97372-94-6; **32**, 21085-72-3; **33**, 97337-66-1; **34**, 7355-18-2; **36**, 97337-67-2; **37**, 27994-30-5; *β*-**38**, 97337-68-3; *α*-**38**, 97337-69-4; **39**, 3590-59-8; **41**, 97337-70-7; **43**, 97337-71-8; CH_3OSnBu_3, 1067-52-3; $Pd(PPh_3)_4$, 14221-01-3; CH_3OH, 67-56-1; CH_3ONa, 124-41-4; Bu_3SnOPh, 3587-18-6; 1-phenyl-3-(4-bromophenyl)-3-hydroxy-1-propene, 1669-60-9; 4-methylpentan-2-one, 108-10-1; propanal, 123-38-6; 7-methyloct-3-en-5-one, 17577-93-4; cinnamyl alcohol, 104-54-1; 7-oxabicyclo[3.2.1]oct-2-en-6-one, 4720-83-6.

Reductive Alkylation of Illinois No. 6 Coal. Chemical and Spectroscopic Evidence Concerning the Principal Oxygen-Containing Groups in the Coal

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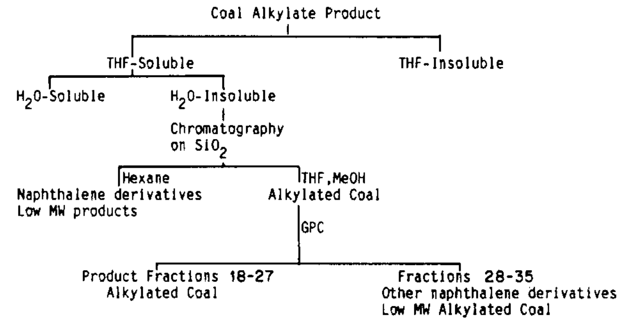
The reductive alkylation of a representative Illinois No. 6 high volatile bituminous coal from the Illinois No. 6 seam has been carried out with potassium naphthalene(−1) as the reducing agent and several primary alkyl iodides as the alkylating agents, and the properties of the soluble products have been investigated. Chemical and spectroscopic studies of the products obtained in reactions with methyl-d_3 and methyl-^{13}C iodide indicate that only 2 ether linkages/100 C are cleaved in the reductive alkylation, that there are 5 C-alkylation and 7 O-alkylation reactions/100 C, and that there are 0.1 primary alkyl methyl ethers/100 C, 2.2 hindered aryl methyl ethers/100 C, 3.3 unhindered aryl methyl ethers/100 C, 0.6 unhindered dihydroxyaryl methyl ethers/100 C, and 0.8 methyl carboxylates/100 C. The nature of the oxygen-containing compounds in this coal is discussed.

Although CP MAS NMR spectroscopy, diffuse reflectance FTIR spectroscopy, and related methods for the study of solids provide important information about the structural elements of coal, it is clear that even more information could be obtained if the coal could be studied in homogeneous solution. Consequently, procedures for the conversion of the intractable solid into soluble products without significant degradation of the structure have long been sought. In some instances, this objective can be realized by reduction or by alkylation. For example, the reduction of a low volatile, bituminous coal from the Lower Kittaning Seam with 88% carbon(daf) with potassium in ammonia yields a product that is 90% soluble in pyridine.[1] Regrettably, the lower rank bituminous coals cannot be successfully solubilized with these procedures.[2] The most suitable method for these coals was discovered by Sternberg and his associates.[3,4] They found that many coals reacted with potassium naphthalene(−1) to form polyanions that could be alkylated. The reaction products are often quite soluble in common organic solvents such as tetrahydrofuran or pyridine and, as a consequence, can be investigated in homogeneous solution.[5]

A systematic study of a low rank bituminous coal from the Illinois No. 6 seam revealed that reductive alkylation with potassium naphthalene(−1) as the reducing agent provided a higher yield of soluble products than reductive alkylation with potassium in liquid ammonia or potassium–sodium alloy in glyme solvents.[2] A study of the reaction variables indicated that the reduction step was most effectively accomplished with potassium rather than lithium or sodium and with biphenyl or naphthalene rather than anthracene or other polycyclic aromatic hydrocarbons.[6] The reactivity patterns observed in the alkylation reactions, methyl iodide > butyl iodide and butyl iodide > butyl bromide > butyl chloride, established that the alkylation reaction was well characterized as an S_N2 process.[6] Although the structure of the alkylating agent often influences the solubility of the product, the methylation, butylation, and octylation of Illinois No. 6 coal yielded only modestly different amounts of soluble products.

Scheme I



The proton and carbon NMR spectra of the reductive methylation and butylation products of this Illinois coal have been reported.[6,7] However, the NMR data did not permit an unequivocal assignment of the interesting oxygen-containing structural elements even when the reactions were carried out with highly enriched reagents such as methyl-^{13}C and butyl-*1*-^{13}C iodide. Accordingly, we have extended our study by the investigation of the alkylated coals prepared with methyl-d_3 and methyl-^{13}C iodide by using both chemical and spectroscopic methods to define the nature and quantity of the O-alkylated products.

Results

The empirical formula of the representative Illinois No. 6 coal used in this study was $C_{100}H_{87.0}O_{13.1}S_{1.9}N_{0.75}$; it contained 8.2% ash. The reductive alkylation reaction was carried out as shown in eq 1 and 2.

$$\text{coal} \xrightarrow[\text{5 days, 25 °C}]{\text{K, } C_{10}H_8\text{, THF}} \text{coal polyanion} \qquad (1)$$

$$\text{coal polyanion} \xrightarrow[\text{2 days, 25 °C}]{\text{RI, THF}} \text{coal alkylate product} \qquad (2)$$

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(1) Mallya, N.; Stock, L. M. *Am. Chem. Soc., Div. Fuel Chem. Prepr. Pap.* **1985**, *30* (2), 291.

(2) Stock, L. M. *Coal Sci.* **1982**, *1*, 210.

(3) Sternberg, H. W.; Delle Donne, C. L.; Pantages, P.; Moroni, E. C.; Markby, R. E. *Fuel* **1971**, *50*, 432.

(4) Sternberg, H. W.; Delle Donne, C. L. *Fuel* **1974**, *53*, 172.

(5) The results obtained from several laboratories have been reviewed in ref 2.

(6) Alemany, L. B.; Stock, L. M. *Fuel* **1982**, *61*, 250.

(7) Alemany, L. B.; Stock, L. M. *Fuel* **1982**, *61*, 1088.

