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HIGH TEMPERATURE PROTON EXCHANGE REACTIONS
BY HYDROXIDE IN WATER

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ABSTRACT

The ability of hydroxide ion to produce carbanions at 170°C in water has been determined by measuring the extent of deuteration and reexchange of deuterium labels for several organic acids and phenols. The results of the exchange reactions provide a rough estimate of the types of reactions that are possible between hydroxide ion and wood components during alkaline pulping. It has been estimated that NaOH/H₂O at 170° can deprotonate organic acids having pK_a values of about 35 and can produce polyanion intermediates. Several experiments were directed toward understanding the effects of α-hydroxyl groups and zinc ions on carbanion formation. Exchange reactions involving Na₂S at 170° showed that this species is largely dissociated to NaOH and NaSH and that the latter does not contribute to the basicity of the solution.

INTRODUCTION

The chemical pulping of wood often employs strongly alkaline solutions and, in the case of kraft pulping, also sodium sulfide (Na₂S). During kraft pulping roughly one-half of the wood constituents are solubilized either by the action of (a) hydroxide ion as a base or (b) OH⁻ and SH⁻ ions as nucleophiles.¹ Some hydroxide reactions also stabilize constituents; for example, the carbohydrate "stopping" reaction¹ appears to be favored by high concentrations of hydroxide.^{2,3} An important aspect of understanding the reactions of wood components during pulping is therefore a fundamental understanding of the chemistry of OH⁻ at 170°.

An experimental program was set up to examine the deuterium exchange and back proton exchange of deuterated substrates by $\text{OD}^-/\text{D}_2\text{O}$ and $\text{OH}^-/\text{H}_2\text{O}$, respectively. The conditions employed here, namely 1N NaOD in D_2O at 170°C for 2 hours, were selected to simulate soda pulping conditions. The substrates employed generally contained alcohol, phenol and/or carboxylic acid groups; these groups are commonly found in wood components and impart solubility in aq. alkali.

Several methods are available to determine the extent of deuteration; these include mass spectroscopy and both proton (^1H) and carbon-13 (^{13}C) nuclear magnetic resonance (NMR). The NMR techniques not only provide information on the extent of deuteration, but also on the location of deuterium atoms. The frequency used to decouple ^1H - ^{13}C interactions does not decouple D - ^{13}C interactions during acquisition of ^{13}C -NMR spectra. A $-\overset{\text{H}}{\underset{\text{D}}{\text{C}}}-$ group will appear as a three line signal (deuterium spins of +1, 0, -1) and at reduced intensity (poorer spin relaxation) in the ^{13}C -NMR spectrum of proton decoupled samples. A $>\text{CD}_2$ group correspondingly displays a 1:2:3:2:1 pattern of greatly reduced intensity. Thus, ^{13}C -NMR spectra show which carbons are deuterium substituted and to what approximate extent.

RESULTS AND DISCUSSION

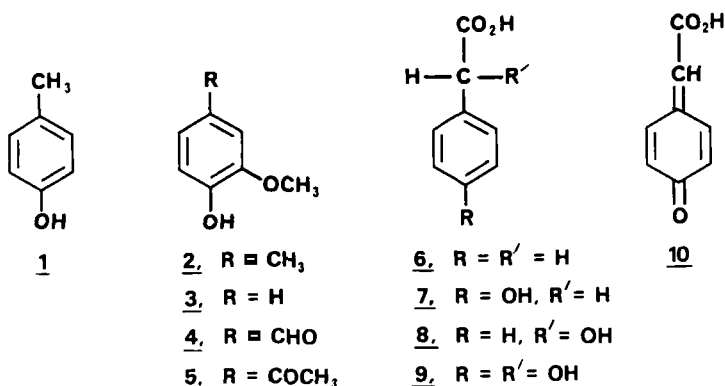
Simple Phenols

Samples of *p*-cresol (1) and creosol (2) were completely deuterium exchanged at the available ortho and para positions by treating each with 1N NaOD in D_2O at 170° for 2 hours. These strenuous conditions were probably not needed,⁴ since guaiacol (3) and vanillin (4) are readily deuterated and acetoguaiacone (5) slowly deuterated when treated with 0.5N NaOD in D_2O at 100° for 20-24 hours.⁵

