This result can be explained by considering the reactions in Scheme II. Excess AHQ^{-2} should drive equation 4 back to ion 3a and thus greatly lower the level of quinonemethide 2a. With low levels of 2a, step 8 which produces compound 10 will be disfavored. Consequently, ion 11^{-2} builds to a high level and leads to 11 upon protonation.

The proposed reduction mechanism (Scheme II) involves radical anion intermediates. Reactions which depend on radical anion intermediates to achieve a desired transformation can frequently be altered or terminated by the addition of a radical anion quencher, such as dinitrobenzene.[8] The latter is effective in organic solvents but may not be in an aqueous system. We reasoned that 3,5-dinitrobenzoic acid (DNBA) would be soluble in aqueous alkali and act as a radical anion quenching reagent. Its effect on the reduction of 3a by AHQ^{-2} was examined.

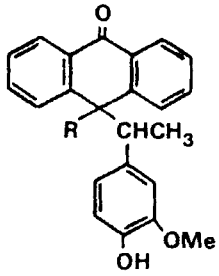
The reaction between 3a and AHQ^{-2} was repeated in the presence of DNBA and no reduction occurred; anthraquinone, along with regular and oxidized condensation products, and 4-hydroxybenzaldehyde were produced. Several control experiments involving DNBA were performed and it was learned that DNBA is capable of accepting two electrons from AHQ^{-2} to give AQ (see Experimental for additional discussion). Thus, it is not certain whether DNBA is quenching radical anion processes or just removing AHQ^{-2} from the system.

Landucci has reported that one electron redox reactions of AQ and $AHQ^{\cdot-}$ (eq. 9) differ significantly in their energetics in organic solvents, but occur simultaneously in water.[3] Consequently, the further search for a compound which would quench $AHQ^{\cdot-}$ and not AHQ^{-2} in an aqueous media seems fruitless.

$$AQ \overset{e^-}{\rightleftharpoons} AHQ^{\cdot} \overset{e^-}{\rightleftharpoons} AHQ^{-2} \quad (9)$$



12, R=CH_2Ph
13, R=$CH_2CH_2COCH_3$



14, R=OH
15, R=H

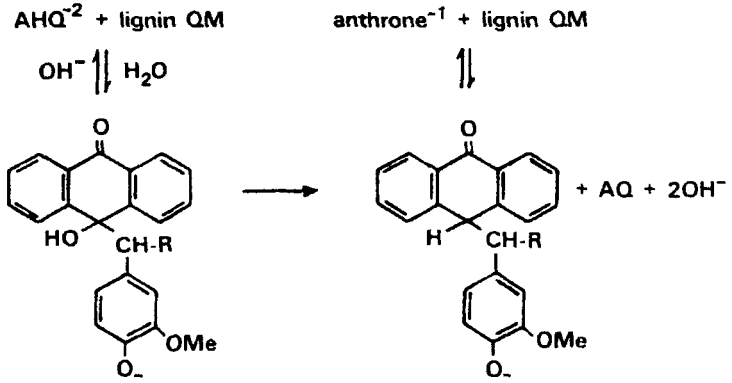
Scope and Significance of AHQ^{-2} Reductions

How general are these AHQ^{-2} reductions? Simple carbonyl compounds do not appear to be reduced by AHQ^{-2}. Recovered without change from reaction with AHQ^{-2} were: acetone, benzaldehyde, acetovanillone (4-OH-3-OMe-$PhCOCH_3$), benzophenone (PhCOPh), anthrone and ferulic acid (4-OH-3-OMe-$PhCH{=}CHCO_2H$). For a successful reduction by AHQ^{-2}, the transfer of electrons to the substrate has to be favorable energetically or the substrate radical anions able to further decompose irreversibly, as described in equation 6, to new species. Apparently the simple carbonyl compounds examined do not meet these criteria.

The AHQ reductions of models 12 and 13 were next examined. These compounds would be expected to undergo an exchange of OH at C_{10} for H in the presence of AHQ^{-2}, without the complication of the C_{10}-alkyl substituent coming off and going on. Unfortunately, 12 and 13 were not reduced by AHQ^{-2} in aqueous alkali, presumably because of their low solubility. The adducts were also not reduced by AHQ^{-2} in aqueous dioxane, a solvent system in which they were somewhat soluble. Surprisingly, adduct 3a was also not reduced when aqueous dioxane was employed as the solvent. Apparently dioxane interferes with the reduction process.