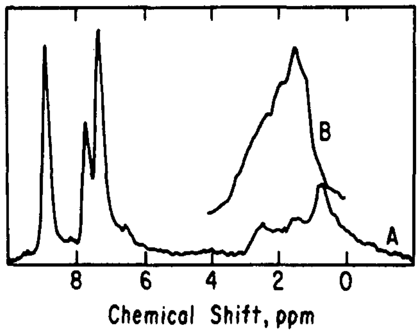

Figure 1. The ^{2}H NMR spectra of reduced Illinois No. 6 coal. (A) The coal anion was prepared with potassium naphthalene(−1) in tetrahydrofuran–tetrahydrofuran-d_8 and treated with water. (B) The coal anion was prepared in the usual way and treated with heavy water.

The product isolation sequence, Scheme I, was developed to separate the desired coal products from the unwanted byproducts formed by the reductive alkylation of naphthalene. Several tests demonstrated that the procedure was suitable for this purpose.[2,8] More than 90% of the tetrahydforuan-soluble alkylated coal was eluted in the first nine product-containing fractions during gel permeation chromatography. Mass spectra analyses confirmed that these fractions were free of naphthalene, bitetralyl, reductively alkylated naphthalene, and related kinds of compounds. These substances were present in small amounts in subsequent fractions.

The conversion of the coal to tetrahydrofuran-soluble products ranged from 46 to 64% in 15 experiments with methyl, ethyl, and 1-butyl iodide. Reductive alkylation of the tetrahydforuan-insoluble byproduct yielded another 50 to 60% tetrahydrofuran-soluble material. Thus, 80–90% of the organic carbon atoms in the original coal can be observed in soluble products. The existence of a new absorption in the infrared spectrum of the product near 1740 cm^{-1} (ester carbonyl stretch) and the absence of broad absorption near 3300 cm^{-1} (oxygen–hydrogen stretch) indicated that the alkylation reaction was complete.

The reduction of Illinois No. 6 coal consumed 22.4 ± 0.6 equiv of potassium/100 C.[6] The number of methyl groups added to the coal was determined by measurement of the deuterium content of a highly soluble sample of coal alkylated with methyl-d_3 iodide. Combustion of this material and measurement of the deuterium content of the water indicated that 9.9 methyl-d_3 groups/100 C had been added to the coal.[9] Analysis of the same material by ^{2}H NMR spectroscopy provided a somewhat higher value, 12.6 ± 0.7 methyl-d_3 groups/100 C. These observations are in reasonable accord with the finding of Larsen and Urban that the reductive ethylation of Illinois No. 6 coal under the same conditions with ethyl-^{14}C iodide led to the incorporation of 11 alkyl groups/100 C.[8] Inasmuch as the combustion–mass spectral analyses generally provided results that were 10% low, we conclude that 12 methyl-d_3 groups/100 C were added to the coal during the reaction.

The imbalance between the degree of reduction and alkylation was investigated. Several lines of evidence suggested that the difference originated in the abstraction of hydrogen from tetrahydrofuran by transient coal radicals or carbanions.[10,11] Accordingly, the reduction step was carried out in a mixture of tetrahydrofuran and tetrahydrofuran-d_8. The residual potassium was removed and water was added to the mixture. The portion of the product that was soluble in pyridine was obtained as described in the Experimental Section and the ^{2}H NMR spectrum of the material was recorded, Figure 1 part A.

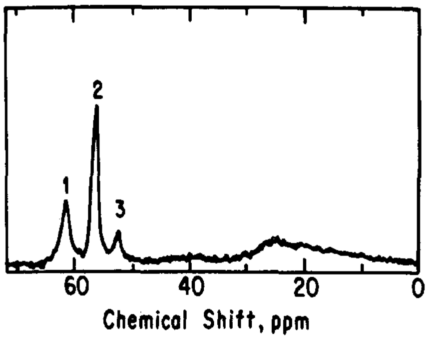

Figure 2. The ^{13}C NMR spectrum of the reductive methylation product of Illinois No. 6 coal.

There were no significant resonance signals downfield of 4 ppm. Hence, tetrahydrofuran-d_8 fragments were neither chemically nor physically incorporated into the product. However, there was a broad signal upfield of 3 ppm indicative of the addition of the label to hydroaromatic and aliphatic structures. It was established in a separate experiment that this high field signal was about 20-fold more intense than the signal in the aromatic region. Thus, few labeled aromatic hydrocarbons were produced in the reactions of the transient intermediates with tetrahydrofuran-d_8. Quantitative work indicated that 2.4 ^{2}H/100 C were introduced into the reduced coal. The primary kinetic isotope effects, k_H/k_D, for the reactions of ethers with bases are significant ranging from 3 to 5.[12] Adoption of the midrange value, 4, implies that 9.6 H/100 C are introduced into the coal from the etheral solvent. The coal sample also contains 0.82% iron pyrite; the reduction of this substance would consume an additional 0.4 equiv of potassium/100 C. The sum of these three reactions, 21 equiv/100 C, is in reasonable accord with the measured consumption of potassium.

The coal polyanion formed in the customary way was also treated with heavy water. The product of the reaction was washed with water to replace all readily exchangeable protons. Quantitative analysis of the ^{2}H NMR spectrum, Figure 1 part B, indicated that the pyridine-soluble product contained 4.2 ^{2}H/100 C.

The NMR spectrum of a typical GPC fraction obtained by reductive methylation with 98% methyl-^{13}C iodide is shown in Figure 2. Examination of the spectra of all the GPC fractions indicated that the average *O*-methyl/*C*-methyl ratio was about 1.4 and that only traces of *N*-methyl groups were present.

The resonances of the O-methylation products appear in three distinct regions which are designated 1, 2, and 3 for convenient discussion. Plausible assignments of the resonances based exclusively on chemical shift correlations are presented in column A of Table I. Since the spectroscopic observations do not define the character of the oxygen-containing compounds adequately we exploited the differences in chemical reactivity to characterize them more completely.

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[8] Larsen, J. W.; Urban, L. O. *J. Org. Chem.* **1979**, *44*, 3219.

[9] This determination was performed by the Gollab Analytical Services.

[10] Ignasiak, B.; Fryer, J. F.; Jadernik, P. *Fuel* **1978**, *57*, 578.

[11] Ignasiak, B.; Carson, D. *Fuel* **1979**, *58*, 72.

[12] Zielinski, M. "Supplement E, The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups, and Their Sulfur Analogues"; Patai, S., Ed.; J. Wiley and Sons: New York, 1980; Chapter 10.

