Nucleophilicities of Selected Ions in Water at 195 °C

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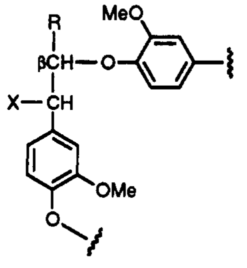
The reaction of a benzyl aryl ether (3) with selected ions was studied to determine relative nucleophilicities at 195 °C in water. Nucleophilic displacement by the ions occurred at the benzyl carbon to liberate a phenolic group. The primary products of the displacement were independently synthesized and reacted in alkali to determine their stability. Hydrosulfide ion was 20 times more reactive than hydroxide ion with this substrate, while anthrahydroquinone ion was 17 times more reactive.

Introduction

Wood is principally composed of fibrous carbohydrate material and amorphous polymeric lignin. The goal of chemical pulping is to separate and remove the lignin component from the carbohydrate fibers. Lignin monomer units are held together largely by alkyl aryl ether bonds, with the β-O-4 type (A) accounting for 50–60% of the intermolecular linkages and the α-O-4 type (B) for 6–8%.[1] Reagents are present during pulping to promote the cleavage of these other bonds and the formation of alkali-soluble phenolic products.



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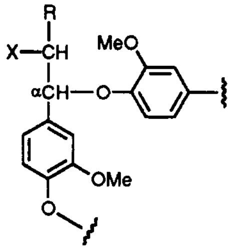

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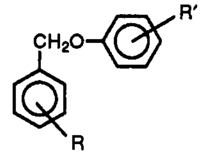

1; R = H, R′ = *p*-COOH
2; R = *p*-COOH, R′ = *p*-NO_2
3; R = *m*-COOH, R′ = *m*-CF_3

One way pulping reagents can promote delignification is by functioning as nucleophiles.[2] The effectiveness of pulping reagents may be related to their relative nucleophilicities in water at 170 °C, the conditions of pulping. This report addresses the relative nucleophilicities of selected ions at high temperatures in aqueous alkali toward a saturated carbon site. A corresponding study involves the relative nucleophilicities of pulping ions toward a conjugated unsaturated carbon site.[3] Attack of reagents at both types of sites could be important to effective delignification.

Nucleophilicity not only depends on the type of substrate under attack but on many other factors, including solvent type and reaction temperature.[4] It is not clear how effectively nucleophiles will be solvated at 170–200 °C and whether the nucleophilic orders observed at room temperature will apply at high temperatures. A fundamental understanding of these issues is important to developing better pulping systems.

Results and Discussion

Substrate Selection. A model compound was needed which exhibited good reactivity at 170 °C, would not undergo competing base-promoted elimination reactions, and represented the abundant ether linkages present in lignin. The alkali-soluble benzyl aryl ether compound 1 was the first model selected for study. It was anticipated that the benzyl ether would be more reactive than an alkyl aryl ether toward S_N2 reactions[4] and provide more latitude for reaction temperature variation. However, 1 was found to be relatively stable at 170 °C in aqueous alkali.

Compound 2, which contains a nitro group on the phenolate portion of the molecule, was sufficiently reactive in sodium hydroxide solutions at 170 °C. The electron-withdrawing group enhances the reactivity of the site under attack and provides additional stabilization of the negative charge on the leaving phenolate ion. The nitro group, however, was not stable to hydrosulfide ion at 170 °C. Therefore, 2 was not a suitable model.

Structure–reactivity studies indicate that the trifluoromethyl group is a relatively strong electron-withdrawing group, though not as strong as the nitro group.[4] Therefore, benzyl ether 3 was synthesized and studied. The *m*-trifluoromethyl group was chosen to avoid undesirable steric effects of an ortho position and possible quinone methide formation at the para position. Quinone methide formation of the liberated phenolate ion would hamper product analysis.

Mechanistic Studies. The reactions of ether 3 were investigated in oxygen-free water solutions which contained hydroxide, hydrosulfide, and anthrahydroquinone ions. The expected reaction pathway of 3 is shown in eq 1. The disappearance of 3 and formation of products was followed using GC techniques. The identities of all products were confirmed by synthesizing or purchasing the products and comparing their GC and GC-MS properties.

• Abstract published in *Advance ACS Abstracts*, October 15, 1993.

(1) Sjostrom, E. *Wood Chemistry: Fundamentals and Applications*; Academic Press: New York, 1981.