Arylacetic Acids

The exchange reactions of a few simple arylacetic acids have been reported.^{4,6} We were interested, however, in the exchange

efficiencies at C_{α} when hydroxyl groups were present. A previous study suggested that α -OH groups would retard carbanion formation.⁷ The protons on the α -carbons of phenylacetic acid (6) and *p*-hydroxyphenylacetic acid (7) were largely exchanged (92 and 87%, respectively) for deuteriums under the standard conditions. The ring protons ortho to the phenolic group of 7 were also exchanged (87%). Reexchange of the deuterated compounds by NaOH/H₂O at 170° for 2 hours was nearly complete.



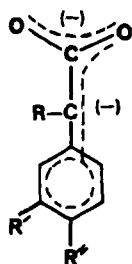
Mandelic acid (8) was also exchanged at the α -carbon position. The exact extent of exchange could not be determined from the ¹H-NMR spectrum because of an overlapping of the HOD and α -protons. However, the ¹³C-NMR spectrum clearly showed that extensive exchange had occurred; the C_{α} -carbon appeared as a weak 1:1:1 triplet ($-\overset{\text{D}}{\underset{\text{H}}{\text{C}}}$), with almost no remaining $-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}$ singlet. [The deuterated carbons are shifted to slightly lower frequencies than the protonated carbons.] Back exchange of the deuterated mandelic acid with NaOH at 170° removed all the deuteriums.

Mandelic acids substituted with phenol groups were subjected to deuteration to determine if an additional charge on the aromatic ring would inhibit exchange at the C_{α} -carbon. The first compound examined, *p*-hydroxymandelic acid (9), gave after deuteration,

a complex ^{13}C -NMR spectrum which indicated that new components were present. This result can be explained by the formation of a quinonemethide (10) and its subsequent reactions to produce undesirable by-products.¹

The behavior of *m*-hydroxymandelic acid (11) to deuteration and reexchange was normal; the α -proton was roughly 98% exchanged, completely reexchanged with NaOH, and no by-products were observed. The extent of deuteration on the ortho and para ring protons were roughly 70%. Figure 1 shows the ^{13}C -NMR spectra of *m*-hydroxymandelic acid before and after exchange. Like all others, the spectra were recorded in NaOD/D₂O and therefore are of anions rather than neutral species.

In summary, the phenylacetic acid derivatives are easily deuterium exchanged at the α -carbon via carbanion intermediates which have to be multicharged species. Based on the expected acidity scale of $\text{RCO}_2\text{H} > \text{ArOH} > \text{ROH} > \text{-CH}$,^{9,10} the carbanions may be as highly charged as a tetraanion (11⁻⁴). Since the exchange reactions at the various acidic sites are equilibrium reactions, carbanion formation might preclude some oxyanion production. For example, the α -exchange observed with *m*-hydroxymandelic acid may have involved 11⁻³ rather than 11⁻⁴. The probable intermediates in the exchange reactions observed for the tested arylacetic acids are shown below.



The resonance stabilization provided to the carbanion by the carboxylate anion must be substantial. The ortho and para proton exchange reactions were less (70 vs. 98%) than α -proton exchange