Table I. The Relative Abundances of the O-Alkylation Products Defined by Chemical Conversions and Carbon NMR Spectroscopy

A. possible NMR assignments	B. relative abundance^a	*O*-methyl/ 100 C^a
1. Region Centered at 61 ppm		
vinyl ethers		
primary alkyl ethers	primary alkyl ethers	0.1
primary benzyl ethers		
hindered aryl ethers	hindered aryl ethers	2.2
2. Region Centered at 55 ppm		
secondary alkyl ethers		
unhindered aryl ethers	unhindered aryl ethers	
dihydroxyaryl compounds	dihydroxyaryl compounds	0.6
simple aryl ethers	simple aryl ethers	3.3
3. Region Centered at 51 ppm		
tertiary alkyl ethers		
aryl- and alkylcarboxylic acid esters	aryl- and alkylcarboxylic acid esters	0.8

[a] The results have been normalized on the basis of the finding that there are 7 *O*-methyl groups/100 C in the alkylated product.

Table II. Results for the Demethylation of Ethers with Lithium Iodide and 2,4,6-Collidine at 170 °C for 24 h

compound	recovery, %
2-phenylethyl methyl ether	100
benzyl methyl ether	100
4-methoxybenzoic acid	100
9-anthryl methyl ether	76
anisole	0
2,6-dimethylanisole	0

First, the relative contributions of methyl esters and methyl tertiary alkyl ethers to the region 3 resonance at 51 ppm were determined by mild basic hydrolysis. Tetrahydrofuran-soluble, ^{13}C-enriched reductively methylated coal was treated with tetrabutylammonium hydroxide in aqueous tetrahydrofuran for 24 h at room temperature. The hydrolyzed product, which was recovered from the reaction in a conventional way, was completely soluble in tetrahydrofuran and chloroform. The signal at 51 ppm in the starting material was reduced by 98% in the product. Thus, the region 3 resonance arose from methyl carboxylates. Neither the hydrolysis experiment nor chemical shift correlation studies distinguish between aryl and alkyl methyl carboxylates.

Second, Haenel and co-workers suggested that a portion of the signal near 61 ppm in region 1 of the ^{13}C NMR spectrum of a reductively methylated bituminous coal from the Ruhr coal field was due to the formation of enolic methyl ethers.[13,14] To test this suggestion, ^{13}C-enriched reductively methylated Illinois No. 6 coal product was treated with hydrochloric acid in aqueous tetrahydrofuran for 48 h at room temperature. The product, which was fully soluble in tetrahydrofuran, was examined by ^{13}C NMR spectroscopy. There were no significant changes in the relative or absolute intensites of the two most downfield O-alkylation signals (regions 1 and 2). Thus, vinyl ethers were not formed to a measurable degree in the reductive methylation reaction.

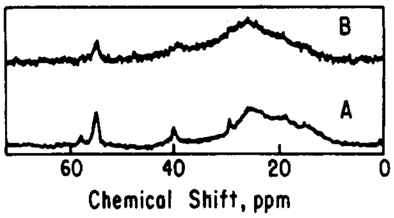

Figure 3. The ^{13}C NMR spectrum of the reductive methylation product shown in Figure 2 following (A) treatment with lithium iodide in collidine and (B) treatment with this reagent and boron trifluoride etherate–1,2-ethanedithiol.

Third, aryl methyl ethers and alkyl methyl ethers can be distinguished by selective demethylation with lithium iodide in 2,4,6-collidine.[15,16] This reaction is quite selective. The information available in the literature and the representative results presented in Table II indicated that aryl methyl ethers and methyl esters are cleaved after 24 h at 170 °C. However, alkyl methyl ethers are cleaved only very slowly and aryl butyl ethers and dialkyl ethers (including alkyl methyl ethers) are stable under the reaction conditions.

The soluble ^{13}C-enriched reductively methylated coal and anhydrous lithium iodide were heated to 170 °C in 2,4,6-collidine under nitrogen for 48 h. The solvent was removed in vacuo and the demethylated product was washed with 2 N hydrochloric acid and dried under nitrogen. This treatment altered the physical as well as the chemical character of the alkylated coal. Specifically, only 30% of the recovered material was soluble in tetrahydrofuran. Several observations indicated that the loss in solubility arose from demethylation. For example, reductively butylated coal can be recovered virtually unchanged from the same reaction. Fortunately, the demethylated product was about 80% soluble in pyridine. This behavior is consistent with the notion that pyridine, by virtue of its basicity, disrupts intermolecular hydrogen bonding and, by virtue of its aromatic character, also overcomes intermolecular π interactions. The intensity of the resonances of the *O*-methyl groups in the ^{13}C NMR spectrum, Figure 3 part A, was greatly decreased in this reaction product. The losses in intensities in regions 1, 2, and 3, relative to the presumably constant C-alkylation intensity, were 96%, 89%, and 100%, respectively. It is notable that primary benzyl methyl ethers were not formed during reductive methylation as evidenced by the absence of intensity downfield of 60 ppm in the spectrum of the demethylated product.

Fourth, alkyl methyl ethers can be cleaved selectively by boron trifluoride-etherate and a thiol or dithiol.[17,18] These reagents are effective for the demethylation of primary and secondary alkyl methyl ethers and benzyl methyl ethers, but aryl methyl ethers and tertiary alkyl methyl ethers are stable. A reductively methylated coal sample, which had been previously demethylated with lithium iodide, was treated under argon with boron trifluoride–etherate and ethanedithiol in a sealed tube for three days. The recovered, thoroughly washed product was 95% soluble in chloroform. The ^{13}C NMR spectrum is shown in Figure 3 part B. Acid-catalyzed ether cleavage

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(13) Haenel, M. W.; Mynott, R.; Niemann, K.; Richter, U. B.; Schanne, L. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 636.

(14) Fried, J.; Abraham, N. A.; Santhanakrishnan, T. S. *J. Am. Chem. Soc.* **1967**, *89*, 1044.

(15) McMurry, J. E. *Org. React.* **1976**, *24*, 187.

(16) Several recent applications are presented in the following articles: (a) Snyder, C. D.; Rapaport, H. *J. Am. Chem. Soc.* **1974**, *96*, 8046. (b) Welch, S. C.; Prakasa Rao, A. S. C. *J. Org. Chem.* **1978**, *43*, 1957. (c) McCarthy, J.; Moore, J.; Cregge, R. *Tetrahedron Lett.* **1978**, *52*, 5183. (d) Kitamura, T.; Imagaura, T.; Kiauinisi, M. *Tetrahedron* **1978**, *34*. (e) Colombo, L.; Gennari, C.; Potenza, D.; Scolastico, C.; Aragoczini, F. *J. Chem. Soc., Chem. Commun.* **1979**, 1021. (f) Kende, A. S.; Rizzi, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4247.

(17) Node, M.; Hori, H.; Fujita, E. *J. Chem. Soc., Perkin Trans. 1*, **1976**, 2237.

