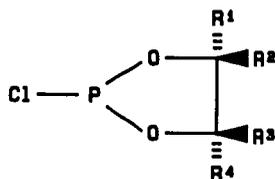


IDENTIFICATION OF LABILE-HYDROGEN FUNCTIONALITIES  
IN COAL-DERIVED LIQUIDS BY  $^{31}\text{P}$  NMR SPECTROSCOPY

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INTRODUCTION

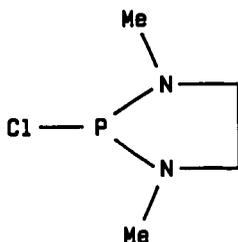
In recent publications from our laboratories<sup>1-3</sup>, the application of  $^{31}\text{P}$  Fourier transform nmr spectroscopy to the analysis of -OH, -NH and -SH functionalities in coal extracts and pyrolysis condensates has been described. We initiated these studies with a series of reagents 1a-e which contain two oxygen atoms in the five-membered phospholane ring system, and varying degrees of ring substitution.



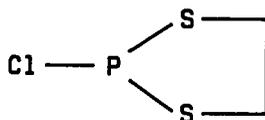
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
1a	H	H	H	H
1b	Me	Me	Me	Me
1c	H	H	H	Me
1d	H	Me	Me	H
1e	Et	Et	Et	Et

These reagents react under mild conditions with the above labile-hydrogen functionalities,  $\text{R}_\text{X}\text{EH}$  to give  $\text{R}_\text{X}\text{EP}$  linkages in which the phospholane ring remains intact. The HCl liberated is neutralized by triethyl amine in the reaction mixture. In the series 1a-e, reagents 1a and 1b emerged as optimum in terms of minimum overlap of the ranges for each functional group and for maximum resolution within each range of the chemical shifts due to the various R groups attached to the functional group heteroatom E (Figure 1).

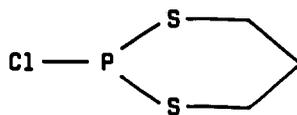
To determine the role of the heteroatoms within the ring system of the reagent and the size of the ring system, we are extending our investigations to include reagents such as 2 - 4. Here we describe our preliminary results with a series of model compounds derivatized with these reagents, and also with a coal low-temperature pyrolysis condensate which was allowed to react with 3.



2



3



4

## EXPERIMENTAL

Reagents 2,<sup>4</sup> 3<sup>5</sup> and 4<sup>6</sup> were prepared according to published syntheses. Chemical shift data for derivatized model compounds were obtained by using a procedure described previously.<sup>2,3</sup> For 2 and 3, chemical shift data for the individual model compounds were recorded. For reagent 4 only chemical shift ranges for model compounds were recorded by derivatizing mixtures of phenols, alcohols, acids or amines. The compositions of the mixtures are given in Table I.

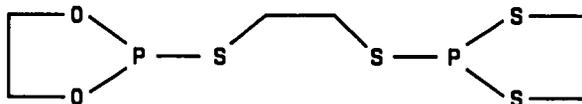
A low-temperature pyrolysis condensate of a Illinois No. 6 coal sample was obtained as described previously.<sup>2,3</sup>

## RESULTS AND DISCUSSION

The chemical shift data for selected model compounds derivatized with 2 - 4 are given in Table II. The regions associated with the <sup>31</sup>P nmr resonances for the model phenols, aliphatic alcohols, carboxylic acids, amines and thiols derivatized with 2 - 4 are shown in Figure 1.

Derivatization of phenols with 2 - 4 gives the corresponding phospholanes (2, 3) or phosphoranes (4) instantaneously. The observed chemical shift range of 15.2 ppm for phenols derivatized with 3 constitutes a significant improvement over the chemical shift range of approximately 6 ppm reported earlier for dioxaphospholanes 1a - 3.<sup>3</sup> Alcohols derivatized with 3 display chemical shifts in the region 143.4 - 151.8 ppm with most of the signals appearing in the 143.4 - 147.2 ppm range. This range is well separated from the chemical shift range observed for derivatized phenols.