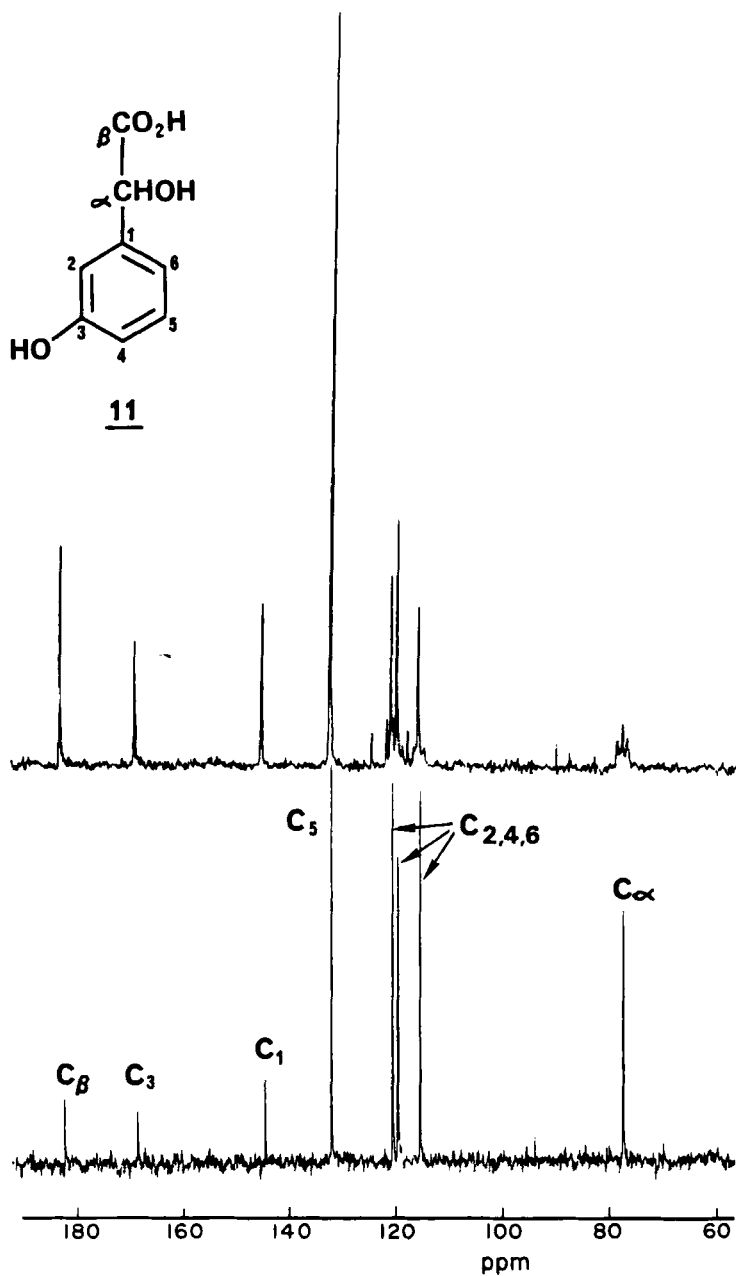
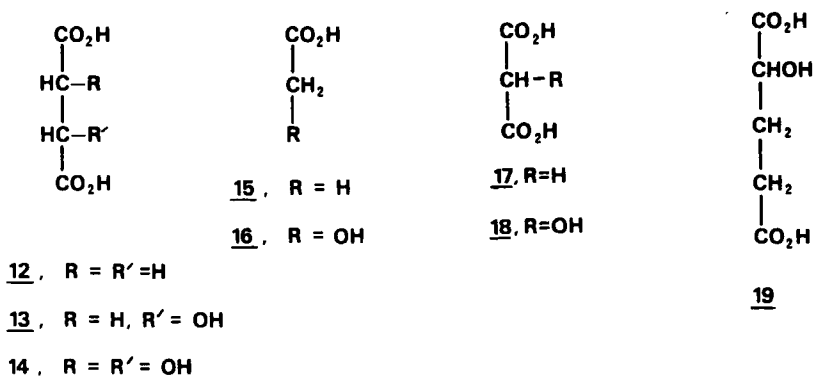


Figure 1. ¹³C-NMR spectra of *m*-hydroxymandelic acid in NaOD/D₂O before heating (bottom) and after 2 hrs at 170° (top).

ion 11 and less (70 vs. 98%) than o-exchange of p-creosol. This suggests that a phenolate ion has less effect on benzyl exchange than a charged benzyl carbon has on o,p-phenol exchange. The next set of compounds examined has no aryl rings attached to the exchange site and, therefore, tests the necessity of this group for stabilizing effects.

Aliphatic Carboxylic Acids

Succinic acid (12), malic acid (13) and tartaric acid (14) were completely exchanged under the standard deuteration conditions. The deuterated succinic acid was also completely reexchanged by NaOH/H₂O at 170°. Some dehydration occurred with malic acid. Acetic acid (15) and glycolic acid (16) were also readily exchanged and reexchanged.