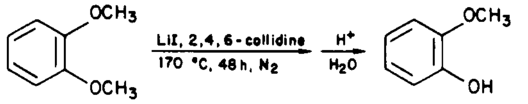
(18) Fuji, K.; Ichikawa, K.; Node, M.; Fujita, E. *J. Org. Chem.* **1979**, *44*, 1661.

Table III. Relative Abundances of the Carbon and Oxygen Alkylation Products Determined by Analysis of the ^2H NMR Spectra[a]

	relative abundance, %			*O*-methyl-d_3/*C*-methyl-d_3
fraction	aryl O	alkyl O	C	
20	53	9	38	1.6
22	55	4	41	1.4
24–25	56	2	42	1.4
26–27	47	4	49	1.0

[a] The uncertainty is estimated to be 7%.

eliminated the *O*-methyl resonances in region 1, but not in region 2. The residual intensity in this region of the spectrum can best be rationalized on the basis of 1,2-dimethoxyaryl compounds, eq 3. These compounds undergo monodemethylation with iodide ion, even when the reagent is in great excess,[16a,16b] and also resist acid-catalyzed demethylation.



(3)

The ^2H NMR spectra of the reductive alkylation products prepared with methyl-d_3 iodide were also recorded over the temperature range from 25 to 145 °C with 2-bromopyridine as the solvent. The weak resonance signal was readily discernible at 3.4 ppm. The assignment of this signal to alkyl methyl-d_3 ethers was confirmed in two ways. First, the widths of all the resonances narrowed perceptibly as the temperature increased but the resonance at 3.4 ppm was especially sharp compared to the resonances of the aryl methyl-d_3 ethers and *C*-methyl-d_3 compounds. This observation is compatible with the idea that the relaxation properties of the ^2H nuclei in the methylated coal depend upon segmental motion with the ^2H nuclei in closer proximity to the large anisotropic structures exhibiting slower internal motions and, as a consequence, broader lines.[19,20] We postulate that the ^2H nuclei in CoalAlkyl-OCD_3 structures are located in more mobile segments than the ^2H nuclei in CoalArOCD_3 or CoalCCD_3 structures and they should, therefore, exhibit the narrowest resonance signals. Second, and more directly, treatment of this alkylated coal with boron trifluoride–etherate and ethanedithiol eliminated the resonance at 3.4 ppm.

The ^2H NMR spectra obtained at 145 °C were analyzed by curve fitting techniques to determine the relative abundances of the carbon and oxygen methylation products. The results are summarized in Table III for four different GPC fractions.

The results are entirely consistent with the ^{13}C NMR data for the coal. Specifically, the *O*-methyl-d_3/*C*-methyl-d_3 ratio was in the range from 1.6 to 1.0 with the largest value recorded for the highest molecular weight product. In addition, the results presented in Table III suggest that the ratio changes because there is a larger quantity of alkyl methyl-d_3 ethers in the higher molecular weight fractions.

Discussion

Aspects of Reductive Alkylation. An equilibrated mixture of coal anions is formed during the slow, 5 day reduction of Illinois No. 6 coal with potassium naphthalene(−1) in tetrahydrofuran, eq 1. These anions react readily with water, alkyl iodides, and other electrophilic agents. Unfortunately, the products of the reactions with proton acids such as water and ammonium ion exhibit only limited, 25%, solubility in pyridine. In contrast, the products of the reactions of the coal anions with methyl iodide are almost 70% soluble in this solvent. The reductively alkylated coal is much more soluble than the material obtained by the sequential reduction, protonation, and O-methylation of the coal.[2] Clearly, both C- and O-alkylation are essential for high conversion of this coal to a soluble material suitable for spectroscopic study.

The outcome of the reduction reaction is determined by kinetic as well as by thermodynamic considerations. This feature is well illustrated by the results obtained in the study of the reactions of the coal anions with hydrogen donors. Thus, the partially soluble product obtained by treatment of the anions with heavy water contains 4.2 $^2H/100$ C. The level of deuterium incorporation in this material is comparable with the degree of C-alkylation, about 5 methyl groups/100 C. We infer that the same anions are undergoing reaction in each instance. Inasmuch as the resonance of the ^2H nuclei appear almost exclusively at high field, it seems safe to conclude that there are few, if any, vinyl or aryl carbanions in the equilibrated reaction mixture. Rather, the observation that the maximum intensity of the broad, ^2H signal appears at 1.6 ppm suggests that relatively stable anions and dianions of aromatic compounds and benzylic carbanions are present at the end of the reduction step and that these substances are converted into dihydroaromatic compounds and arylmethanes by alkylation. Although some progress has been made in the definition of the structures of these compounds,[21] much more remains to be done.

The reactions that occur between the reactive intermediates and the solvent provide different products. As already discussed, the imbalance between the consumption of potassium and the degree of alkylation of the coal can be accounted for by the reactions of radicals and anions with tetrahydrofuran. Additional information about the nature of the intermediates can be obtained from the ^2H NMR spectra of the products. Virtually, all the ^2H nuclei in the sample exhibit resonances at high field, and more importantly, the maximum intensity appears at 0.8 ppm. These observations are more compatible with the occurrence of carbon–carbon and carbon–oxygen bond cleavage reactions that lead to alkyl and arylalkyl anions and radicals rather than to aryl anions or radicals. Although this feature of the chemistry deserves more attention, these preliminary results imply that few aryl radicals, such as those that could be formed by the carbon–oxygen or carbon–carbon bond cleavage reactions of diaryl ethers[22] or diarylmethanes[2], eq 4–6, are formed or, if formed, are not

$$\text{CoalArOArCoal} \rightarrow [\text{CoalArOArCoal}]^{-\cdot} \rightarrow \text{CoalAr}\cdot + \text{CoalArO}^- \quad (4)$$

$$\text{CoalArCH}_2\text{ArCoal} \rightarrow [\text{CoalArCH}_2\text{ArCoal}]^{-\cdot} \rightarrow \text{CoalAr}\cdot + \text{CoalArCH}_2^- \quad (5)$$

$$\text{CoalAr}\cdot + \text{ThF-}d_8 \rightarrow \text{CoalArD} + \text{THF-}d_7\cdot \quad (6)$$

sufficiently mobile to react with the solvent. The observations are more consistent with the related cleavage reactions of aryl alkyl ethers and 1,2-diarylalkanes as illus-

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(19) Allerhand, A.; Doddrell, D.; Komoroski, R. *J. Chem. Phys.* **1971**, *55*, 189.