Compounds 14 and 15 had been prepared earlier by us, the former by alkylation of AHQ^{-2} by chloroacetate 8 and the latter by a similar alkylation of anthrone (9).[2] Dialkylation of anthrone does not occur here, presumably because of the bulky nature of the alkylating agent. In other words, the reaction analogous to equation 8, Scheme II, can not occur in this system. Treatment of 14 with excess AHQ^{-2} at 100°, under nitrogen, gave 15. Based on these results, one can speculate that the following reactions of lignin could be occurring during pulping:

The above set of reactions offer an explanation as to how anthrone (found in trace amounts[9]) is formed during AQ pulping. Anthrone adduct 10 has been used as a source of quinonemethides;[2] consequently, anthrone adducts appear to mimic AHQ-adducts in that they enter into equilibria with their constituent parts. Anthrone adducts, or derivatives thereof, may account for other losses of AQ during pulping.[10,11]



(10)

The reduction of adducts by AHQ^{-2} may not be a significant reaction in pulping because of concentration effects. Adduct concentrations should be low due to the reversible nature of the reactions which produce adducts and the alternative chemistry available to AHQ^{-2}. One could imagine that there is a sea of quinonemethides for AHQ^{-2} to react with (causing fragmentation or retardation of condensation, along with AQ liberation), but only an occasional adduct to reduce.

173° Adduct Reactions

Of prime interest is the chemistry displayed by the adducts at 173°, a typical pulping temperature. Adduct 3a was mixed with aqueous alkali inside a sealed container under nitrogen for 2 hours at 173°. The products, after exposure to air and work-up, consisted of AQ, a solid and a small amount of viscous liquid. A ^{1}H-NMR spectrum of the solid indicated that it was probably a mixture of AQ, condensation products and materials that absorb strongly in the 7.2-8.2δ aromatic region. Absorptions in this region have been observed for vanillyl alcohol cooks done in the presence of AHQ^{-2} and are of unknown origin.[5]

A portion of the solid was derivatized with dimethyl sulfate and analyzed by GC-MS. The results are shown in Fig. 1. It should be emphasized that the GC-MS analysis will only provide information on the *volatile* components present in the solid sample. The most prominent signal (D) is due to AQ, which most likely arose during the air oxidation of the bright red (AHQ^{-2}) product solution. The other signals, for which assignments could be made,[7] were condensation products or forms of the starting material, as indicated on Fig. 1. A discussion of how condensation products form can be found elsewhere.[5]

It is apparent that at 173° adduct 3a underwent extensive fragmentation, liberating AHQ^{-2}. Very little of the adduct survived. Likewise, during vanillyl alcohol/alkali reactions in the presence of AHQ^{-2}, adduct 3b is produced, but very little is present at the end of cooking at 173° for 2 hours.[5]

Much of the QM portion of the QM-AHQ adducts, after the 173° reaction, can not be accounted for by the GC-MS analysis technique, although some condensation products were observed.

The amount of AQ recovered after the 173° cook of 3a was only about 50% of theory. Where did the remainder go? Some is still present in adduct form. There is still much to be learned about the fate of adducts and AQ under pulping conditions. It seems reasonable to assume, however, that a small percentage of the orig-

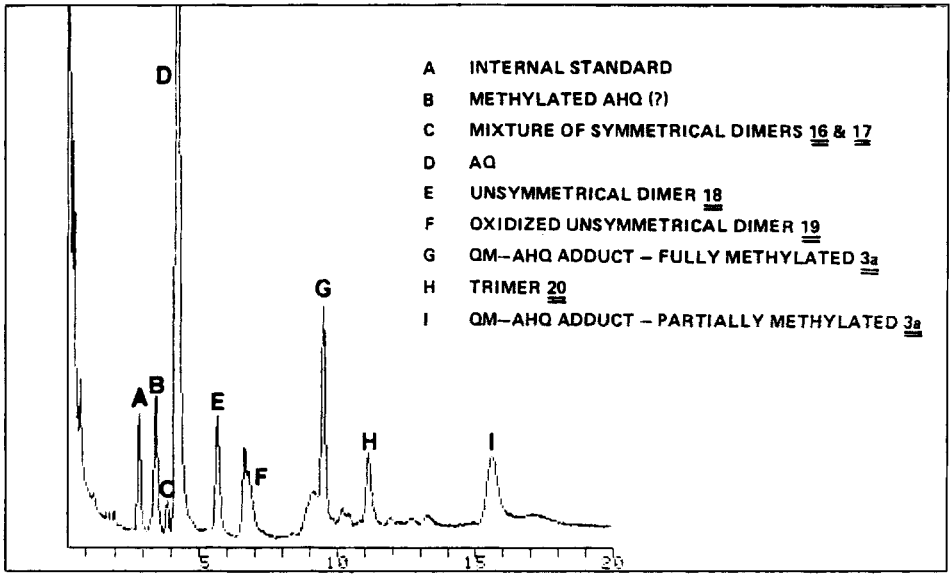
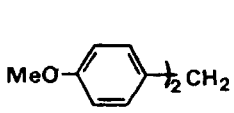
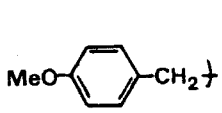