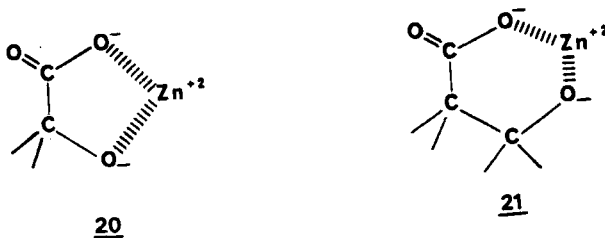
For the compounds discussed so far, the placing of a hydroxyl group on the carbon undergoing exchange does not retard the exchange reactions. If a hydroxyl group is ionized, it should become an electron-donating group and, thus destabilize an attached carbanion. In order to verify that α -hydroxyl groups inhibit carbanion formation,⁷ we investigated the exchange reactions of malonic acid (17) and tartronic acid (18).

The exchange of malonic was so rapid that it was complete in a matter of minutes at room temperature. On the other hand, 54

hours at room temperature were required to fully exchange tartaric acid. The increased resonance stability provided by the gem-carboxylic acids of 17 and 18 must account for the ease of exchange at room temperature. The difference in reactivity of the two demonstrates that an α -hydroxyl group inhibits carbanion formation at C_α .

The zinc salt of α -hydroxyglutaric acid (19), which was both commercially available and has potentially exchangeable $>CHOH$ and $-CH_2-$ groups separated sufficiently to avoid complicating dehydration reactions, was heated at 170° in $NaOH/D_2O$ and only the C_4 -methylene group exchanged. Because of the insolubility of $Zn(OH)_2$, the pH may have been lower than expected. Yet, the results indicated again that an α -hydroxyl group inhibits exchange.

Could the zinc ion have played a role? Cyclic complexes, such as 20 and 21 have been postulated to be present in pulps (carbohydrates).¹¹ Alkaline earth hydroxides, such as strontium hydroxide, are known to increase the extent of carbohydrate "stopping" reactions.^{3,12} The latter increase pulp yield. To determine the effects of zinc ion on exchange reactions, we examined the extent of $C_\alpha-H$ exchange for tartaric acid, with and



without zinc ion present. The aromatic protons of mandelic acid were used as an internal reference for the ^1H-NMR area measurements.

The $NaOD/D_2O$ exchange was performed in duplicate for 15 minutes at 170° . The amount of deuterium exchange at the alpha $CHOH$ group was, in one case, 97.5% (no Zn^{+2}) and 90.3% (Zn^{+2}) and, in

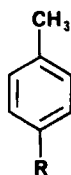
the other case, 91.4% (no Zn^{+2}) and 79.7% (Zn^{+2}). The addition of zinc ion reduced but did not prevent the exchange of an α -hydroxy-carboxylic acid and suggests that divalent ions may play a role by affecting the degree of ionization with such compounds. The preferential exchange results observed for zinc α -hydroxyglutarate (19) must be largely attributed to carbanion retardation by an α -OH group rather than a zinc ion effect.

Benzyl Exchange

The exchange capacities of benzyl sites not directly attached to strong stabilizing groups were examined next. In these cases the resonance stabilization was provided by simply the attached aromatic ring or by conjugation through the aromatic ring to a carboxylic or sulfonic acid group.

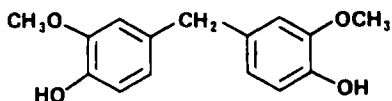
Under the standard 2 hour, 170° conditions, *p*-toluenesulfonic acid (22) was deuterated on the methyl group to 78%; reexchange, even after 12 hours, only reduced the deuterium content to 76%. Likewise, *p*-toluic acid (23), for which exchange data at $180^\circ C$ are known,⁶ was 34% deuterated in 2 hours and 5% deuterated after reexchange for 24 hours. The lack of complete removal of deuterium on reexchange with NaOH/H₂O can be attributed to solvent and C-D isotope effects.^{12,13} A compound which undergoes deuterium exchange and limited proton reexchange provides an example of the limits of carbanion production by NaOH.

Diguaiacylmethane (24) did not undergo deuteration at 170° even after 24 hours. However, 4-hydroxydiphenylmethane (25) exhibited some deuteration at 170° - 26% at the benzyl carbon after 2 hours and 70% after 24 hours; reexchange over a 24-hour period reduced

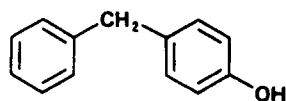


22, R = SO₃H

23, R = CO₂H



24



25

the deuterium content to 61%. The difference in reactivity of these two compounds can be understood by assuming that a benzene ring provides some stabilizing effects to an adjacent carbanion but a phenolate ring does not. Toluene was not deuterated after 54 hours at 170° probably because of poor solubility.