(20) The influence of segmental motion on the ^{13}C NMR spectra of reductively butylated coal is discussed: Alemany, L. B.; King, S. R.; Stock, L. M. *Fuel* **1978**, *57*, 738.

(21) Stock, L. M.; Willis, R. S. *Am. Chem. Soc., Div. Fuel Chem. Prepr. Pap.* **1985**, *30(1)*, 21.

(22) Patel, K. M.; Baltisberger, R. J.; Stenberg, V. I.; Woolsey, N. F. *J. Org. Chem.* **1982**, *47*, 4250.

trated in reactions 7 and 8. Base-catalyzed elimination reactions, eq 9, may also occur during the degradation of the coal macromolecule.[2] The radicals and carbanions produced in these ways would react with the labeled solvent to yield substances with resonances in the highfield region of the ^{2}H spectrum.

$$\mathrm{CoalArOAlkylCoal} \rightarrow [\mathrm{CoalArOAlkyl}]^{-}\cdot \rightarrow \mathrm{CoalArO}^{-} + \mathrm{CoalAlkyl}\cdot \quad (7)$$

$$\mathrm{CoalArCH_2CH_2ArCoal} \rightarrow [\mathrm{CoalArCH_2CH_2ArCoal}]^{-}\cdot \rightarrow \mathrm{CoalArCH_2}^{-} + \mathrm{CoalArCH_2}\cdot \quad (8)$$

$$\mathrm{Ar(ArCH_2)CHCH_2Ar} \rightarrow \mathrm{Ar(ArCH_2)CH\bar{C}HAr} \rightarrow \mathrm{ArCH_2}^{-} + \mathrm{ArCH{=}CHAr} \quad (9)$$

The ^{13}C signals of the C- and O-alkylation products appear in two broad bands in the solid-state CP MAS NMR spectra of isotopically enriched, reductively methylated and butylated coals.[23] The three principal resonances of the O-methylation products that are evident in the liquid-phase spectra, Figure 2, have not yet been resolved in solid coals.[23] Thus, this solubilization reaction is effective for the production of coal molecules suitable for spectroscopic study. While the resolution of these three bands is important, it is necessary to recognize that even when fully resolved the chemical shift information is inadequate to define many significant structural characteristics. Fortunately, chemical methods can be conveniently used to transform the soluble coals and to obtain desirable additional information about the oxygen-containing compounds. The results of the chemical and spectroscopic study are summarized in column B of Table III. The ^{2}H NMR studies of the related products containing methyl-d_3 groups support the conclusion that aryl methyl ethers are the most abundant products and provide independent evidence for the presence of alkyl methyl esters.

The Oxygen-Containing Compounds. Interest in challenging problems such as the discovery of methods for the selective depolymerization of coal under mild conditions have prompted work on the structure of coal. The oxygen-containing compounds of the high volatile bituminous coals, for example, Illinois No. 6 coal, have received special attention because the carbon–oxygen linkages in these substances provide an obvious target for specific chemical degradation reactions. Davidson reviewed the early structural work on the oxygen compounds in coal, but important additional contributions have appeared since the publication of his article.[24] In brief, there seems to be little doubt that between 50 and 55% of the oxygen atoms in Illinois No. 6 coal occur in hydroxyl groups. This feature is secured by several lines of evidence including titration data[25] and quantitative assays of the degree of methylation.[26] The nature of the other oxygen atoms is less securely established. NMR spectroscopists often assign the signal intensity in the low field region of the solid-state spectra of coal (downfield of 162 ppm) to carbonyl carbon atoms.[23,27] About 5% of the ^{13}C signal intensity for Illinois No. 6 coals occur in this region. However, this assignment can not be literally accepted for two reasons. First, as Maciel and co-workers point out,[27] the line widths of the ^{13}C resonances of the lower rank coals are relatively large. As a consequence, the resonances of the ipso carbon atoms in hydroxy- and methoxyaromatic compounds with "normal" chemical shifts may be broadened into the downfield region. Second, the resonances of some ipso carbon atoms in oxygen-rich ethers and phenols do, in fact, appear at fields below 160 ppm.[28] Clearly, the NMR data cannot, without additional evidence, be taken as indicative of 5% carbonyl carbon atoms. Indeed, there is no correspondingly intense absorption in the infrared spectrum of the Illinois No. 6 coal. In this connection, it is interesting to compare the FTIR spectrum of the coal and its O-methylated derivative. The methylated product contains less than 1 methyl ester/100 C, yet the carbonyl absorption near 1740 cm^{-1} is readily evident in conventional spectra. For the native coal, rather sophisticated curve analysis techniques are required to even detect the absorptions of esters.[29] We infer, therefore, that acid and ester carbonyl groups contribute no more than 1% of the intensity in the ^{13}C solid-state spectrum. Classical methods for the assessment of the quantities of other carbonyl groups in coal imply that these groups are less abundant than carbonyl groups (<1/100 C).[30] Some workers have suggested that these carbonyl groups appear in strongly hydrogen bonded quinones, e.g., 1-hydroxyanthraquinone.[25] These observations and the solid-state NMR data can be reconciled if it is presumed that certain sp^2 carbon atoms bonded to hydroxyl groups or etheral oxygen atoms have chemical shifts at fields lower than 162 ppm and that line broadening effects disperse other ^{13}C resonance signals into the low field region. In summary, the 13 oxygen atoms in the Illinois No. 6 coal under study apparently are distributed among 5 or 6 phenolic groups, 1 acid group, 5 or 6 etheral groups, and possibly one other carbonyl group.

Our observations, Table III, column B, indicate that the reductively methylated coal contains 7 labeled methoxyl groups/100 C distributed among esters, 0.8/100 C, and ethers, 6.2/100 C. The quantity of carboxyl groups found in this material is in reasonable accord with the observations outlined in the previous paragraph. It is pertinent, however, that more carboxyl groups are detected in the reductive methylation product than in the methylated coal extract. The modest increase may be the consequence of the entrapment of small molecules[31,32] within the cross-linked macromolecular structure[33] of the coal. We infer that these acids are liberated during the reductive cleavage reactions which disrupt the matrix.[31]

The new results provide much more information about the ethers and phenols in this coal. We observe merely 0.1 primary alkyl ethers/100 C and no discernible quantities of secondary or tertiary alkyl ethers or primary benzylic ethers. These results indicate that the corresponding alcohols are not present in the original coal, but they do not exclude the presence of other dialkyl ethers, which would not cleave under the reaction conditions, or

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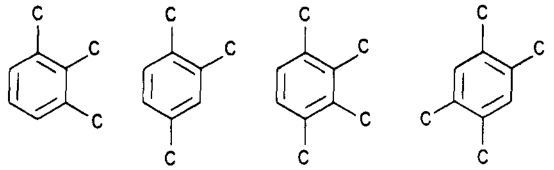
benzylic ethers, which would cleave to produce alkylaromatic compounds, eq 10.