(2) Gierer, J. *Holzforschung* 1982, *36*, 43.

(3) Reed, G. A.; Dimmel, D. R.; Malcolm, E. W. *J. Org. Chem.*, preceding paper in this issue.

(4) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 2nd ed.; McGraw-Hill: New York, 1977.

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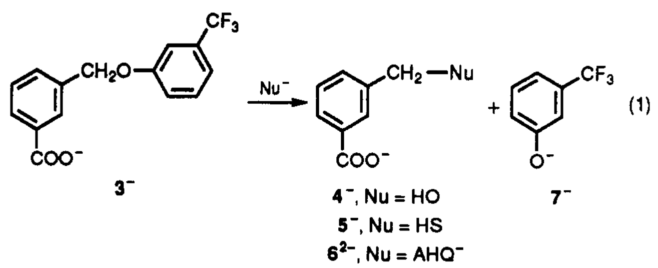


(1)

Benzyl ether 3 was heated in aqueous sodium hydroxide, simulating soda pulping reactions, to give 3-(hydroxymethyl)benzoic acid (4) and 3-(trifluoromethyl)phenol (7) (eq 1, Nu = HO$^-$). Analysis of the reaction products, shown in Figure 1, indicated roughly a 100% mass balance when adding the concentrations of 3 and 4; less than a perfect balance existed when adding the concentrations of 3 and 7.

The stabilities of products 4 and 7 were investigated. Benzyl alcohol 4 did not react with hydroxide ion to form secondary products. Phenol 7, however, degraded after extended reaction times. Its concentration decreased by approximately 40% over a 6-h period at 195 °C. The rate of disappearance of 7 was not increased by the presence of hydrosulfide ion. Products from the reaction of 7 were not found by GC-MS. Resorcinol, a possible product of hydroxide substitution at the site of the trifluoromethyl group on 7, was not observed. Resorcinol was also found to degrade under similar conditions except at a slower rate.

Reactions similar to those which caused the degradation of 7 did not appear to consume the starting benzyl ether 3. The mass balance between 3 and the primary product 4 was constant while that between 3 and the product phenol 7 was not constant at extended reaction times. This indicated that only 7 was unstable.

Compound 3 was heated in solutions containing sodium sulfide; the latter should be completely hydrolyzed to hydroxide and hydrosulfide ions.[3,5] Conditions were chosen to simulate kraft pulping reactions. The primary products of the reaction were expected to be 3-(mercaptomethyl)benzoic acid (5), from HS$^-$ displacement, 3-(hydroxymethyl)benzoic acid (4), from HO$^-$ displacement, and phenol 7 (eq 1, Nu$^-$ = HO$^-$ and HS$^-$). Analysis of the reaction mixture showed a good mass balance between 3 and 7 (Figure 2); the reaction time was shorter than in the HO$^-$ case, meaning that 7 had less time to undergo secondary degradation reactions.

The relative amounts of products 4 and 5 reflect the relative nucleophilicities of HO$^-$ and HS$^-$. For example, if the two ions have identical nucleophilicities, the ratio of 4:5 should be 11:1 on the basis of the 11:1 ratio of HO$^-$ to HS$^-$ employed. Benzyl alcohol 4, already shown to be stable in 195 °C alkali, was observed in only trace amounts. Benzyl mercaptan 5 was not detected, but secondary products derived from 5 were observed. On the basis of product analyses, HS$^-$ appears to be superior to HO$^-$ as a nucleophile in displacement reactions of 3 at 195 °C.

The hydrosulfide reaction gave rise to three new products, 3-toluic acid (8), isophthalic acid (9), and 3-(((3′-carboxybenzyl)thio)methyl)benzoic acid (10), all of which were suspected to be secondary reaction products of mercaptan 5. An independently synthesized sample of 5 was degraded at a moderate rate at 195 °C to form primarily 8 with small amounts of 9.