Sodium Sulfide

The kraft pulping of wood employs sodium sulfide (Na_2S) to effect a rapid production of strong pulps.¹ Limited previous work indicates that the Na_2S dissociates in water to give NaOH and NaSH .¹⁴ A simple experiment was conducted to verify the degree of dissociation of Na_2S and to determine the basicity of SH^- at 170°.

Three deuterium oxide solutions of p-toluic acid (23) were prepared and heated under identical conditions for 6 hours at 170°. The solutions contained 1.5 equivalents of anh. Na_2S , and 1.5 and 3.0 equivalents of NaOD , respectively. The ratios of the integrated proton NMR areas for the methyl signal relative to the aryl signals were nearly identical (0.57 and 0.58) for the solutions containing the same number of equivalents of Na_2S and NaOD , but nearly one-half (0.30) for the solution containing double the equivalents of the others. [The theoretical ratio of methyl/aryl signals for no exchange is 3/4 or 0.75.] It is apparent from these results that (a) Na_2S is completely dissociated in water at 170° to hydroxide and hydrosulfide at 170°, (b) the hydrosulfide ion is not a strong base and (c) the extent of toluic acid exchange is sensitive to alkali concentration.

In order to verify the importance of alkali in our exchange reactions, we heated sodium p-toluenesulfonate (p- MePhSO_3Na) with D_2O for 3 1/2 hours at 170°C. No H/D exchange was observed at any site; in contrast, 78% H/D exchange of the three methyl protons was observed with 1N $\text{NaOD}/\text{D}_2\text{O}$ at 170° after 2 hours.

Werstiuk and Timmins have reported several examples of H/D exchange for heteroaromatics in D_2O and polycyclic aromatics with dilute acid (DCl) catalyst; very high temperatures (300°C) were commonly employed.^{15,16}

CONCLUSIONS

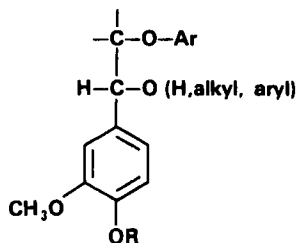
The acidity and basicity of compounds should change with temperature. As the temperature increases, reaction rates generally increase; (additional vibrational energy is imparted to the CH and OH bonds. Also, because of the breakdown of hydrogen bonding, hydroxide ion should be less solvated and, thus, more reactive as the temperature increases. The combination of these effects probably accounts for hydroxide ion being an apparent very strong base at 170° in water. The acidity of the methylene protons of 4-hydroxydiphenylmethane (25) should be considerably less than that of diphenylmethane (pK_a 35),⁹ and yet the former underwent partial exchange at 170° by hydroxide ion (pK_a of H₂O is 15.74).^{9,10}

The results for the compounds tested verify⁷ that carboxylate anions contribute significantly to the stability of a carbanion, aryl groups exhibit only moderate stabilizing effects, and attached hydroxyl groups have negative stabilizing effects. It should, however, be pointed out that the small negative effect of an α -OH group was generally overcome by the severity of reaction conditions employed here.

What are the implications of our results to wood chemistry problems? The reducing end of carbohydrates contains hemiacetal or hemiketal groups in equilibrium with aldehyde or ketone groups and, of course, many alcoholic OH groups. The stabilization of a carbanion by an α -aldehyde or ketone group should be better than that of a carboxylate group. Since our carboxylic acid model compounds readily formed α -carbanions at 170° with hydroxide, even in the presence of several hydroxyl substituents (ArOH and ROH), carbohydrates should as well. Our exchange results indicate that dianions could be intermediates in alkaline carbohydrate reactions. [Actual model polyhydroxyketones and carbohydrates were not tested for fear of complications due to reactions such as aldol condensations, eliminations, etc.]

