bottle was then allowed to cool overnight and vented, and the contents were filtered through a small fritted-glass filter. The filtrate was transferred to a distilling flask and most of the acetic acid and acetic anhydride was removed by distillation at 50 mm (bp 42–58 °C). The distillation residue was cooled, dissolved in ether (250 mL), washed with water and saturated sodium carbonate solution, dried ($MgSO_4$), and filtered, and the ether was removed on a rotary evaporator. The residue, a pale brown oil, weighed 28.8. Distillation gave 24.6 g of colorless oil, bp 103–147 °C (16 mm), which was analyzed by GLC on an F&M Model 720 gas chromatograph using a 5-ft. 20% Carbowax 20M on Chromosorb column operated isothermally at 175 °C. The product contained 4.1 g (23.7 mmol) of 3,4-diacetoxy-1-butene, 1.8 g (10.4 mmol) of 1,4-diacetoxy-*cis*-2-butene, and 18.7 g (108.9 mmol) of 1,4-diacetoxy-*trans*-2-butene.

Registry No. **1**, 40390-49-6; **2**, 764-41-0; **3**, 18085-02-4; **4**, 35125-19-0; **5**, 18085-01-3; **7**, 25260-60-0; **8**, 1576-98-3; **9**, 70940-89-5; butadiene, 106-99-0; acetic acid, 64-19-7; 4-vinyl-4-butyrolactone, 21963-38-2; sodium acetate, 127-09-3; 1,4-dibromo-*trans*-2-butene, 821-06-7; *cis*-2-butene-1,4-diol, 6117-80-2; acetyl chloride, 75-36-5; butadiene monoepoxide, 930-22-3.

Incorporation of Naphthalene and Tetrahydrofuran during the Reductive Alkylation of Illinois No. 6 Coal

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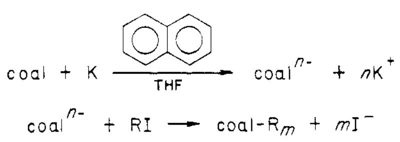
Naphthalene and THF containing ^{14}C were prepared and used in the reductive alkylation of Illinois No. 6 coal. The reductively alkylated coal was fractionated by chromatography on silica gel. Small amounts of ^{14}C from THF are found in the products. This is in part due to tightly bound THF. Naphthalene is incorporated during the reaction, but is found only in the first nonpolar fractions eluted from the silica gel column. Ethyl groups were incorporated in all fractions. Chromatography on silica gel can be used to isolate the alkylated coal cleanly, giving material which does not contain significant amounts of naphthalene or THF. However, if all of the reaction products are used without separation, the mixture contains significant amounts of material derived from naphthalene and small amounts of material derived from THF.

Coals are solid, insoluble, complex mixtures of polymeric organics and minerals.[1] Most organic spectroscopic techniques do not work well on solids, so one major thrust of coal research has been to solubilize coals by carrying out known, selective chemical reactions. Perhaps the reaction most used for solubilizing coals is the Sternberg reductive alkylation procedure[2,3] outlined in Scheme I. Its early use has been reviewed.[4] It is capable of converting greater than 90% of many coals into material extractable into pyridine or benzene. The products of this reaction have been used in many further studies such as measurements of molecular weight distributions[4] and NMR structural investigations.[5] Because of its wide use, it is important that the chemistry of this solubilization process be thoroughly understood.

The interactions of alkali metals with aromatics and other groups thought to be present in coals are quite complex. The cleavage of aryl ethers by alkali metals in THF has been reported.[6] Lithium arenes[7] and lithium biphenyl in THF[8] also cleave ethers. Reductive cleavage of carbon–carbon bonds in diarylalkanes may also occur.[9-12]

