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FACILE REACTION/EXTRACTION OF COAL WITH
SUPERCRITICAL FLUIDS

Quarterly Technical Progress Report for the Period
January 1-March 31, 1984

By
C. G. Venier
T. G. Squires

April 20, 1984

Work Performed Under Contract No. FG22-82PC50786

Energy and Mineral Resources Research Institute
Iowa State University
Ames, Iowa

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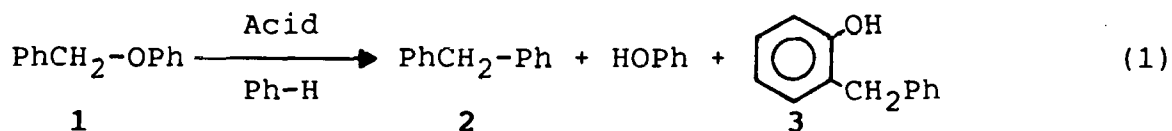
Energy and Mineral Resources Research Institute
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Ames, Iowa 50011

Date Transmitted: April 20, 1984

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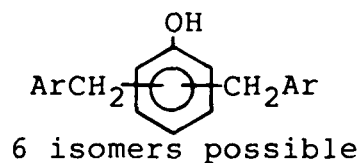
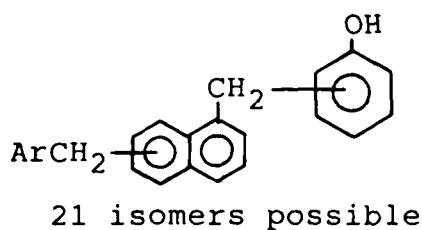
RESULTS

Arylmethyl phenyl ethers undergo competing reactions when treated with Lewis acids. A partitioning of arylmethyl groups between an intramolecular pathway (a rearrangement) and an intermolecular one was previously reported. Studies of benzyl phenyl ether show that, regardless of the choice of acid or temperature, essentially one-half of the starting phenylmethyl phenyl ether, **1**, ends up as rearranged product. Table 1 shows that generally



the same result holds for 1-naphthylmethyl phenyl ether, **4**. However, a previously unrecognized complication shows up in the products of the acid-catalyzed reaction of **4**.

Despite the fact that solvent benzene is in great excess, substrate or product or both, effectively compete for the 1-naphthylmethyl moiety. Capillary gc-ms reveals that at least five products of molecular weight 374 are produced in these reactions. This corresponds to structures containing two 1-naphthylmethyl groups and one phenol. These products can arise by substrate capture of a 1-naphthyl-methyl followed by ether-to-phenol rearrangement or, alternatively, by capture of 1-naphthyl-methyl by products **5**. Even under conditions where the molar



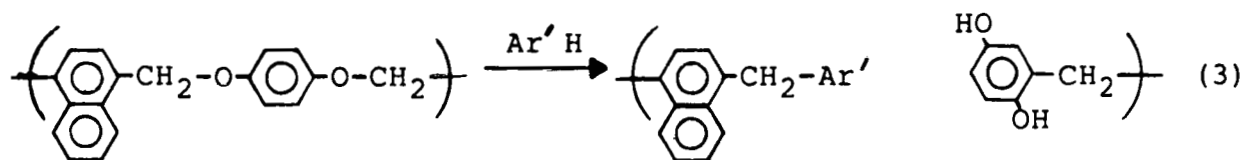
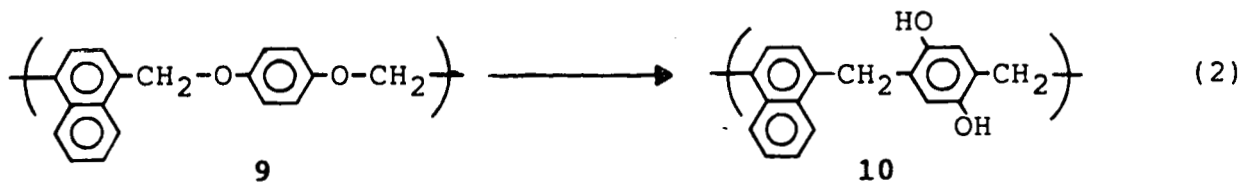
ratio of benzene to starting material exceeds 1000, a significant number of product molecules derive from more than one molecule of starting ether.