An interesting observation can be made from inspection of the data of derivatized pinacol. Derivatization with 3 gives signals at 108.77 and 214.75 ppm. These signals are outside the range of the other derivatized alcohols. The signal at 108.77 ppm is in the range of thiols derivatized with 3 and the peak at 214.75 ppm is in the range of thiols derivatized with 1a - e<sup>3</sup>. These results are consistent with the suggestion that with 1,2-diols, transesterification occurs to give 5.



5

Carboxylic acids react rapidly with reagents 2 - 4. The chemical shift range for carboxylic acids derivatized with 4 could be obtained for a mixture of acids but within a few minutes signals in the range 61.7 - 1.7 ppm started to appear. It is presently not clear what further reactions may be leading to these signals. The chemical shift range observed for carboxylic acids derivatized with 3 overlaps with the region observed for derivatized phenols (Figure 1).

Amines derivatized with dioxaphospholanes of type 1 (e.g., 1a and 1b in Figure 1) generally give signals in the  $^{31}\text{P}$  nmr spectrum in regions that overlap with signals observed for derivatized -OH functionalities. Amines derivatized with 3, however, give signals well outside the region for -OH functional groups.

Thiols derivatized with 3 display chemical shifts upfield from derivatized -OH functional groups and downfield from derivatized amines. There also appears to be a separation between aromatic and aliphatic thiols similar to the separation between alcohols and phenols.

Preliminary results with coal-derived liquids derivatized with 3 appear promising. Thus, with an Illinois No. 6 low-temperature pyrolysis condensate (Figure 2) peaks in the 152 - 163 ppm region appear well resolved for identification of specific phenols.

#### CONCLUSIONS

Of the three new reagents, reagent 2 does not give an improvement over reagents of type 1. Reagent 2 gives broader  $^{31}\text{P}$  peaks, probably owing to the presence of quadrupolar nitrogen nuclei near the nmr-active phosphorus nucleus.

The resolution obtained with reagent 3 is substantially better than any of the reagents investigated so far, paving the way for identification of functional groups and their organic substituents in coal-derived liquids.

Increasing the ring size of the derivatizing reagent from 3 to 4 does not improve the chemical shift ranges observed nor does it lead to less overlap of the functional group chemical shift ranges.

#### ACKNOWLEDGEMENTS

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Table I. Model Compound Mixtures Used With Reagent 4.

Functional Group Class	Model Compounds in the Mixture
Phenols	<u>m</u> -cresol, <u>p</u> -cresol, 2,3-xyleneol, 2,4-xyleneol, 2,5-xyleneol, 2,3,5-xyleneol, <u>p</u> -methoxyphenol, 2,4,6-xyleneol, 3,4,5-xyleneol, catechol, resorcinol, 2-methylresorcinol, $\alpha$ -naphthol, <u>o</u> -cresol, hydroquinone, <u>m</u> -methoxyphenol, $\beta$ -naphthol, 3-ethylphenol, 2,6-xyleneol, 3,5-xyleneol, phenol.
Alcohols	methanol, benzyl alcohol, benzhydrol, isoamyl alcohol, mandelic acid, 2,3-butanediol, menthol, cyclohexanol, <u>t</u> -butanol, <u>t</u> -amyl alcohol, pinacol.
Acids	benzoic acid, <u>p</u> -toluic acid, 2,4,6-trimethoxybenzoic acid, mandelic acid, terephthalic acid, $\alpha$ -methylcinnamic acid, succinic acid.
Amines	aniline, <u>o</u> -toluidine, proline, carbazole, 2,6-methylaniline, diisopropylamine, N-ethylaniline, pyrazole.

Table II.  $^{31}\text{P}$  Chemical Shifts of Phenols, Alcohols, Acids, Amines and Thiols Derivatized with 2 and 3.