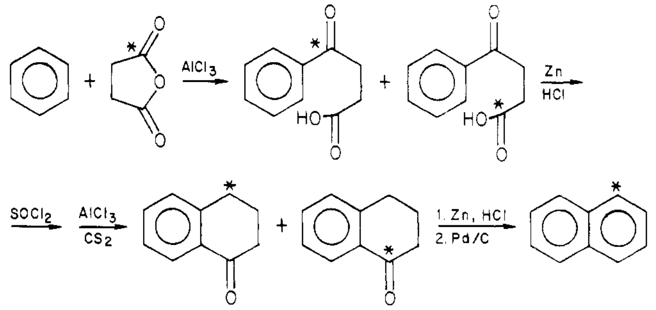
Scheme I



$$\text{coal} + \text{K} \xrightarrow[\text{THF}]{} \text{coal}^{n-} + n\text{K}^{+}$$

$$\text{coal}^{n-} + \text{RI} \rightarrow \text{coal-R}_{m} + m\text{I}^{-}$$

Scheme II



The interaction of polycyclic aromatics with alkali metals gives hydrogen and, presumably and initially, a radical anion.[13] The reductive alkylation of a number of aromatics has been studied in detail.[14-18] It is clear that it

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Table I. Amount of Naphthalene Incorporated during the Reductive Ethylation of Illinois No. 6 Coal[a]

fraction	eluting solvent	mass eluted, g	dpm/mg of dissolved sample	wt % of fraction which is naphthalene derived	dpm/mg of sample counted as CO_2	wt % of fraction which is naphthalene
1	hexanes	0.662	1304	52.0	1121	45.2
2	transition between hexanes and C_6H_6/hexanes	0.797	1344	53.6	1447	58.3
3	benzene/hexanes (1:1)	1.409	1046	41.7	1148	46.3
4	THF	2.454	68	2.7	40	1.6
5	left on column	0.518	36	1.5	20	0.8
6	insolubles	1.787			15	0.6

[a] Coal (4.294 g) was reacted with 1.481 g of naphthalene, 53.28 g of THF, and 9.75 g of ethyl iodide.

Table II. Amount of THF Incorporated during the Reductive Ethylation of Illinois No. 6 Coal[a]

fraction no.	mass eluted, g	dpm/mg of dissolved sample	wt % of fraction which is THF derived	dpm/mg of sample counted as CO_2	wt % of fraction which is THF derived
1	0.929	1.93	0.6	2.93	0.9
2	0.327	1.98	0.6	2.20	0.7
3	0.882	8.00	2.5	5.88	1.8
4	0.654	16.23	5.1	15.36	4.8
5	0.110	16.31	2.3	2.65	0.8
6	0.463			2.36	0.7

[a] Coal (1.682 g) was reacted with 24 g of THF and 0.61 g of naphthalene in 9.75 g of ethyl iodide.

is a very complex process, with both radical and nucleophilic substitution reactions occurring.[15,16] There are so many competing reactions occurring that mixing and workup procedures can have a significant effect on the product distribution.[17]

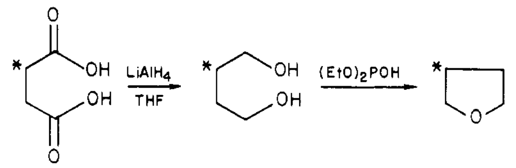
A flurry of papers has appeared recently in which reductive alkylation is applied to coal or other heavy hydrocarbons. Both Gaines[19] and Stock[5] have studied the NMR spectra of coals solubilized by this method. Franz[20] has demonstrated the occurrence of numerous side products derived from naphthalene. The interesting and effective application of reductive alkylation to Athabasca asphaltenes has been reported.[21] Ignasiak has used this reaction to solubilize both a high rank vitrinite[22] and Rasa lignite.[23] Incorporation of naphthalene occurred during the reductive alkylation of an asphaltene.[21] It has also been reported without providing experimental details that THF is incorporated during the reaction.[23]

Since reductive alkylation is being used extensively to solubilize coals and since the structure of the reaction products is being scrutinized carefully with the aim of learning about the structure of the parent coal, detailed knowledge of this reaction is necessary. One major question is the role of the naphthalene and THF in the reaction. We began our studies by determining the degree to which these materials are incorporated into the reaction products.