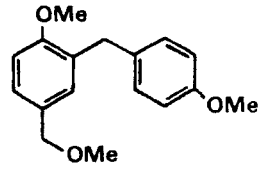
Figure 1. Gas chromatogram of the methylated product obtained from heating 3a in alkali for 2 hours



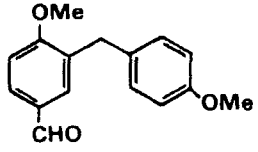
16



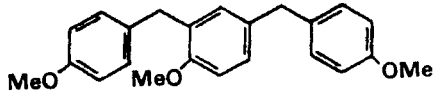
17



18



19



20

inal AQ charge added to pulping liquors will end up as C_{10}-alkylated AHQ or anthrone derivatives after a wood cook. One such derivative, a benzanthrone, has been isolated from pulping liquors.[12,13] A C_2-substituted anthraquinone has also been isolated from pulping liquors.[14]

Competition Experiments

The thermal reactions just discussed point out that the weakest link in the adducts is the C_{10}-benzyl bond. Yet this bond is *relatively* strong compared to alternative p-hydroxybenzyl bonds. The quinonemethides derived from p-hydroxybenzyl substituted compounds are quite reactive. For example, the half-life of a simple substituted QM in neutral methanol at 25° is reported to be 17 seconds.[15] One would expect that the half-life of QM 2a in aqueous alkali to be extremely short, especially at elevated temperatures. Yet, adduct 3a can be prepared in aqueous alkali at 60° and reacts cleanly at 100° to give 10.

Hydrosulfide ion (SH^-), one of the principal components of kraft pulping, is a very good nucleophile. Yet, the reaction of AHQ^{-2} with quinonemethide 2a in the presence of excesses of OH^- and SH^- gave a 87% yield of adduct 3a. If adducts play a major role in delignification, it is now understandable how AQ is capable of functioning at catalytic levels even in the presence of large excesses of hydroxide and hydrosulfide ions, as is the case for kraft-AQ pulping.

Spectroscopic Results

In an attempt to observe adduct dissociation, we have examined the visible and nuclear magnetic resonance (NMR) spectral changes which occur when adduct 3a is heated in alkali.

The visible spectra were recorded in a solvent system which contained sodium hydroxide and dithionite. The alkali served the purpose of promoting reaction and insuring that AHQ existed as its red dianion form. The dithionite was needed to reduce AQ to AHQ;

the former could result from air oxidation of the sample while in the unsealed quartz sample cell.

A solution of adduct 3a in aqueous alkaline dithionite was heated in a quartz cell and the 417 nm absorption measured (Fig. 2); AHQ^{-2} absorbs strongly at this wavelength (Fig. 3). The production of AHQ and/or AQ began above 60° and increased as the temperature was increased. Whether the heating produced AHQ^{-2} (by dissociation of 3a) or AQ (by the reaction described by equation 3) could not, unfortunately, be determined because of the presence of the sodium dithionite. Solubility problems also made the study qualitative, rather than quantitative.

A solution of 3a in D_2O/DMSO-d_6, containing NaOD, was heated while observing its NMR spectrum. The spectrum, which was that of $3a^-$, showed no significant change after one hour at 30° and one hour at 60°. However, when the temperature was increased to 90°, the signals associated with $3a^-$ gradually disappeared and new signals appeared.

Even though the signals were somewhat broad, most could be assigned to 10^{-2}, based on a comparison to a NMR spectrum of 10 in D_2O/DMSO/OD^- at 90°. The signals remaining comprised an AB system with one doublet at 6.34 and another at 6.84δ. These signals are not due to AHQ^{-2}, for which a spectrum was obtained. At no time during the course of heating of 3a did signals due to AHQ^{-2} appear. Nor were there any signals produced which could be attributed to a QM.