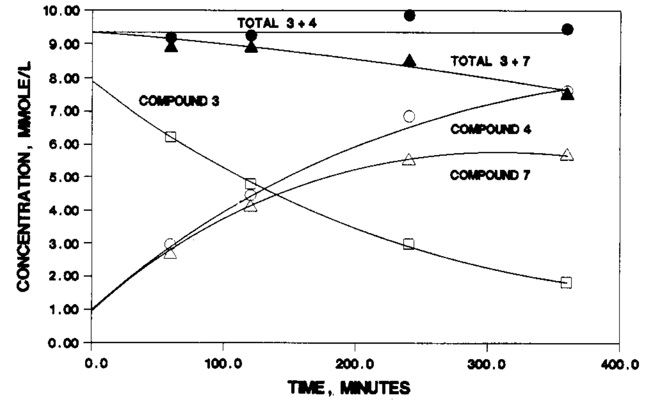


Figure 1. Mass balance for the reaction of 3 in 1.04 M NaOH at 195 °C.

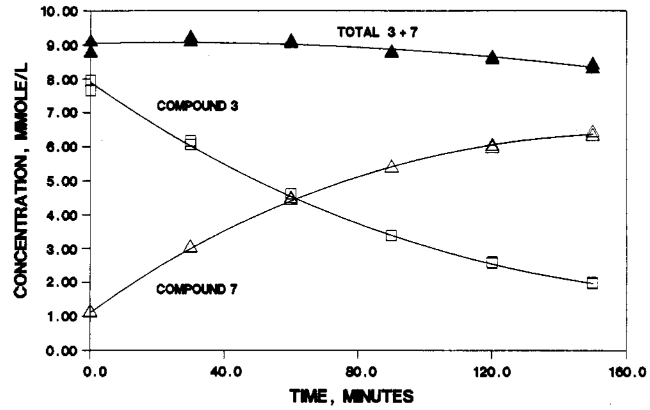
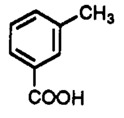


Figure 2. Mass balance for the reaction of 3 in 0.958 M NaOH and 0.0874 M NaSH at 195 °C.



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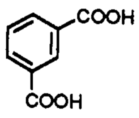

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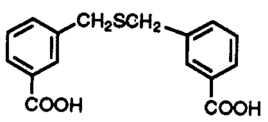

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When mercaptan 5 was heated in a deuterium oxide solution containing sodium deuteroxide, one deuterium atom was incorporated into the methyl group of toluic acid. This evidence suggested that toluic acid (8) was formed from 5 by the loss of elemental sulfur, followed by protonation of the resulting carbanion (Scheme I). In the presence of hydrosulfide ions or elemental sulfur, however, 5 was very rapidly converted to 9, with lesser amounts of 8. Polysulfide, formed from elemental sulfur, may act as an oxidant to form 9 (Scheme I).

Heating mercaptan 5 at 195 °C in the presence of 3 led to a product mixture consisting of 8 and 9 as well as 10; the latter apparently is formed by the nucleophilic attack of 5 on the starting material. Sulfide 10 was shown to be stable in solutions containing hydroxide and hydrosulfide ions. In addition, the degradation rate of benzyl ether 3 was virtually unaffected by the presence of the dimer. Therefore, 10 was considered to be a stable end product.

Benzyl ether 3 was heated in solutions containing both hydroxide and anthrahydroquinone ions to simulate soda-AQ pulping reactions. The expected primary products were alcohol 4, 10-hydroxy-10-(3′-carboxybenzyl)-9(10*H*)-

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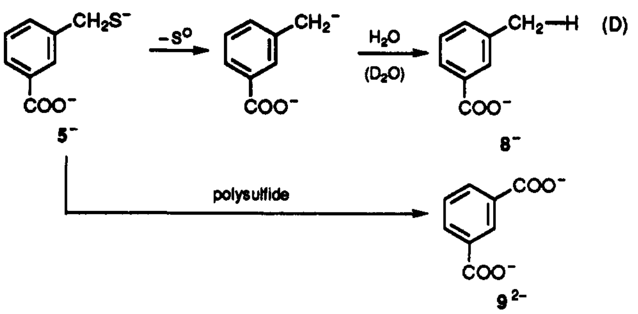
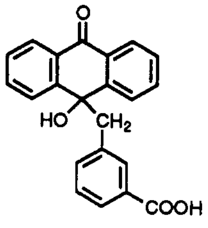
(5) Blythe, D. A.; Schroeder, L. R. *J. Wood. Chem. Technol.* 1985, *5*, 313.