$$\mathrm{CoalArCH_2OArCoal} \rightarrow [\mathrm{CoalArCH_2OArCoal}]^{-\cdot} \rightarrow \rightarrow \mathrm{CoalArCH_3} + \mathrm{CoalArOH} \quad (10)$$

The phenolic ethers in the reductive methylation product are distributed among conventional methoxy aromatic compounds, 3.3/100 C, hindered methoxy aromatic compounds, 2.2/100 C, and dimethoxy aromatic compounds, 0.6/100 C. This reaction, as discussed subsequently, also produces 2 new hydroxyl groups/100 C. The greatest change appears to be in the quantity of hindered ethers. While the finding that aromatic ethers are predominant is hardly surprising, the relatively large quantities of the hindered ethers and diethers is notable. The chemical shift data for the hindered ethers in region 1 of the ^{13}C NMR spectrum, Figure 2, are compatible with the methoxy groups in compounds such as 2,6-dimethylanisole, 2-methyl-1-methoxynaphthalene, and 9-methoxyacridine.[34] Hence, peri interactions as well as ortho substituents may both be important. Other work in our laboratory suggests that the carbocyclic structures in this coal are rather highly substituted and highly condensed with a preponderance of 1,2,3-, 1,2,4-, 1,2,3,4-, and 1,2,4,5-substitution patterns.[35] Consequently, there are ample opportunities for steric perturbations of the methoxy carbon atoms in the methylated products.



The detection of 0.6 dimethoxy compounds/100 C is nicely in accord with the observations obtained in oxidation studies by the research groups at Pennsylvania State University[36] and the Argonne National Laboratory.[37] Both groups have shown that selective oxidation reactions yield 4-hydroxy- and 3,4-dihydroxybenzoic acid and related this observation to the presence of hydroxy- and dihydroxyphenyl groups in the most probable coal precursor, lignin.[36,37] The new quantitative results of the present work imply that such fragments are more abundant than implied by the oxidation studies.

Three lines of evidence suggest that there are two more hydroxyl groups in the reduced coal than in the native material. First, as already mentioned, Illinois No. 6 coals contain 5 hydroxyl groups/100 C.[24-26] Second, methylation of this coal and subsequent extraction also yields a product with about 5 methyl groups/100 C. Third, the reductive methylation product can be compared directly with the methylation product of the toluene-insoluble, pyridine-soluble extract from the same coal.[36,37] The extract, which has an elemental composition very similar to that of the coal, undergoes methylation readily to provide a soluble substance containing 0.6 methyl esters/100 C, 0.7 hindered methyl ethers/100 C, 0.4 dihydroxyaryl methyl ethers/100 C, and 2.8 aryl ethers/100 C. Approximately 50% of the oxygen atoms in the extract are accounted for in this analysis. We postulate, therefore, that there are five other etheral groups in the raw material and that two of them are cleaved in the reductive methylation to produce additional esters, 0.2/100 C, hindered aryl ethers, 1.5/100 C, dihydroxylaryl ethers, 0.2/100 C, and conventional aryl ethers, 0.5/100 C. Significantly larger quantities of hindered aryl methyl ethers appear in the products of the reductive alkylation reaction. If these results can be taken as representative of the native coal, it is possible to infer that at least 3 ether groups/100 C did not cleave during the reduction. This feature of the chemistry has previously received attention for other coals.[2,38,39] In brief, Wachowska and Pawlak[38] suggested that the unreacted ethers might be heterocyclic compounds and Carson and Ignasiak[39] emphasized the deactivating influence of oxyanions on the rates of ether cleavage reactions of oxyaryl ethers, e.g., $^{-}$OArOR. Broadly speaking, four classes of compounds—benzofurans, xanthenes, hydroxyaryl ethers, and dialkyl ethers—need to be considered on the basis of the criteria that they are plausible constituents of Illinois No. 6 coal and that they resist reductive cleavage under the reaction conditions. Dibenzofurans often undergo reduction rather than cleavage.[40] Xanthanes and hydroxyaryl ethers form relatively stable anions, which do not cleave, under the experimental conditions.[41] The reduction potentials for the dialkyl ethers are so great that these compounds do not cleave.[42] There is not independent evidence for the existence of non-benzylic dialkyl ethers in this coal. Moreover, the fact that our attempts to increase the solubility of the reduced coal by acid-catalyzed ether cleavage reactions were unsuccessful suggests that these contituents are not present in significant quantity. In contrast, the fact that the reductively alkylated coal and the methylated coal[43] are more readily reduced and fragmented than the original coal strongly implies that the removal of anion-forming components is particularly important for further solubilization as illustrated in eq 11 and 12. Further support for the view that

$$\text{original coal: } \mathrm{CoalOArOArOH} \rightarrow \mathrm{CoalOArOArO^-} \nrightarrow \mathrm{CoalOArOArO^{2-}} \quad (11)$$

$$\text{methylated coal: } \mathrm{CoalOArOArOCH_3} \rightarrow [\mathrm{CoalOArOArOCH_3}]^{-\cdot} \quad (12a)$$

$$[\mathrm{CoalOArOArOCH_3}]^{-\cdot} \rightarrow \rightarrow \mathrm{CoalOArO^-} + \mathrm{ArOCH_3} \quad (12b)$$

certain of the unreactive ethers are hydroxyaryl ethers is provided by the finding that the treatment of the insoluble residue with boron tribromide–dimethyl sulfide and subsequent methylation did not increase the solubility of the material. This conclusion finds support in other results for Illinois No. 6 coals including the oxidation work described in the previous paragraphs and detailed analyses of the titration curves. Dutta and Holland point out that certain of the phenolic groups in this coal exhibit rather low p*K* values and note that such observations are compatible with the occurrence of *o*-dihydroxy compounds.[25] In addition, Winans and Hayatsu and their associates found that the vigorous oxidation of an Illinois bituminous coal provided xanthonecarboxylic acids.[44]

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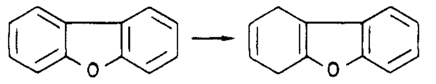
The observations are also compatible with the presence of dibenzofurans and related oxygen heterocycles that selectively undergo reduction, eq 13. The Argonne group has demonstrated that oxidation produces six different dibenzo- and naphthobenzofurancarboxylic acids in readily detectable amounts.[44]



(13)