Quite obviously the equilibrium between $3a^-$ and QM 2a and AHQ^{-2} lies strongly on the side of $3a^-$, since neither 2a or AHQ^{-2} appeared in the NMR spectrum of warm solutions of $3a^-$. However, both 2a and AHQ^{-2} must have been formed since they are prerequisites for the production of 10^{-2}, which was observed.

The NMR sample at the conclusion of the experiment contained a large amount of solid, presumably AQ. The spectrum did not, however, show typical AQ signals, probably because AQ was not in solution. The pair of AB signals at 6.3 and 6.8δ observed at 90° could be an anthraquinone phenolate charge transfer complex. Quinones

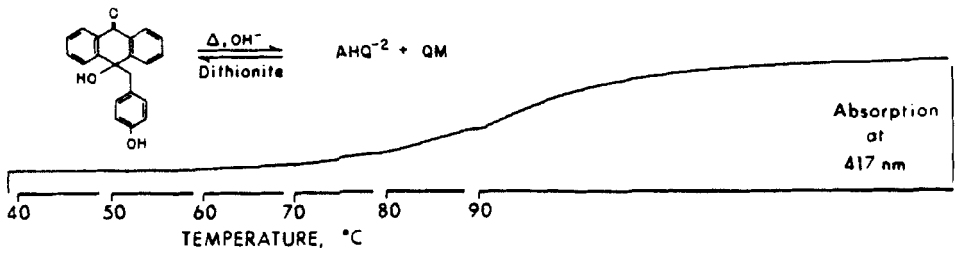


Figure 2. The change in absorbance at 417 nm as a solution of adduct in alkaline dithionite is warmed rapidly from one temperature to another and then held for a time, before warming another 10°C

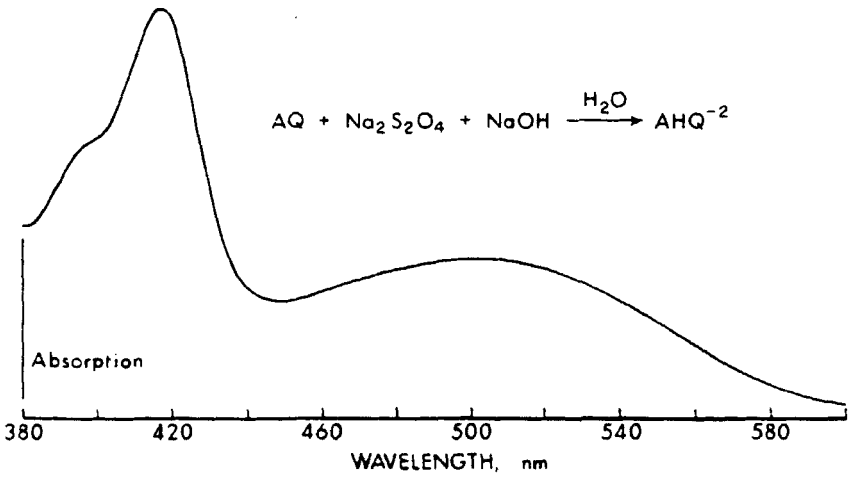


Figure 3. Visible spectrum of a solution of anthraquinone in alkaline dithionite

are known to complex with phenols.[16] The AQ portion of a phenolate charge transfer complex would be expected to show upfield NMR signals due to a greater electron density in the AQ ring.

In attempts to generate AQ-phenolate charge transfer complexes, we added AQ to solutions of 10 and of p-cresol in D_2O/OD^-/DMSO-d_6 and recorded NMR spectra. Even though the solutions were saturated with suspended AQ particles, no signals other than

solvent, 10^{-2} and p-cresolate ion were observed. These results do not, however, rule out the possibility of a soluble AQ-phenolate complex growing from low concentrations of AQ produced during the thermal reactions of $3a^{-}$.

Conclusions

Adducts of simple quinonemethides and AHQ enter into an equilibrium with their constituent parts at temperatures above 60° in aqueous alkali. At 100°, in the absence of oxygen, the adducts are reduced by AHQ to give anthrone adducts. At 173° the adducts largely, but not completely, decompose, releasing about 1/2 of the trapped AHQ back to the medium.

The lack of interference by hydroxide and hydrosulfide, the crossover experiment and the spectral results all suggest that the equilibrium which exists between QM-AHQ adducts and their QM and AHQ^{-2} constituent parts at elevated temperatures lies strongly on the side of the adduct. This preference could, however, change as the QM increases in bulk and the adduct acquires some steric strain.