Scheme I



anthracenone (6), and phenol 7 (eq 1, Nu⁻ = HO⁻ and AHQ²⁻). Analysis of the reaction mixture showed a good mass balance between 3 and 7 (Figure 3). Once again, only trace amounts of 4 were detected, indicating anthrahydroquinone ion was a much stronger nucleophile than hydroxide ion. The expected AHQ addition product 6 was also observed in only trace amounts. A number of secondary products were observed; these included previously discussed 8 and 9, together with moderate amounts of compounds 11, 12, and 13.



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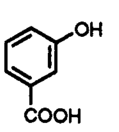

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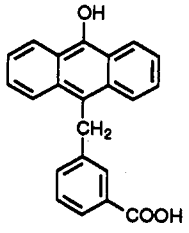

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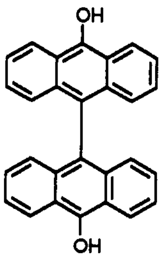

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The reactions of AHQ adduct 6 were investigated to determine its degradation pathways. A sample of 6 was synthesized by methods previously reported by us.[6] The synthetic 6 was found to degrade to 8 and 9 under soda and soda–AHQ reaction conditions. Minor components of the reaction mixture included 11, 12, and 13. Dimer 13 was also formed under reaction conditions in AHQ solutions which did not contain model compounds or their degradation products. On the basis of these findings, we conclude that anthrahydroquinone reacted with benzyl ether 3 to form primary product 6, which subsequently decomposed to form a variety of secondary products.

Kinetic Studies. Benzyl ether 3 was heated at 195 °C in oxygen-free aqueous solutions which contained sodium hydroxide and combinations of sodium hydroxide and sodium hydrosulfide, disodium anthrahydroquinone, sodium sulfite, and sodium thiosulfate. Because changes in the ionic strength of the medium could alter the observed rate constants, efforts were made to maintain a constant ionic strength level (1.1 M).

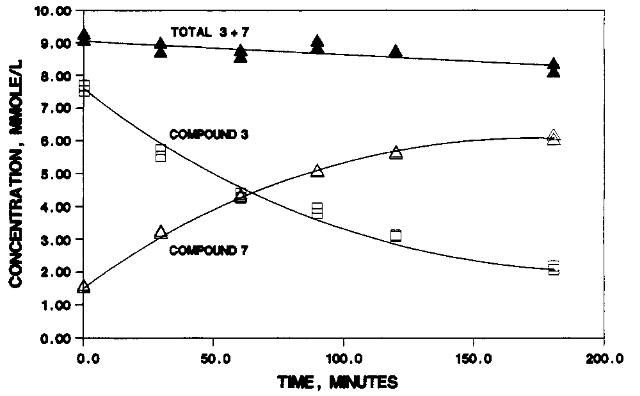

Figure 3. Mass balance for the reaction of 3 in 0.785 M NaOH and 0.0872 M AHQ at 195 °C.

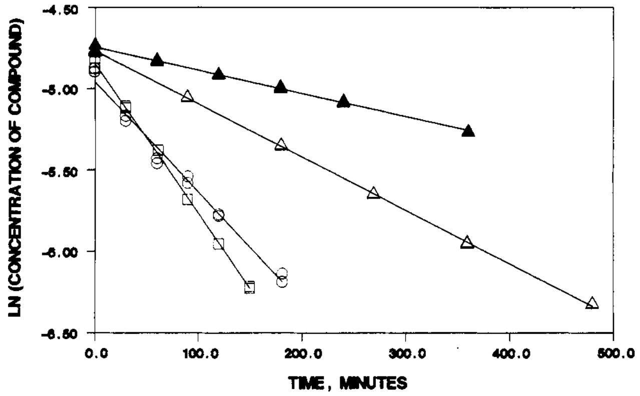

Figure 4. Pseudo-first-order reactions of 9.0 mM compound 3 at 195 °C: △, 1.05 M NaOH; ▲, 0.519 M NaOH; □, 0.958 M NaOH and 0.0874 M NaSH; and ○, 0.785 M NaOH and 0.0872 M AHQ.

Excesses of each reagent were used so that their concentrations remained essentially constant. This allowed use of pseudo-first-order rate expressions to follow the reaction.[7] An excellent fit of data over 2 half-lives with each additive was observed (Figure 4). The reactions between 3 and other nucleophiles were assumed to be first order with respect to the nucleophile.