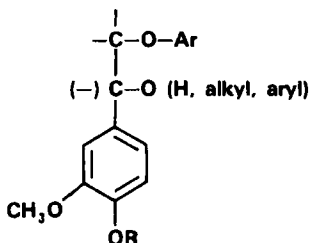
A unit that appears often in lignin is that shown by structures 26 and 27.¹ Based on the exchange results with diguaiacyl-

methane (24) and 4-hydroxydiphenylmethane (25), a carbanion such as 29 would appear possible during pulping, while 28 would be quite unlikely. Carbanion 29 could undergo elimination and condensation reactions which might be contributing to "bulk delignification" and "residual lignin," respectively.^{1,17}



26, R = H

27, R = alkyl



28, R = (-)

29, R = alkyl

Finally, it should be noted that the use of NaOD/D₂O at high temperature in sealed metal containers offers a convenient way to deuterate mildly acidic $-\overset{|}{\text{C}}-\text{H}$ groups in compounds which are otherwise stable to alkali. A compounds such p-toluenesulfonic acid, which only underwent partial deuteration when treated at 170° for 2 hours, could probably have been completely deuterated by raising the temperature and/or extending the time at 170°. Based on the toluene result, we suspect that water insoluble compounds can not be exchanged by our procedures. Amos and Eckert, however, have recently reported¹⁸ that the methyl groups of 2,3- and 1,4-dimethylantraquinone, both of which have low water solubility, can be completely deuterated in NaOD/D₂O solution at 170° for 90 minutes.

The room temperature NaOD/D₂O exchange of malonic acid offers a much simpler way of preparing the deuterated analog than previous methods.^{19,20}

EXPERIMENTAL

Spectra were recorded on a Jeol FX-100 instrument for solutions in NaOD/D₂O with the sodium salt of 3-(trimethylsilyl) propane

sulfonic acid (DSS) as the internal standard. Except for diguaiacylmethane (24),²¹ all compounds were commercially available.

The chemical shift and extent of exchange for many of the compounds studied are given in Tables 1 and 2. The extent of exchange of the aryl rings of the phenols examined were: *p*-cresol (1), ortho-98%; creosol (2), ortho-100%; *p*-hydroxyphenyl acetic acid (7), ortho-87%; *m*-hydroxymandelic acid (11), ortho-67 to 77% and para-67 to 77% (the range is for duplicate runs).

Deuteration. - A model compound was added to 1.5 g of D₂O so that the ratio of deuteriums to all exchangeable protons was 40:1. To this was added enough 40% NaOD to completely ionize the carboxylic, sulfonic, phenolic and hydroxyl groups and then have a 1N NaOD solution left. The solution was transferred to a 5-mL bomb of moderately thick stainless steel. One to three of these small bombs were placed in a larger Parr bomb and water was added to near the top of the Parr bomb. The Parr instrument took from 30-60 minutes to reach 170 ± 3°C and was held at this temperature for 2 hours, unless stated otherwise. After the heating at 170°C was complete, the Parr bomb was allowed to cool in air to room temperature. The solution was freeze-dried to remove as much HOD as possible and the proton and carbon-13 spectra obtained. An example of deuteration is given below in the case of zinc α-hydroxyglutarate.

Reexchange. - The deuterated sample and residual alkali, obtained by freeze-drying the NMR solution, were dissolved in 1.5 g of H₂O. The solution was heated, cooled and freeze-dried in the previously described manner.

Deuteration of Zinc α-Hydroxyglutarate. - The title compound (0.1985 g) was dissolved in 1.503 g of D₂O and 0.276 g of 40% NaOD in D₂O. After heating (as described above), the solution was freeze-dried and the residue dissolved in D₂O. The ¹H-NMR spectrum showed three signals: HOD at 4.78 δ, >CHOH at 3.85 δ as a triplet (J = 6 Hz) with shoulders, and -CH₂CH₂- at 1.73 δ as a broadened singlet; the ratio of the 3.85 to 1.73 signals was 0.43.