Compounds	Reagents	
<u>Phenols</u>	2	3
2-methoxy-6-methyl phenol	138.4, 136.5	165.24
2,3,6-dimethyl phenol	132.4	160.72
2,6-dimethyl phenol		160.98
guaiacol	135.0	160.45
phenol	131.2	152.51
$\beta$ -naphthol	132.5	154.32
8-quinolol	135.9	167.38
<u>o</u> -cresol		154.78
<u>p</u> -cresol		152.11
<u>m</u> -cresol		152.87
3,5-dimethyl phenol		153.33
2,4-dimethyl phenol		154.20
<u>Alcohols</u>		
methanol	126.4	145.98
benzyl alcohol	127.3	145.11
isoamyl alcohol	126.5	143.41
menthol	133.1	151.78
<u>t</u> -butanol	124.3	145.66
cyclohexanol	129.1	147.17
pinacol	143.4, 114.1, 113.7	108.77, 214.75
<u>Acids</u>		
terephthalic acid	132.7	insoluble product
benzoic acid	131.2	154.55
<u>d</u> -mandelic acid	132.4	152.18
2,4,6-trimethoxybenzoic acid	130.9	159.83
$\alpha$ -methylcinnamic acid	130.3	153.19
<u>Amines</u>		
2,6-dimethylaniline		103.88
<u>o</u> -toluidine		100.61
di-isopropylamine		92.63
N-ethylaniline		99.97
pyrazole		91.43
<u>Thiols</u>		
2-propanethiol		102.16
thiophenol		113.43
<u>o</u> -thiocresol		112.31
3,4-dimethylthiophenol		112.94