Conclusion

Reductive methylation converts about 65% of Illinois No. 6 coal into tetrahydrofuran soluble products. The ^{2}H and ^{13}C NMR spectra of these products can be studied in homogeneous solution even though the molecular weights are large ($\bar{M}_n$ = 1800–2200). The resonances of the *O*-methyl compounds are particularly well resolved and these spectroscopic data provide a basis for the discussion of the principal oxygen-containing compounds. Even more definite information can be obtained by the study of the chemical transformations of these soluble compounds. The results obtained in the current study and in previous studies are in reasonable accord and suggest that the 13 oxygen atoms/100 C in this Illinois No. 6 coal are distributed among 5 or 6 aryl hydroxyl groups, 5 or 6 ethers, 1 carboxylic acid, and probably less than 1 other carbonyl groups. Only minor amounts of aliphatic alcohols appear to be present in the coal macromolecules. The aromatic hydroxyl groups are distributed among hindered (two peri interactions are adequate) and unhindered phenols and aromatic dihydroxy compounds. The reduction reaction selectively cleaves ethers that form hindered phenols. Several lines of evidence suggest that the uncleaved ethers are benzofurans, hydroxyaromatic compounds, and xanthene-like compounds. The results of this study provide a basis for new efforts to selectively depolymerize this material.

Experimental Section

Materials. The Illinois No. 6 coal was obtained from the Peabody No. 10 mine in Pawnee, IL. The bulk sample was stored under water until it was ground and seived and stored under argon. Blind duplicate analyses obtained by the Commercial Testing Laboratory were in excellent agreement.

Tetrabutylammonium hydroxide (50% in water), boron trifluoride–etherate, 1,2-ethanedithiol, lithium iodide, chloroform-*d*, pyridine-d_6, naphthalene, and the chemicals used in model compound studies were purchased and used without further purification. Methyl-d_3 iodide (99% isotopic purity) and methyl-^{13}C iodide (90% isotopic purity) were obtained from Cambridge Isotopes. Tetrahydrofuran was distilled from sodium benzophenone ketyl. 2,4,6-Collidine, 2-bromopyridine, and the alkyl iodides were distilled prior to use.

Spectroscopy. The infrared spectra were recorded with a Perkin Elmer Model 283 spectrophotometer. Samples were prepared by adding the coal product (2–5%) and dry potassium bromide (98–95%) to a stainless steel vessel (12 × 26 mm) containing a steel ball (4-mm diameter). The vessel was shaken vigorously with a Wig-L-Bug (Crescent Dental Mfg. Co.) for 30 s. A portion of the resultant fine powder was made into a pellet with a Perkin Elmer hand press. The pellet was dried in vacuo at 65 °C for 20 h. The spectra were recorded immediately after the pellet was removed from the Abderbalden apparatus in a nitrogen atmosphere. The ^{13}C and ^{2}H NMR spectra were recorded with a Nicolet NTC/200 spectrometer. Pyridine-d_5 and chloroform-*d* were used for carbon experiments and pyridine, 2-bromopyridine, and tetrahydrofuran were used for deuterium experiments. Most experiments were carried out in 12-mm tubes at ambient temperature.

The Reductive Alkylation of Coal with Methyl-^{13}C Iodide. A typical procedure for the reductive alkylation of Illinois No. 6 coal is described. Potassium (1.01 g, 26.3 mmol) was added to a stirred solution of naphthalene (0.400 g, 3.12 mmol) in tetrahydrofuran (40 mL) under argon. After 30 min, coal (1.02 g) was added. The mixture was stirred for 120 h before unreacted potassium (0.30 g, 7.2 mmol) was removed. Methyl-^{13}C iodide (4.5 g, 31.5 mmol) was added dropwise over a period of 5 min. The reaction was exothermic and the flask was cooled in an ice bath for 30 min. The bath was removed and the mixture was stirred for an additional 48 h under argon. The mixture was quantitatively transferred to a centrifuge tube with tetrahydrofuran. The methylated product was centrifuged and the supernatant was filtered below 15 μm. Fresh tetrahydrofuran was added to the residue which was stirred and centrifuged. This process was repeated several times until the supernatant was pale yellow. The tetrahydrofuran-insoluble residue was collected on a 0.9–1.4 μm fritted funnel and washed repeatedly with water until the washings were free of potassium iodide as determined by the addition of sodium tetraphenylborate solution. In a similar fashion, the tetrahydrofuran-soluble residue was washed with water. The tetrahydrofuran-insoluble, water-insoluble product was dried in vacuo at 65 °C for 20 h. The dried product weighed 0.421 g. Hence, not less than 64% of the original coal was converted to soluble products.

The tetrahydrofuran-soluble, water-soluble material was mixed with silica gel (60–200 mesh, 5 g) and tetrahydrofuran and the tetrahydrofuran was removed with a rotary evaporator. This mixture was added to a 25 × 2.2 cm silica gel column prepared from a slurry of the gel in hexane and eluted with hexane (250 mL), tetrahydrofuran (250 mL), tetrahydrofuran–methanol (50:50 mL), and methanol (150 mL). The materials that eluted in tetrahydrofuran, tetrahydrofuran–methanol, and methanol were combined. The solvents were removed with a rotary evaporator, the sample weighed 0.765 g after drying in vacuo at 65 °C for 4 h. The mass increase was 14.5%.

A portion of the water-soluble, hexane-insoluble, tetrahydrofuran-soluble alkylated coal (140 mg) was filtered through 1.4 μm frit in preparation for gel permeation chromatography. This sample was dissolved in tetrahydrofuran (1 mL) and injected onto the column. Fifty 3.7-mL fractions were collected; the coal products were concentrated in fractions 18–35. Study of the fractions by pyrolysis mass spectroscopy revealed that fractions 18–27 were free of reduced and reductively alkylated naphthalene derivatives. These fractions were combined, the solvent was removed by rotary evaporation, and the sample was dried in vacuo at 65 °C for 20 h. The weight of the combined fractions was 120 mg and the mass balance was 100%. Portions of fractions 18–27 (20 mg) were combined and dissolved in chloroform-*d* (5 mL) and the ^{13}C NMR spectrum was recorded, Figure 2.

Reductive Alkylation with Methyl-d_3 Iodide. An analogous procedure was used for this preparation. The purified product, which weighed 11% more than the original coal, was isolated as described in the previous paragraph. The substance was 52% soluble in tetrahydrofuran. Gel permeation chromatography of a portion of the product was carried out as described. The infrared spectrum of the tetrahydrofuran-soluble, hexane-insoluble product was recorded. Carbon–deuterium stretching absorptions were observed at 2040, 2092, 2198, and 2325 cm^{-1}. The ^{2}H NMR spectra of six fractions (5 mg dissolved in 2-bromopyridine (5 mL)) were recorded over the temperature range from 25 to 145 °C.