EXPERIMENTAL

The equipment employed, procedure for preparing AHQ^{-2} and procedure for derivatizing by methylation are explained elsewhere.[2,5]

Low Temperature Air Cook of 10-Hydroxy-10-(4'-hydroxybenzyl)-9(10H)-anthracenone (3a). - In a small Erlenmeyer flask was placed 1.7 g of $3a^{2}$ and about 20 mL of 1N sodium hydroxide. The flask was flushed with nitrogen, stoppered and heated on a hot plate. The clear solution became red colored upon heating. Opening the flask to air caused the red color to change to light orange and a precipitate to form. After about 20 minutes the orange tint had disappeared and the pale yellow solution was rich in precipitate.

The flask was cooled and the contents filtered to afford 0.97 g of anthraquinone. The filtrate was acidified and refiltered to

give 0.35 g of 80% pure 10,10-di(4'-hydroxybenzyl)-9(10H)-anthracenone (10), as shown by ^{1}H-NMR and IR.[2] The filtrate of this last filtration was extracted several times with ether. The combined ether extracts were dried (Na_2SO_4) and evaporated to give 0.30 g of an oil. The ^{1}H-NMR spectrum of the oil in DMSO showed 9.04 (ArOH), 6.6-7.0 (Aryl) and 3.4-3.7δ (Ar-CH_2-Ar) which suggested that the material was composed of phenolic condensation products derived from p-hydroxybenzyl alcohol (4).

A sample of 4[17] was treated with aqueous alkali under the conditions described above. Acidification, ether extraction, drying and evaporation gave a gummy residue which exhibited as ^{1}H-NMR similar to the oil described above.

Low Temperature Air Cook of 10-Hydroxy-10-(4'-hydroxy-3'-methoxybenzyl)-9(10H)-anthracenone (3b). - A solution of 1.33 g of 3b[2] in 20 mL of 1N sodium hydroxide was stirred at 85-90° for 4 hours, during which time the dark orange colored solution became light yellow and a precipitate had formed. The solution was cooled and filtered to give 0.72 g of solid AQ. The filtrate was acidified to produce a red-brown precipitate, which was collected by filtration; the weight was 0.26 g. A portion of this sample was methylated and analyzed by gas chromatography - mass spectroscopy (GC-MS). The sample was similar in its GC-MS to the methylated product which results from heating vanillyl alcohol (5) with aqueous alkali,[5] in that both contained condensation products 17, 18, and 20.

Visible Absorption Spectra of AHQ^{-2} and Decomposing Adduct (3a). - Sodium dithionite (3.4 g of 90% technical grade) was dissolved in 100 mL of distilled water and then filtered through Celite to remove fine particles. Sodium hydroxide (1.0 g) was added to the filtrate and the volume brought to 250 mL by the addition of distilled water. Anthraquinone (2.5 mg) was weighed into a 100 mL volumeteric flask, and then diluted to volume with the alkaline dithionite solution. The visible spectrum from 380 to 600 nm was

recorded, relative to an alkaline dithionite blank solution. The results are shown in Fig. 3.

A 2.5 mg sample of 10-hydroxy-10-(4'-hydroxybenzyl)-9(10H)-anthracenone (3a)[2] was weighed into a 100 mL volumetric flask and the alkaline dithionite solution added to bring the volume to 100 mL. The spectrometer was set at 417 nm and the absorption of the above solution measured as a function of temperature (30-90°). The results are shown in Fig. 2.

Crossover Experiment Between 3a and 6. - A mixture of 0.5 g (1.6 mmoles) of 10-hydroxy-10-(4'-hydroxybenzyl)-9(10H)-anthracenone (3a)[2], 0.34 g (1.6 mmoles) of 4-acetoxy-3-methoxybenzyl chloride (6)[2] and 0.25 g (6.2 mmoles) of sodium hydroxide in about 100 mL of water was stirred under nitrogen while warming. The temperature was raised from 25° to 90-100° and then held there for 2 hours. The solution was cooled and filtered to give 0.24 g of solid (A). The filtrate was acidified and filtered to give 0.32 g of solid (B). Ether extraction of this filtrate produced only a very small residue.

Solids A and B were methylated and analyzed by ^{1}H-NMR and GC-MS. Solid A was predominantly adduct 3a while solid B contained roughly a 2:1 ratio of 3a:3b, along with phenolic condensation products. The gas chromatogram of derivatized solid B and interpretation of the mass spectra of the condensation products have been incorporated into an earlier publication.[7] The identification of the products rests on comparison of NMR and GC-MS data of known samples and analogous materials.