If substrate and/or products can trap the electrophilic 1-naphthylmethyl species with such efficiency, it stands to reason that other aromatic compounds will likely be better than benzene also. Table 2 shows data demonstrating that this is the case. The fact that the relative rate constant measured for the naphthalene-benzene competition remains constant over a 100-fold change in naphthalene concentration, confirms that the change in product slate arises by the simple partitioning of an intermediate between the two traps. The straightforward behavior of the system was further checked by allowing diphenylether and 2,6-dimethylphenol to compete directly. The rate constants determined when three traps are present are sensibly the same as those found in binary competition (see last line of Table 2).

One would expect the same sort of behavior for the trapping of intermediates generated from insoluble materials. Naphthalene should be a substantially better capping agent than benzene. The results of the BF_3 -catalyzed arylations of polymer 9 with benzene, naphthalene, or phenanthrene as traps in CH_2Cl_2 solvent are given in Table 3, along with the results from some reactions

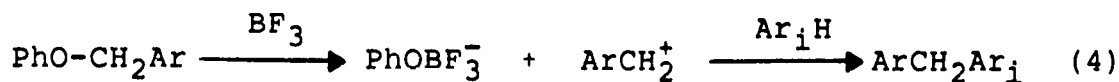
carried out in benzene solvent.

Of particular importance is the fact that the solubilities of products generated in the presence of naphthalene and phenanthrene differ markedly from that produced by BF_3 treatment alone. Infrared spectra (Figure 1) clearly establish that the ether functions present in the starting polymer are no longer present in the products. Apparently, in the absence of a trap, polymer 9 is converted to a new polymer, whose structure is best approximated as 10, equation 2, although we recognize that substantial amounts of interchain crosslinking might occur. The enhanced solubility in the presence of arene, therefore, signals the lowering of molecular weight by capping reactions, equation 3.



DISCUSSION

The results reported here are best interpreted on the basis of a model in which carbonium ions generated from arylmethyl phenyl ethers are partitioned between the various nucleophiles present. In this system, aromatic rings are the most nucleophilic functional groups. The 1-naphthylmethyl cation is much more stable than is the simpler benzyl cation, and, consequently, much more selective in its reactivity(1). Thus, in the case of



benzyl phenyl ether, 1, solvent benzene effectively traps all generated carbonium ions. However, the more stable 1-naphthylmethyl cation generated from 4, is sufficiently stable to discriminate between the poorly nucleophilic benzene and the more nucleophilic molecules, 4 and 5. Naphthalene, on the other hand, is much more nucleophilic than benzene(2), and in sufficient concentration, suppresses "self-trapping".

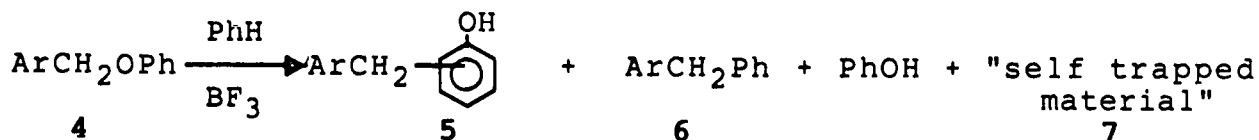
The same picture emerges from work with polymer 9. Apparently, benzene is insufficiently reactive to compete with intramolecular (intrapolymer) nucleophiles and, consequently, no increase in solubility accompanies the cleavages of ether links in 9 upon addition of benzene. When better nucleophiles, naphthalene and phenanthrene, are provided, carbonium ions generated from ether cleavages are capped and the product is lower in molecular weight and more soluble.

It is worth noting that the naphthalene ($k_{\text{rel}}=300$) is nearly as good a trap as the phenol ($k_{\text{rel}}=450$). Since hydroxylic solvents will level the acid strength of BF_3 to that of $\text{ROBF}_3^-\text{H}^+$ and hydrocarbons would not, the acid-catalyzed bond cleavages necessary for unlinking coal may in fact be faster in BF_3 -arene than in BF_3 -phenol. While we have not yet extended these results to coals, we believe that the combination of a relatively mild Lewis acid catalyst, BF_3 , with a good carbonium ion trap, naphthalene, will allow selective cleavage and capping of aryl alkyl ether bonds.