The slopes of the lines (Figure 4) were calculated from regression analysis to obtain the observed rate constants. Second-order rate constants were calculated using eq 2,[3] where [HO⁻] = concentration of hydroxide ion (M) and [Add⁻] = concentration of additive (M).

$$k_r = k_{HO}[HO^-] + k_{Add}[Add^-] \qquad (2)$$

Correlation factors (R^2) were 0.996 or better for NaOH and NaOH/NaSH reactions and 0.985 for NaOH/AHQ. Triplicate runs were performed in these cases. Only single runs with a limited number of data points were done for Na_2SO_3 and $Na_2S_2O_3$. Only crude estimates of nucleophilic strengths were needed in the latter cases.

In the sodium hydrosulfide case, two corrections were made to the observed rate constant for disappearance of benzyl ether 3 in order to arrive at a value of k_{HS}. These corrections were a result of reactions of 3 with nucleophiles in the system, other than HS⁻ and HO⁻. Primary product 5 reacted with 3 to give dimer 10. The rate of formation

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(6) Dimmel, D. R.; Shepard, D. *J. Org. Chem.* **1982**, *47*, 22.

(7) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; John Wiley and Sons: New York, 1981; pp 37–82.

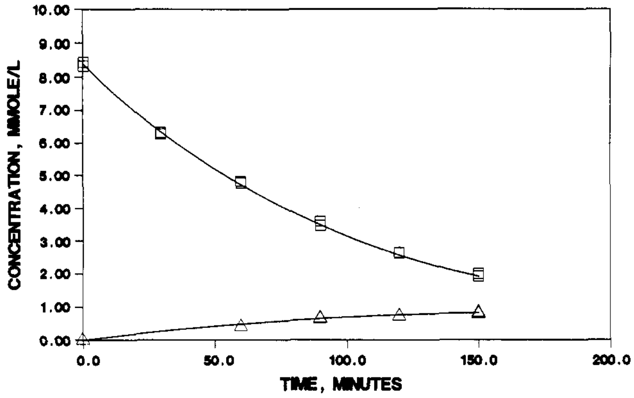

Figure 5. Concentration vs time profiles for the disappearance of compound **3**, □, and appearance of dimer **10**, △, for the reaction of **3** with NaSH/NaOH at 195 °C.

of **10** was followed (Figure 5) to get an estimate of the contribution of reaction of **5** to the overall disappearance of **3**.

The sodium sulfide solutions employed contained small amounts of sodium sulfite and sodium thiosulfate as impurities; the effect of these sulfoxy species on the degradation of **3** was also investigated. Starting material **3** was heated with a 100-fold excess of sodium hydroxide and a 10-fold excess of sodium sulfite in one case and sodium thiosulfate in another case. Analysis of the data showed that both sulfide and thiosulfate ions were more reactive than hydroxide ion. Large 95% confidence intervals were calculated for these second-order rate constants because (1) duplicates were not performed, (2) only three time periods (including the zero time) were used to calculate the rate constant, and (3) the experimental error associated with the hydroxide ion rate constant is propagated through the calculations.

Second-order rate constants of the reaction of **3** with the various nucleophiles studied are shown in Table I. The experimental errors for the various nucleophiles are larger than those for hydroxide, since hydroxide ion is present during the other nucleophilic reactions and the error limits associated with hydroxide ion are propagated through the calculations. Although precautions were taken to eliminate oxygen during the experimental setup, low levels of oxygen could affect AHQ^{2-} and HS^- concentrations and help contribute to the larger 95% confidence limits in these cases.

Table I. Reaction Rate Constants of 3 at 195 °C

nucleophile	10^5k, M^{-1} s^{-1} (±95% CI)[a]	k_{rel}
NaOH	5.2 ± 0.1[b]	1
NaSH	103 ± (5–10)[b,c]	20
Na_2AHQ	90 ± 8.5[b]	17
Na_2SO_3	43 ± 12[d]	8
$Na_2S_2O_3$	47 ± 23[d]	9

[a] CI signifies the confidence interval. [b] Average of triplicate kinetic determinations, each involving duplicates at six time periods. [c] The observed rate constant of 125 ± 5 × 10^{-5} M^{-1} s^{-1} was reduced 15% and 3%, respectively, by contributions due to secondary reactions of **3** and **5** and to the presence of 6% sodium sulfite and 2% sodium thiosulfate in the solution. [d] Based on very limited data; see text for discussion.