Preparation of Adduct 3a in the Presence of Sodium Sulfide. - A procedure identical to before,[2] except with the inclusion of 2 equivalents of sodium sulfide, gave an 87% yield of crude adduct 3a.

100° Anaerobic Reactions of 10-Hydroxy-10-(4'-hydroxybenzyl)-9(10H)-anthracenone (3a). - A solution of 1.02 g (3.2 mmoles) of

3a[2] in 20 mL of 1N NaOH was stirred under nitrogen at reflux for 7 hours, cooled and exposed to air. Filtration gave anthraquinone which, after drying, weighed 0.33 g (1.6 mmoles). Acidification of the filtrate with concentrated hydrochloric acid gave a precipitate. Filtration and air drying afforded 0.60 g (1.4 mmoles) of 10,10-di(4'-hydroxybenzyl)-9(10H)anthracenone (10), mp 211-214° (methanol-water), identical to a sample of the same material prepared by alkylation of anthrone (9) with 2 equivalents of 6.[2]

The reaction was repeated and aliquots withdrawn at 3, 5, 10, 15, 20, 30, 60, 120, and 240 minutes after the start. Each sample was worked-up as described above. After methylation, the samples were analyzed by GC and in some cases GC-MS.

The 100° anaerobic reactions of adduct 3a were repeated several times with different levels of AHQ^{-2} present. The ratios of 3a to AHQ^{-2} examined were 1:1, 1:4, and 1:8. The products were worked-up as described above and analyzed by ^1H-NMR.[2] The level of 10-(4'-hydroxybenzyl)-9(10H)-anthracenone (11)[2] increased as the ratio of AHQ^{-2} increased. With 8 equivalents of AHQ^{-2}, 11 accounted for roughly 50% of the product, with the remainder being mostly starting material 3a and a little 10. No reduction product 11 was observed (performed twice) when the 1:8 ratio of 3a to AHQ^{-2} was employed in a solvent system of 50:50 dioxane-water.

Reactions Involving 3,5-Dinitrobenzoic Acid (DNBA). - A mixture of 1.34 g (6.3 mmoles) of DNBA,[17] 0.53 g (13 mmoles) of sodium hydroxide and 1.05 g (3.15 mmoles) of 3a in 100 mL of water was stirred at reflux under nitrogen for 5 hours, cooled, exposed to air and filtered to remove AQ. The filtrate was acidified to produce a precipitate "A", which was isolated by filtration. The filtrate produced here was extracted with ether, which in turn was washed with water, dried (Na_2SO_4) and evaporated to a residue "B". Recrystallization of "B" from methanol-water gave as a first crop DNBA and later 4-hydroxybenzaldehyde, the structures of which were established by comparing IR and NMR spectra to authentic samples.[17]

Precipitate "A" was dissolved in ether and extracted with sodium bicarbonate solution. The ether was dried (Na_2SO_4) and evaporated to give a sirup (0.06 g). The bicarbonate solution was acidified to give 0.71 g of DNBA. The sirup was methylated and analyzed by GC-MS; components which were observed were AQ, dimers 16 and 19, trimers (20 was the major one, but several aldehyde trimers were also present) and a tetramer of p-hydroxybenzyl alcohol (4). Details of the mass spectra are provided elsewhere.[7]

Nitrobenzene is a known oxidizer of benzyl alcohol.[1] Apparently, 3,5-dinitrobenzoic acid is also performing a similar role, since the levels of aldehydic products were relatively high.

The dropwise addition of a solution of DNBA in aqueous alkali to an aqueous solution of AHQ^{-2} rapidly discharged the red color (AHQ^{-2}) and resulted in a grey-green colored solution containing precipitated AQ. The addition of p-acetoxybenzyl chloride (6) to an aqueous alkaline solution of DNBA gave rise to phenolic condensation products, derived from 6, but no p-hydroxybenzaldehyde.

These experiments suggest that, during the thermal decomposition of adduct 3a, DNBA accepts electrons from AHQ^{-2}, transforming the latter to AQ, and the electron rich DNBA causes some oxidation of phenolic products. Because AHQ^{-2} is removed from solution, the reduction of 3a by AHQ^{-2} can not proceed.