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2. Dewar, M.J.S.; Mole, T.; Warford, E.W.T. J. Chem. Soc. 1956, 3581, report $k(\text{naphthalene})/k(\text{benzene})=350$ for nitration.
3. Bunnett, J.F. In "Investigations of Rates and Mechanisms of Reactions"; Lewis, E.S., Ed.; Wiley-Interscience: New York, 1974; Chapter IV, pp. 158 ff.

Table 1. Products of BF_3 -Catalyzed Cleavage of 1-Naphthylmethyl Phenyl Ether.^a

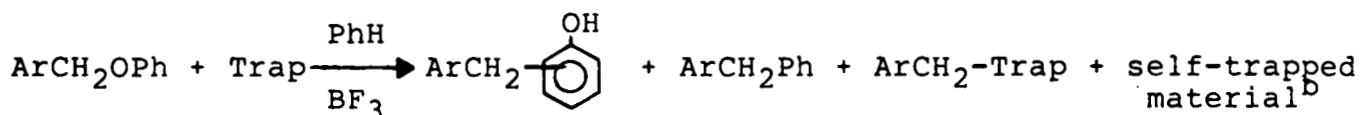


<u>ArCH₂OPh</u>	<u>o-5</u>	<u>p-5</u>	<u>6</u>	<u>recovery</u>	<u>7^b</u>
0.2M	30	12	<1	43%	(1.00)
0.02M	37	15	6	58%	.76
0.002M	50	16	12	78%	.27

^aRoom temperature, benzene solvent

^bRelative yield of several products from liquid chromatographic analysis.

Table 2. Relative Trapping Ability of Aromatic Compounds in BF₃-Catalyzed Cleavage of 1-Naphthylmethyl Phenyl Ether.^{a,3}



Trap	Trap, M	5	6	8	7	k _{rel} ^c
		<u>o-5</u>	<u>p-5</u>	<u>6</u>	<u>8</u>	
Benzene	0	38	13	7	--	(1)
Naphthalene	.020	33	14	7	3	280
Naphthalene	.20	37	14	3	17	310
Naphthalene	2.0	32	8	1	46	260
Diphenyl Ether	.20	41	13	4	4	50
2,6-Dimethylphenol	.20	39	12	2	17	450
Diphenyl Ether	.20	28	9	1.5	15	500
2,6-Dimethylphenol	.20				1.3	45

^aRoom Temperature, benzene solvent.

^bSee Figure 1 for relative yields of self-trapped material.

$$\frac{k_{\text{trap}}}{k_{\text{PhH}}} = \frac{[\text{ArCH}_2\text{-Trap}]}{[\text{ArCH}_2\text{Ph}]} \times \frac{[\text{PhH}]}{[\text{Trap}]}, \text{ see reference 3.}$$

Table 3. BF₃-Catalyzed Arylation of Polymer 9.

ArH/solvent	Acid	Temp.	Product solubilities ^a		
			CH ₂ Cl ₂	PhH	Acetone
CH ₂ Cl ₂	BF ₃ ·H ₂ O	23°			0% ^b
CH ₂ Cl ₂	BF ₃	20°	<5%		
PhH/CH ₂ Cl ₂ ^c	BF ₃	20°	<5%		
naphthalene/CH ₂ Cl ₂ ^c	BF ₃	20°	29%		
phenanthrene/CH ₂ Cl ₂ ^c	BF ₃	20°	24%		
PhH	BF ₃ ·CH ₃ OH	80°		11%	39%
PhH	BF ₃	23°		19%	76%

^aDetermined by weight of insoluble product.

^bIR shows complete loss of ether functionality.

^c0.4 M Arene.