Conclusions

Hydrosulfide and anthrahydroquinone ions were much more reactive than hydroxide ion at 195 °C toward displacement reactions at the saturated carbon center in 3-[[3′-(trifluoromethyl)phenoxy]methyl]benzoic acid. This conclusion is based on relative rate constants (Table I) and the very low levels of hydroxide displacement product **4** observed in competitive experiments where the level of NaOH was much greater than that of the other nucleophiles.

Depending on the medium pH, the principal nucleophiles under investigation could exist as H_2S, HS^-, or S^{2-} and as AHQ, AHQ^-, or AHQ^{2-}. At the pH employed in this study, HS^- and AHQ^{2-} should be the dominant ions.[3] However, reactions of minor ionic forms may contribute to the reported rate constants. Our data do not address this issue. However, from the point of view pulping efficiency, the important issue is how well a species performs, regardless of its ionic state.

An alternative interpretation of the rate differences might argue that the values reflect differences in single electron transfer (SET) abilities; several previously suspected nucleophilic substitution reactions have been shown to possess SET chemistry.[8] Testing for an SET mechanism is difficult in high temperature aqueous NaOH because the reagents often used to detect SET chemistry are generally not water soluble and/or degraded under our conditions. One reagent that seemed appropriate, *m*-nitrobenzoic acid, rapidly oxidized AHQ to AQ, thus, circumventing intercepting possible SET reactions.

Previous work in our laboratory has shown that NaOH and NaSH did not electron transfer to quinone methides at 150 °C in 1 M NaOH; however, AHQ^{2-} did electron transfer.[9] It is likely, therefore, that the relative reactivities of NaOH and NaSH observed with compound **3** reflect relative differences in nucleophilicities. The picture is less clear in the case of AHQ^{2-}; however, $\mathbf{3}^-$ is not very electron poor and, therefore, is probably a poor substrate for a SET reaction.

The efficiency of the kraft pulping process appears to be related to the high nucleophilicities of hydrosulfide ion and lignin-attached mercaptide groups which can promote direct and neighboring group displacements at aryl ether bonds.[1] The high efficiency of anthraquinone pulping processes appears to be related to the high nucleophilicity of AHQ^{2-}, efficient internal fragmentation processes, and/or the existence of low energy, electron transfer fragmentation processes.[9–11] Both sodium sulfite and sodium thiosulfate appear to be good nucleophiles in reactions at either a saturated or unsaturated[3] carbon. Thiosulfate is present during kraft pulping and may assist in the delignification process. Pulping with sulfite has been a commerically viable process for several decades; the apparent good nucleophilic properties of the sulfite ion at high temperatures obviously contribute to its effectiveness in promoting delignification.

Experimental Methods

Specific instrumentation employed has been previously described.[3]

3-[[3′-(Trifluoromethyl)phenoxy]methyl]benzoic Acid (3). The following procedure was modified from Haslam and co-workers who synthesized similar compounds.[12] Methyl α-bro-

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(8) Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414.

(9) Smith, D. A.; Dimmel, D. R. *J. Org. Chem.* **1988**, *53*, 5428.

(10) Dimmel, D. R. *J. Wood Chem. Technol.* **1985**, *5*, 1.

(11) Dimmel, D. R.; Perry, L. F.; Chum, H. L.; Palasz, P. D. *J. Wood Chem. Technol.* **1985**, *5*, 15.

(12) Haslam, E.; Haworth, R. D.; Mills, S. D.; Rogers, H. J.; Armitage, R.; Searle, T. *J. Chem. Soc.* **1961**, 1836.

mo-3-toluate[13] (10.0 g, 43.6 mmol) and potassium carbonate (6.7 g, 48.3 mmol) were dissolved in acetophenone (50 mL). The solution was heated to 150 °C with stirring. A solution of 3-(trifluoromethyl)phenol (7.8 g, 48.4 mmol) in acetophenone (25 mL) was added dropwise to the heated solution over a period of 0.5 h. The mixture was then allowed to react at 150 °C for an additional 8 h with stirring. The acetophenone was then removed by steam distillation. The remaining residue was extracted into toluene; the toluene extracts were combined and evaporated.