Reactions of Adducts 12 and 13 with AHQ^{-2}. - To a 200 mL aqueous solution of AHQ^{-2} (13.5 mmoles), containing 2.1 g (52 mmoles) of sodium hydroxide, was added 2.0 g (6.7 mmoles) of 10-hydroxy-10-benzyl-9(10H)-anthracenone (12)[2] in small portions under nitrogen. The suspension was stirred under nitrogen for 5 hours at 100°, cooled and filtered. The collected solid was a mixture of AQ and 12. It was possible to separate AQ and 12 by slurrying the mixture in 1N sodium hydroxide containing sodium dithionite (AQ $\longrightarrow$ AHQ^{-2}), filtering and washing with $NaOH/Na_2SO_4$ several times; 75% of the originally added 12 was recovered.

The reaction was also repeated several times with the following variations: (a) a solvent system of 50:50 dioxane-water, (b) a solvent system of 75:25 dioxane water, and (c) a 50:50 dioxane-water system at 185° in a sealed bomb containing 12, AQ and glucose. In each of these cases 12 was recovered and no detectable reduction occurred.

A mixture of 1.5 g of 10-hydroxy-10-(3'-oxobutyl)-9(10H)-anthracenone (13)[2] and 8 equivalents of AHQ^{-2} were stirred at 100° for 4 hours under nitrogen. The suspension was cooled, exposed to air and filtered to give a mixture of 13 and AQ.

Reduction of 10-Hydroxy-10-(4'-hydroxy-3'-methoxy-α-methylbenzyl)-9(10H)-anthracenone (14) with AHQ^{-2}. - To an aqueous solution (150 mL) of AHQ^{-2}, prepared from 1.9 g (9.1 mmoles) of AQ and containing 1.4 g (35 mmoles) of sodium hydroxide, was added 0.4 g (1.15 mmoles) of 14.[2] The mixture was stirred under nitrogen for 4 hours at 100°, cooled, exposed to air and filtered to give 2.0 g of AQ. The filtrate was acidified to give 0.02 g of solid. NMR and GC analysis showed that the product was a complex mixture of components of which 10-(4'-hydroxy-3'-methoxy-α-methylbenzyl)-9(10H)-anthracenone (15) was one. This fact was established by comparing the crude product to that of an authentic sample 15[2] and observing the characteristic doublet at 4.46 ($Ar_2\underline{CH}CH$). Also the GC retention time and mass spectrum of a component in the methylated product mixture matched that of methylated 15.[2]

High Temperature Thermal Reactions of Adduct 3a. - A 1.0 g sample of 3a[2] and 30 mL of 0.5N NaOH were placed in a titanium pressure vessel. The bomb was flushed with nitrogen, capped and rotated for 2 hours in an oil bath heated at 173°. The bomb was then cooled to room temperature and the bright red colored solution removed and stirred in air. Filtration gave 0.27 g of AQ. The filtrate was acidified and 0.54 g of solid collected by filtration. This latter filtrate was extracted with ether, which in turn was dried (Na_2SO_4) and evaporated to afford 0.10 g of residue, which was not further analyzed.

A ^{1}H-NMR of the solid showed a broad set of signals in the 3.2-3.8 range where Ar-CH_2-Ar absorptions come[5] and an even broader set of signals in the 6.6-8.8 range. No significant levels of 3a appeared in the spectrum. A sample of the solid was methylated and analyzed by GC-MS. The results are shown in Fig. 3.

The experiment was repeated twice more to give qualitatively the same results.

NMR Studies. - About 50 mg of 10-hydroxy-10-(4'-hydroxybenzyl)-9(10H)-anthracenone (3a) was dissolved in about 1/2 mL of DMSO-d_6 and diluted with about 1/2 mL of 20% NaOD in D_2O. An hour after preparation of the solution a NMR spectrum at 30° was recorded ($\Delta\delta$ = upfield shift from unionized 3a[2]): 2.85 (s, 2, CH_2, $\Delta\delta$ = 0.21), 5.30 (d, J = 8 Hz, 2, o-Aryl, $\Delta\delta$ = 0.38), 5.78 (d, J = 8 Hz, 2, m-Aryl, $\Delta\delta$ = 0.38) and 7.2-7.9δ (m, 8, anthrone ring protons, $\Delta\delta$ = 0.2).