The Reduction of Coal in Tetrahydrofuran-d_8. Illinois No. 6 coal (0.994 g), naphthalene (0.398 g, 3.1 mmol), and potassium (0.038 g, 26.5 mmol) were added to a mixture of tetrahydrofuran-d_8 (10 mL) and tetrahydrofuran (40 mL). The reaction was carried out and the products were isolated as already described.

Weak carbon–deuterium stretching frequencies were apparent between 2000 and 2500 cm^{-1}, but the deuterium content of the material could not be determined with this method. Accordingly, the ^{2}H NMR spectra were recorded by dissolving weighed quantities of soluble coal in pyridine or tetrahydrofuran. The results are shown in Figure 1 part A.

The Reduction of Coal in Tetrahydrofuran, Heavy Water Quench. The same coal was reduced in unlabeled tetrahydro-

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furan with the same procedure and quenched with heavy water. The ^2H NMR spectrum was recorded, Figure 1 part B.

The coal was also reduced in unlabeled tetrahydrofuran and quenched with unlabeled water. No resonances were observed upfield of 7.2 ppm. Hence, the resonances observed in the spectra shown in Figure 1 originated from labeled materials.

Basic Hydrolysis of Reductively Alkylated Coal. An intermediate molecular weight fraction of the tetrahydrofuran-soluble products obtained in the reductive alkylation of Illinois No. 6 coal with 90% methyl-^{13}C iodide was hydrolyzed. The reaction product (35 mg) was treated with tetrahydrofuran (2 mL) and tetrabutylammonium hydroxide (1 mL, 40% by weight in water). This mixture was stirred at room temperature for 25 h before it was acidified with 2 N hydrochloric acid. The acidified coal product was collected and washed with water and dried under a stream of nitrogen overnight. The entire sample was dissolved in chloroform-*d* (5 mL) and the ^{13}C NMR spectrum was recorded. The resonance in region 3 at 51 ppm was reduced virtually to the base line.

Acid Hydrolysis of Reductively Alkylated Coal. A representative GPC fraction of tetrahydrofuran-soluble, hexane- and water-soluble ^{13}C-enriched reductively methylated coal (18.8 mg) was treated with hydrochloric acid (0.5 mL, 0.2 N) in tetrahydrofuran (2 mL). The mixture was stirred for five days before the coal product was isolated and dried. The entire product was dissolved in chloroform-*d* (5 mL) and the ^{13}C NMR spectrum was recorded. Replicate analyses indicated that the area of the region 1 resonance relative to the region 2 resonance was 1.61 in the product compared to 1.5 in the starting material.

Demethylation of Aryl Methyl Ethers. The methyl ether was reacted with a 5–10 molar excess of lithium iodide and an equimolar amont of naphthalene, which was used as an internal standard, in 2,4,6-collidine (5–7 mL). The solution was stirred for 48 h at 170 °C under nitrogen. The organic products were isolated in the usual way and analyzed by gas chromatography by using an OV101 column (4% on Chromosorb W, $^1/_8$ in. × 20 ft). The results for several representative compounds are summarized in Table II.

Demethylation of Reductively Methylated Coal. A portion of the tetrahydrofuran-soluble, ^{13}C-enriched reductively methylated coal (GPC fractions 18–27, 121 mg), lithium iodide (512 mg, 3.8 mmol) and 2,4,6-collidine (7 mL) were heated at 170 °C under nitrogen; the reaction proceeded for 48 h. The collidine was removed in vacuo and the coal product was collected and washed with 2 N hydrochloric acid and water to remove inorganic salts. The sample was dried in vacuo to give the product (118 mg) which was extracted with pyridine. The dried pyridine-insoluble fraction weighed 28 mg (23%). A portion of the pyridine-soluble fraction (25 mg) was dissolved in pyridine-d_5 (5 mL) and the ^{13}C NMR spectrum was recorded, Figure 3 part A.

The reaction was also carried out for 24 h. The pyridine-soluble fraction (37.4 mg) represented 92% of the recovered product (40.1 mg). A portion of the soluble product (25 mg) was dissolved in pyridine-d_5 (5 mL) and the ^{13}C NMR spectrum was recorded. The *O*-methyl signal strength decreased by 63 ± 2%.

Demethylation of Reductively Methylated Coal under Acidic Conditions. Tetrahydrofuran-soluble, hexane-insoluble, ^{13}C-enriched reductively methylated Illinois No. 6 coal (30 mg) was treated with boron trifluoride–etherate (0.1 mL) and 1,2-ethanedithiol (1.0 mL) under argon in a vial at room temperature for three days. Excess boron trifluoride and 1,2-ethanediol were removed in nitrogen. The coal product was washed with 10% aqueous sodium bicarbonate (100 mL), water (100 mL), and 95% ethanol (50 mL) to remove the residual acid and dithiol. After drying in a stream of nitrogen, the product was suspended in tetrahydrofuran and centrifuged, and the supernatant was collected. The process was repeated until the supernatant was slightly yellow. The insoluble residue was dried under nitrogen and weighed. About 95% of the demethylated coal product was soluble in tetrahydrofuran. The sample was dissolved in chloroform-*d* and the ^{13}C spectrum was recorded, Figure 3 part B.

Acknowledgment. It is a pleasure to acknowledge the support of this work by the United States Department of Energy and by the Illinois State Coal Board. The NMR equipment used in this research was purchased with funds from the National Science Foundation and the National Institutes of Health.

Registry No. Potassium naphthalene (-1), 4216-48-2; methyl iodide, 74-88-4; ethyl iodide, 75-03-6; 1-butyl iodide, 542-69-8.

Reaction of Singlet Oxygen with Enamino Carbonyl Systems. A General Method for the Synthesis of α-Keto Derivatives of Lactones, Esters, Amides, Lactams, and Ketones

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A general method for the introduction of a ketone α to the carbonyl group of a ketone, lactone, ester, substituted amide, or lactam has been developed involving the formation and dye-sensitized photooxygenation of enamino carbonyl intermediates.

The direct introduction of a ketone α to a carbonyl group is an important functional group transformation which has many applications in natural product synthesis.[1] The conversion of a ketone to an α-diketone, for example, has been employed in the synthesis of colchicine,[1a] strychnine,[1b] and other natural products. There have been important applications of α-keto lactam formation in synthesis, ranging from the preparation of senecio[2] and vasicine alkaloids[3] to the synthesis of β-lactams[4] and derivatives of penams and cephams.[5] In addition, there is intrinsic interest in α-ketopyrrolidones as synthetic targets, due to their reported antibiotic activity, e.g., against *Trichomonas*

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