TABLE I

Chemical Shift and Extent Exchange at C_α of R'-CHCO₂H
 $\begin{array}{c} | \\ R \end{array}$

R	R'	Chemical Shifts ^a		Percent Deuterium at α-carbon as given by proton NMR
		α-Proton	α-Carbon	
H	Ph	3.52	45.91	92
H	<u>p</u> -OH-Ph-	3.34	46.09	87
OH	Ph	4.97	77.55	b,e
OH	<u>p</u> -OH-Ph-	4.56	77.19	c
OH	<u>m</u> -OH-Ph-	4.82	77.87	98
H	-CH ₂ -COOH	2.68	36.74	d,e
H	-CHOH-COOH	2.24-2.77	45.17	d,e
OH	-CH ₂ -COOH	4.22-4.84	56.82	d,e
OH	-CHOH-COOH	4.32	76.46	d,e
H	H	1.67	24.61	d,e
H	OH	3.68	64.70	d,e
H	Ph(CH ₃)-	2.21	39.91	45

^aAll NMR data were acquired with NaOH/D₂O solutions.

^bOverlap of the proton signal with the HOD signal prevented a calculation of the percent deuterium by proton NMR.

^cFormation of quinonemethide and its reactions to produce by-products made analysis by NMR impossible.

^dThe compound does not contain a nonexchangeable proton to use as a reference to calculate the percent deuterium from the proton spectrum.

^eThe carbon-13 spectrum showed that deuterium occurred to a greater extent than 90%.

TABLE 2

Chemical Shift and Extent Exchange for R'-CH₂ (Benzyl)

$$\begin{array}{c} | \\ \text{R}'-\text{CH}_2 \\ | \\ \text{R} \end{array}$$

R	R'	Proton	Carbon	Percent Deuterium at Benzylic Carbon
p-SO ₃ H-Ph-	H	2.25	23.05	78
p-CO ₂ H-Ph-	H	2.00	22.95	34
p-OH-Ph-	Ph	3.72	37.42	26
guaiacyl	guaiacyl	3.38	42.49	0

^a See footnote a of Table 1.

The ¹³C-NMR spectrum showed 185.3 and 184.0 (sharp singlets, carbonyl carbons), 74.4 (sharp singlet, >CHOH), 35.5 (overlapping triplet and pentet, weak, -CDH- and -CD₂-) and 33.4 ppm (sharp singlet, -CH₂-). The ¹³C-NMR indicates that the >CHOH group has not incorporated much, if any, deuterium. Assuming no deuterium at this position and the observed ¹H-NMR ratio of 1:2.3, we calculate that the C₄-carbon is roughly 70% -CD₂- and 30% -CHD-.

Zinc Complex Deuteration. - Two solutions containing 0.0940 g (0.63 mmole) of tartaric acid, 0.0245 g (0.16 mmole) of mandelic acid, 0.4950 g of 40% NaOD (4.8 mmoles) in D₂O and 1.6875 g of D₂O (100 mmoles) were prepared. To one of the solutions was added 0.0530 g ZnCl₂. The formation of Zn(OH)₂ was prevented by adding the tartaric acid, mandelic acid, D₂O and ZnCl₂ together, dissolving the solids, and then adding the 40% NaOD. The two solutions were heated together in the Parr bomb for 15 minutes at 170°C, cooled, freeze-dried and dissolved in D₂O. The proton spectra were obtained. The integrated areas of the aryl mandelic acid and aliphatic tartaric acid signals were then compared. Ratios of 100:4 and 100:15 were observed for the nonzinc and zinc-containing solutions, respectively. Correcting for the number of

protons of each type involved and the starting concentrations, we calculate that the aliphatic deuterium exchange was 97.5% (nonzinc) and 90.3% (zinc).

A repeat of this experiment gave deuterium exchange extents of 91.4% (nonzinc) and 79.7% (zinc). The difference between this latter set of data and the former pair is probably a result of differences in the time used to reach 170° and to cool back to room temperature.

Sodium Sulfide Deuteration. - Three solutions, each containing 1.5 g of D₂O and 0.1272 g (0.94 mmole) of *p*-toluic acid, were prepared in a glove bag with a N₂ atmosphere. One of the solutions also contained 0.1110 g (1.42 mmoles) of anhydrous Na₂S, another 0.14 g 40% NaOD (1.42 mmoles) and the third 0.28 g 40% NaOD (2.84 mmoles). The three solutions were heated simultaneously in the Parr bomb for 6 hours, cooled, freeze-dried, and redissolved in D₂O. Two proton spectra of each solution were obtained; the results are discussed in the text.

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