The solution was heated to 60° inside the NMR probe and spectra recorded at 0, 40, and 70 minutes. The last spectrum was still basically identical to the 30° spectrum except for the appearance of low intensity doublets at 6.3 and 6.8δ. The temperature of the probe was increased from 60 to 90° over a 2 minute period. A NMR spectrum after 10 min at 90° showed the appearance of signals at 6.34 and 6.84 (AB doublet, J = 8 Hz), 5.78 (s) and 3.3δ (broad s); the peaks associated with 3a$^-$ had broadened and the doublets were no longer resolved. Spectra were recorded at 45, 80, 110, and 150 min. Except for the 6.34 and 6.84 doublets, the signals were somewhat broad after 150 min at 90°. The signals at 5.30 and 2.85δ, associated with 3a$^-$, were barely detectable above the baseline noise. The sample, upon removal from the NMR probe, was saturated with solid precipitate.

About 50 mg of 10,10-di(4'-hydroxybenzyl-9(10H)-anthracenone (10) was dissolved in about 1/2 mL of DMSO-d_6 and diluted with 1/2 mL of 20% NaOD in D_2O. NMR spectra at 30° and 90° were recorded; they differed slightly in the resolution of the aryl signals and sharpness of the benzyl signals ($\Delta\delta$ = upfield shift from unionized

10^2): 3.42 (s, 2, CH_2, $\Delta\delta$ = 0.21), 5.78 (s, 8, phenolic aryl, $\Delta\delta$ = 0.40) and 6.1-8.0δ (set of sharp signals, the last being a doublet, 8, anthrone ring, $\Delta\delta$ = 0.3-1.2). The previous sample, heated $3a^-$, contained all these signals, only somewhat broadened.

Approximately, 50 mg of AQ was placed in a mixture of NaOD, D_2O, DMSO-d_6 and sodium dithionite. The solution became dark red in color, indicative of AHQ^{-2}; it was filtered into an NMR tube and a spectrum recorded at 90°: 7.05 (about 0.2 ppm wide, area 1) and 8.17δ (about 0.2 ppm wide, area 1). Neither of these two signals were observed in the spectra of $3a^-$, recorded while heating.

Anthraquinone was added to the solution of 10^{-2} described above and NMR spectra recorded at 30 and 90°. The spectra showed only 10^{-2}. Likewise, AQ was added to a solution of p-cresol in D_2O/OD^-/DMSO-d_6 and a spectrum taken at 30°; only sodium p-cresolate was observed.

REFERENCES

1. J. Marton in Lignins, K. V. Sarkanen and C. H. Ludwig Editors, Wiley Interscience, NY, 1971, Chapter 16.
2. D. R. Dimmel, D. Shepard, T. A. Brown, and R. D. McKelvey, Canadian Wood Chemistry Symposium, Harrison Hot Springs, B.C., Sept. 19-21, 1979; J. Org. Chem., 47, 22,29 (1982).
3. L. L. Landucci, Canadian Wood Chemistry Symposium, Harrison Hot Springs, B.C., Sept. 19-21, 1979; Tappi, 63 (7), 95 (1980).
4. J. Gierer, O. Lindeberg, and I. Noren, Holzforschung, 33, 213 (1979).
5. D. R. Dimmel, D. Shepard, and T. A. Brown, J. Wood Chem. Technol., 1, 123 (1981).
6. E. S. Gould, Mechanism and Structure in Organic Chemistry, Holt, Rinehart and Winston, New York, 1959, p. 141.
7. D. R. Dimmel and D. Shepard, J. Wood Chem. Technol., 1, 147 (1981).
8. N. Kornblum, Angew. Chem. Internat. Edit., 14, 734 (1975).
9. I. Gourang, R. Cassidy, and C. W. Dence, Tappi, 62 (7), 43 (1979).

10. W. H. Algar, A. Farrington, B. Jessup, P. F. Nelson and N. Vanderhoek, Appita, 33, 33 (1979).

11. B. I. Fleming, G. J. Kubes, J. M. MacLeod, and H. I Bolker, Tappi, 62 (7), 55 (1979).

12. T. J. Fullerton and S. P. Ahern, J.C.S. Chem. Commun., 457 (1979).

13. D. W. Cameron and E. L. Samuel, Tetrahedron Letters, 3035 (1979).

14. T. J. Fullerton and B. I. Fleming, Svensk Papperstid., 83, 396 (1980).

15. L. J. Filar and S. Winstein, Tetrahedrom Letters, 9 (1960).

16. J. March, Advanced Organic Chemistry, 2nd Ed., McGraw-Hill, N.Y., 1977) p. 79-82 and references cited therein.

17. Aldrich Chemical Company, Milwaukee, Wisconsin.