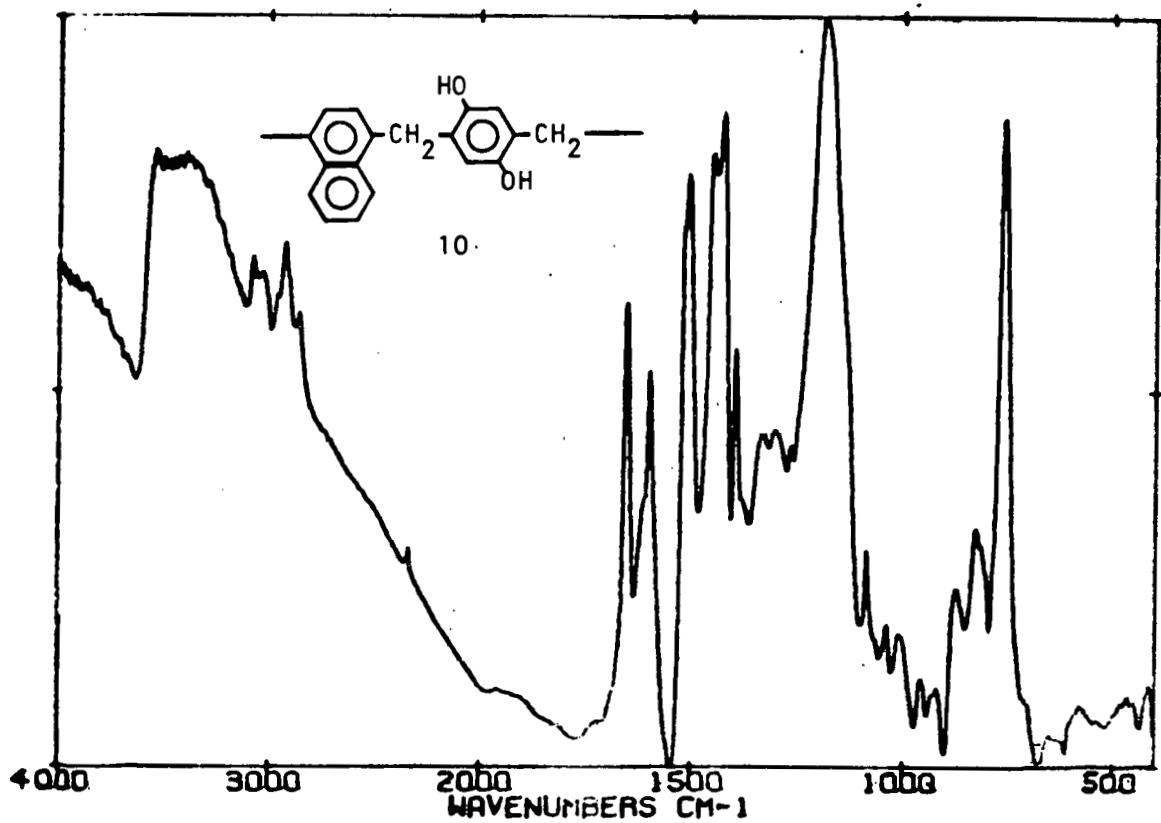
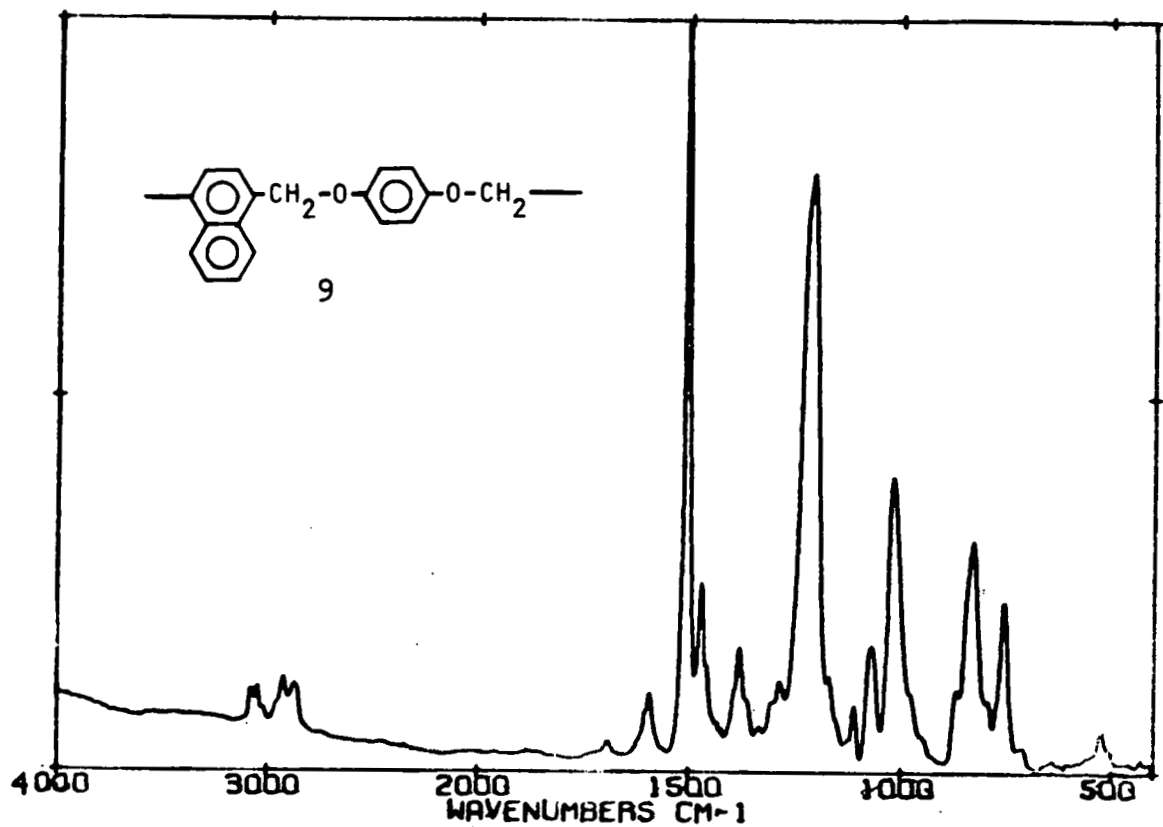