The resulting liquid was added to a solution containing 10% sodium hydroxide (100 mL) and 95% ethanol (20 mL), and the mixture was refluxed for 2 h, acidified, and extracted several times with diethyl ether. The combined dried (anhydrous sodium sulfate) ether extracts were evaporated. The resulting solid was recrystallized from 40% methanol in water to yield 9.2 g (71%) of a yellow-white solid (**3**): mp 116–118 °C; ^{1}H NMR (DMSO-d_2) δ 5.29 (s, 2, ArCH_2O), 7.26–8.09 (m, 8, aryl-H), and 13.06 (s, 1, COOH); ^{13}C NMR (DMSO-d_2) ppm 69.1 (t, ArCH$_2$O), 111.2 (d, $C_{2'}$), 117.1 (d, $C_{6'}$), 118.8 (d, $C_{4'}$), 128.2, 128.5, 128.6, 130.4, 130.9, 131.7 (aryl-C), 136.8 (s, C_3), 158.2 (s, $C_{1'}$), and 166.8 (s, COOH); MS m/z (rel intensity) 296 (12, M$^+$), 135 (100), 89 (7), and 77 (8).

Anal. Calcd for $C_{15}H_{11}F_3O_3$: C, 60.81; H, 3.74. Found: C, 60.78; H, 3.70.

3-(Hydroxymethyl)benzoic Acid (4). The method of Gilman and Melstrom[14] yielded 0.53 g (8%) of the desired product as a yellow-white solid: mp 108–110 °C (lit.[14,15] mp 111 °C, 114.5–115 °C); IR (mull) cm^{-1} 3750 (OH), 1680 (C=O), and 1590 (aryl); ^{1}H NMR (DMSO-d_2) δ 4.59 (s, 2, ArCH_2OH), 5.33 (br s, 1, OH), 7.36–7.96 (m, 4, aryl-H), and 12.89 (br s, 1, COOH); ^{13}C NMR (DMSO-d_2) ppm 62.9 (t, ArCH$_2$OH), 126.9, 127.3, 127.9, 130.3, 130.4 (aryl-C), 142.6 (s, C_3), and 167.0 (s, COOH); MS m/z (rel intensity) 152 (72, M$^+$), 135 (12), 123 (60), 107 (67), 105 (51), 89 (18), 79 (100), and 77 (100).

This compound was also prepared by refluxing a mixture containing methyl α-bromo-3-toluate (4.0 g), concentrated sulfuric acid (6 mL), and water (100 mL) for 4 h. The solution was made basic with 10% sodium hydroxide and extracted with diethyl ether to remove any starting material. The aqueous layer was acidified, extracted into diethyl ether, dried, and evaporated to yield a solid. The solid was recrystallized from water to yield 1.79 g of a product identical to that described above.

3-(Mercaptomethyl)benzoic Acid (5). The method of Folli and Iarossi[16] yielded 3.7 g (85%) of the desired product as a white solid: mp 94–97 °C (lit.[16] mp 105–106 °C); IR (mull) cm^{-1} 1690 (C=O) and 1580 (aryl); ^{1}H NMR (DMSO-d_2) δ 3.81 (s, 2, ArCH_2SH) and 7.34–7.96 (m, 4, aryl-H); ^{13}C NMR (DMSO-d_2) ppm 27.3 (t, ArCH$_2$SH), 127.3, 128.2, 128.7, 130.9, 132.1 (aryl-C), 141.7 (s, C_3), and 166.9 (s, COOH); MS m/z (rel intensity) 168 (45, M$^+$), 135 (100), 89 (11), and 77 (18).

10-Hydroxy-10-(3′-carboxybenzyl)-9(10*H*)-anthracenone (6). The method of Dimmel and Shepard[6] for synthesizing AHQ adducts was used to prepare anthrahydroquinone and the desired adduct. A sufficient quantity of anthrahydroquinone (10–12 mmol) was prepared under a nitrogen atmosphere and dissolved in a mixture containing 30 mL of water and 7.5 mL of 30% sodium hydroxide solution. 3-(Bromomethyl)benzoic acid[17] (2.0 g, 9.3 mmol) was quickly added in solid form to the stirring solution. The solution immediately turned from a red to a tan color. Additional sodium hydroxide was added, and the mixture was heated to 55–60 °C for 1 h and then allowed to cool. The mixture was filtered to remove precipitated anthraquinone. The filtrate was acidified, extracted into diethyl ether, dried over anhydrous sodium sulfate, and evaporated to a yellow solid. Recrystallization from 95% ethanol yielded 1.05 g (33%) of the desired product as a white solid: mp 212–215 °C; IR (mull) cm^{-1} 3480 (H—O), 1680 (C=O), and 1590 (C=C); ^{1}H NMR (DMSO-d_2) δ 3.22 (s, 2, CH_2), 6.22 (dt, J = 1.5, 7.7 Hz, 1, $C_{4'}$-H), 6.48 (br s, 0.7, OH), 6.71 (t, J = 1.5 Hz, 1, $C_{2'}$-H), 6.93 (t, J = 7.7 Hz, 1, $C_{5'}$-H), 7.38–8.03 (m, 9, other aryl-H), and 12.47 (br s, 0.7, COOH); ^{13}C NMR (DMSO-d_2) ppm 54.9 (t, CH$_2$), 72.4 (s, C_{10}), 125.1, 126.4, 126.8, 127.0, 127.4, 129.4, 130.3, 130.8, 133.0, 133.9 (aryl-C), 135.1 (s, $C_{3'}$), 147.1 (s, C_{4a}, C_{5a}), 166.5 (s, COOH), and 181.6 (s, C_9); MS m/z (rel intensity) 344 (M$^+$, 0.2), 209 (100), 152 (14). Assignment of NMR chemical shifts was aided by assignments given in ref 6.

Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.28; H, 4.74.

3-[[(3′-Carboxybenzyl)thio]methyl]benzoic Acid (10). 3-(Bromomethyl)benzoic acid (2.0 g, 9.30 mmol) and 3-(mercaptomethyl)benzoic acid (1.6 g, 9.45 mmol) were dissolved in 1 M sodium hydroxide (40 mL). The solution was refluxed with stirring for 8 h, cooled, acidified with 6 M hydrochloric acid, and extracted into diethyl ether. The combined ether extracts were dried and evaporated to yield a solid, which was recrystallized from 95% ethanol to yield 1.8 g (49%) of **10** as a yellow-white solid: mp 197–198 °C (lit.[18] mp 197 °C); IR (mull) cm^{-1} 1685 (C=O), and 1610 (C=C); ^{1}H NMR (DMSO-d_2) δ 3.77 (s, 4, CH_2), 7.35–7.90 (m, 8, aryl-H), and 12.94 (br s, 1.3, COOH); ^{13}C NMR ppm 34.8 (t, CH$_2$), 127.5, 128.2, 129.3, 130.6, 132.8 (aryl-C), 138.4 (s, C_3), and 166.7 (s, COOH); MS m/z (rel intensity) 302 (M$^+$, 11), 167 (23), 135 (100), 121 (9), 89 (15), 77 (25), and 45 (12).

High Temperature Reactions of 3 and Product Analysis. The same "bomb" and reaction sample workup procedures as those used for the *cis*-cinnamic acid isomerization study[3] were employed here. The only differences used here were that (1) two internal standards were employed, the sample was split, and analyses for carboxylic acids (as methyl esters)[3] and for phenols (as benzoylates)[19] were performed separately. The temperature program used for the analysis of the carboxylic acid methyl esters was 130 °C for 1 min, 10° min^{-1} to 250 °C, 30° min^{-1} to 300 °C, and held at 300 °C. The retention times were methyl 3-tolulate, 2.2 min; methyl 3-hydroxybenzoate, 4.9 min; methyl 3-(hydroxymethyl)benzoate, 6.3 min; dimethyl isophthalate, 6.3 min; methyl 3-(mercaptomethyl)benzoate, 6.7 min; methyl 3-[[3′-(trifluoromethyl)phenoxy]methyl]benzoate, 10.9 min; methyl 4-(benzyloxy)benzoate (internal standard), 12.4 min; methyl 3-[[(3′-carboxybenzyl)thio]methyl]benzoate, 16.8 min; and 10-hydroxy-10-(3′-carboxybenzyl)-9(10*H*)-anthracenone, 22.2 min. The temperature program for analysis of benzoylated phenols was the same as above except the initial column temperature was 160 °C. The retention times (as benzoates) were 3-(trifluoromethyl)phenol, 3.6 min, and 4-isopropylphenol (internal standard), 7.3 min.

High Temperature Reactions of 5 in D_2O and Product Analysis. Mercaptan **5** was reacted in deuterium oxide and sodium deuteroxide under previously described reaction conditions; identical sample workup procedures were also employed. Deuterium incorporation was followed using GC-MS and NMR. Detection of a significant M + 1 peak for methyl 3-toluate indicated deuterium incorporation. Proton NMR indicated replacement of an α-methyl proton.

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