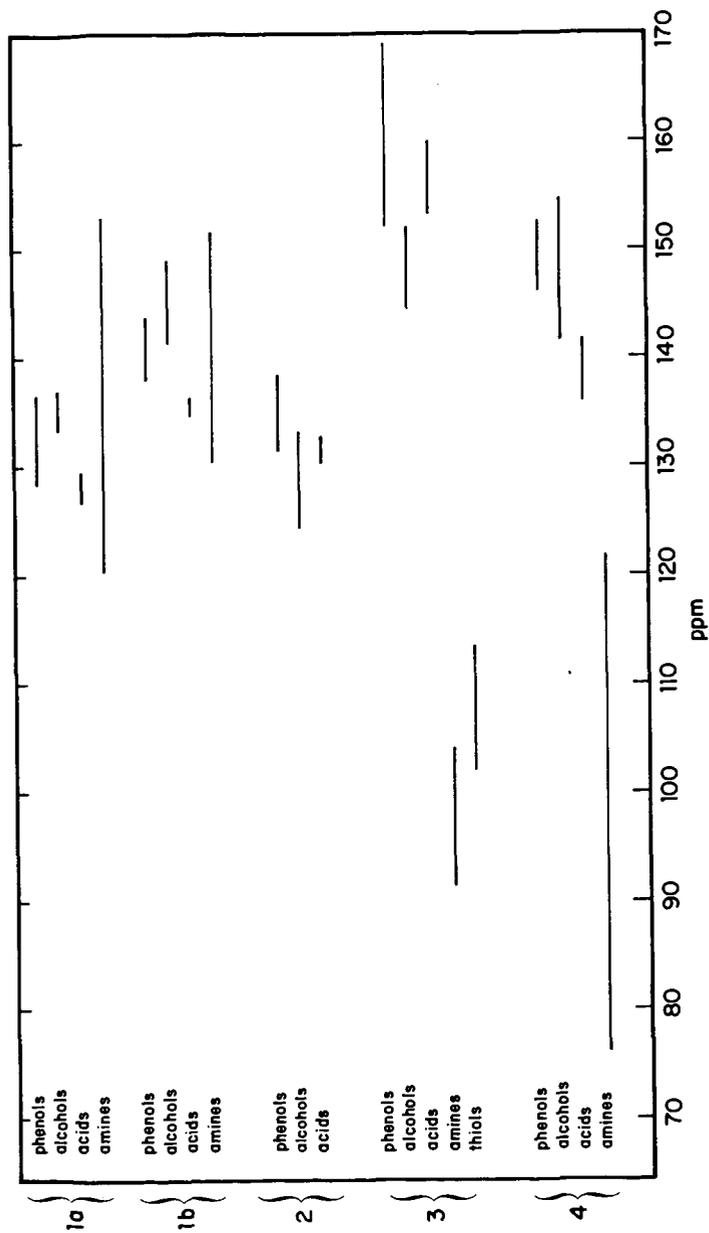


Figure 1. <sup>31</sup>P chemical shift ranges for model compound phenols, alcohols, acids, amines and thiols derivatized with reagents 1a, b and 2 - 4.

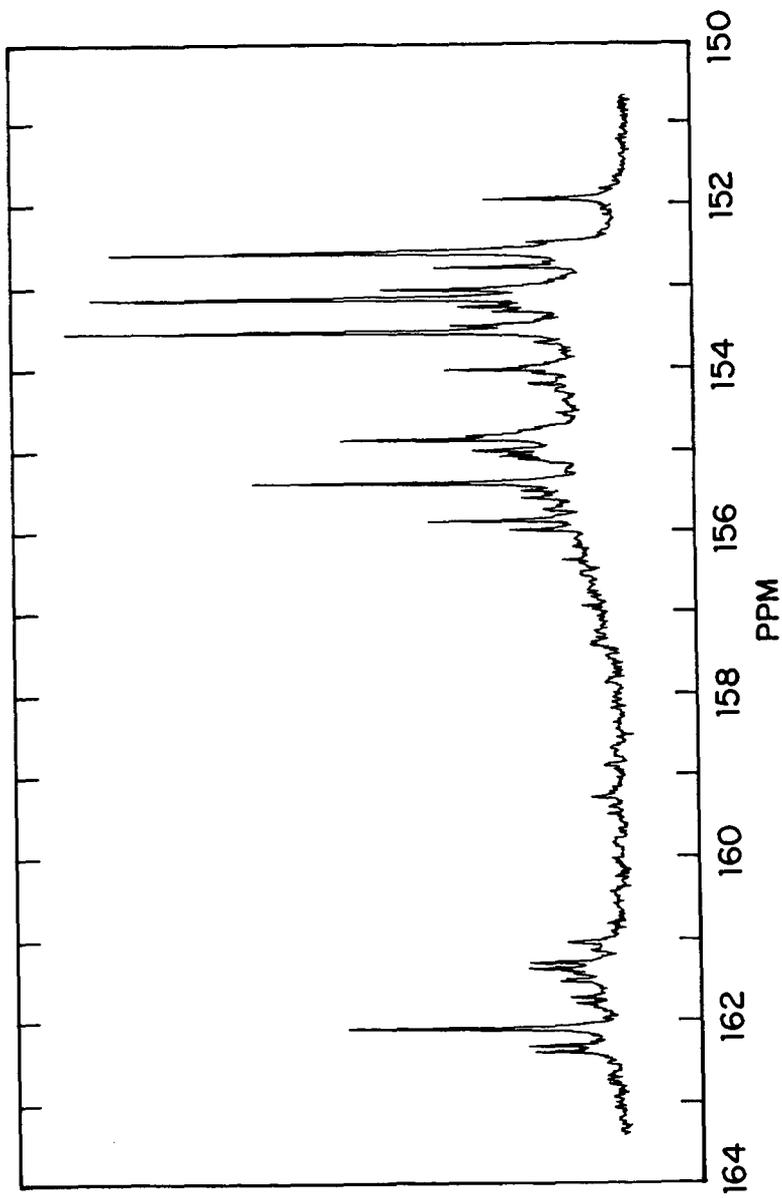


Figure 2.  $^{31}\text{P}$  nmr spectrum of the phenol region of an Illinois No. 6 low-temperature pyrolysis condensate.