FIGURE 1. Infrared spectra of polymer 9 and its rearrangement product, polymer 10.

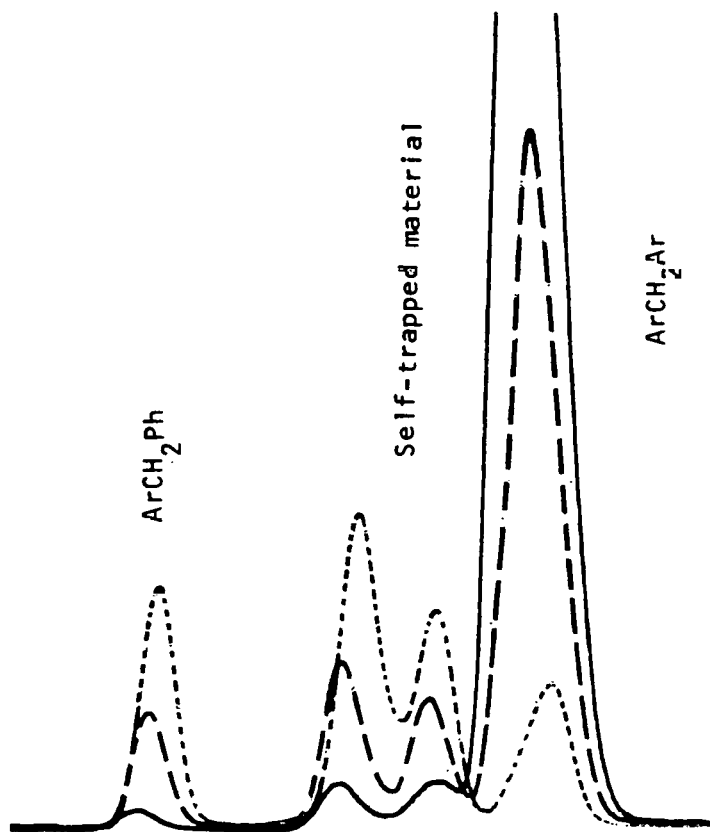


FIGURE 2. Liquid Chromatograms of the Naphthylation of 1-Naphthylmethyl Phenyl Ether, ArCH_2OPh

- 0.020 M Naphthalene (ArH)
- 0.20 M Naphthalene (ArH)
- 2.0 M Naphthalene (ArH)