Results

Naphthalene Incorporation. Naphthalene containing ^{14}C was prepared using the Haworth synthesis (Scheme II). Reductive ethylation of Illinois No. 6 coal was carried out using Sternberg's procedure.[2,3] The resulting alkylated coal was fractionated on a silica gel column using the procedure developed by Burk and Sun.[24] The easiest procedure would be to measure the activity of each fraction directly using liquid scintillation counting. The solutions are colored and the experimental difficulties to be encountered in counting such solutions are well recognized.[25,26] However with proper attention to detail and necessary corrections, such solutions can be counted quite accurately.[27] We had reasonable success counting the colored, coal derived samples. A detailed description of the experimental technique is given in the Experimental Section. In addition to difficulties caused by the color, there was the possibility that the solutions contained colloidal materials which would reduce the counting efficiency and lead to an underestimation of the amount of ^{14}C present. Because of these two factors, we elected also to count the samples by burning and counting the CO_2

Scheme III



Scheme IV

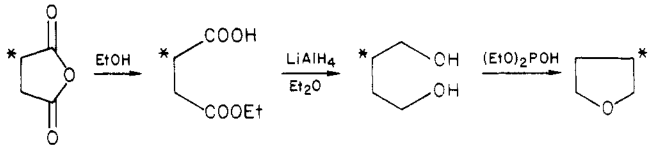


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Table III. Quantity of Ethyl Groups Incorporated during the Reductive Ethylation of Illinois No. 6 Coal[a]

fraction no.	mass eluted, g	dpm/mg of dissolved sample	wt % of fraction which is ethyl	dpm/mg of sample counted as CO_2	wt % of fraction which is ethyl
1	1.329	3656	8.1	2637	6.1
2	0.434	1905	4.2	930	2.2
3	1.506	3699	8.1	3524	8.2
4	2.580	5581	12.2	5753	13.3
5	0.926	5599	12.3	4743	11.0
6	1.909			4670	10.8

[a] Coal (4.525 g) was reacted with 1.416 g of naphthalene and 9.75 g of ethyl iodide in 53.28 g of THF.

produced using a standard procedure.[28] Because the many corrections required with colored solutions lead to nagging uncertainties about the results, the preferred technique is to burn and count CO_2. The amount of naphthalene incorporated into each fraction is shown in Table I. It is obvious that there is a clean separation. The first three fractions contain naphthalene derivatives and the bulk of the coal-derived products are found in fractions 4 through 6 and contain little naphthalene.

THF Incorporation. Labeled THF was prepared by two different routes. The first is shown in Scheme III and the second in Scheme IV. Scheme IV is preferred.

The reductive ethylation was carried out using the same procedure as before. The amount of THF incorporated is shown in Table II. Only fraction 4 contained a significant amount of THF. When the ^1H NMR spectrum of fraction 4 was recorded using pyridine-d_5 as solvent, peaks at positions expected for THF were observed.[29] Since this sample had been dried under vacuum at 80 °C to constant weight, it seemed most unlikely that any THF would still be present in the sample. Since fraction 4 had been eluted with 600 mL of cold (unlabeled) THF, any labeled THF should have been lost by exchange. Nonetheless, we took 120 mg of fraction 4 and stirred it overnight with refluxing THF under N_2. After removal of the THF by distillation, the remaining sample was burned and the CO_2 was counted. Only 57.4% of the ^{14}C remained in the solid sample. Thus about 40% of the THF present in fraction 4 is there as sorbed material which is exchangeable. It is apparent that the reductively ethylated coal has a very strong affinity for small amounts of THF. The nature of the interaction between THF and the alkylated coal remains mysterious.

Ethyl Incorporation. The incorporation of ethyl groups was measured as for naphthalene and THF and the results are shown in Table III. As with naphthalene and THF, agreement between the two counting techniques is satisfactory, given the difficulty in counting colored solutions.

Discussion

The incorporation of naphthalene, THF, and ethyl into the various fractions is expressed in Table IV as number of groups incorporated per 100 carbon atoms of Illinois No. 6 coal. The data from counting CO_2 were used. Fractions 1, 2, and 3 contain, respectively, 48, 39, and 44% of material derived from coal. Probably little can be learned about the structure of the parent coal from these fractions.

The solubilized coal is contained in fractions 4 and 5. It is interesting that as many ethyl groups have been incorporated in the insoluble fraction 6 as were incorporated into fractions 4 and 5. This makes it clear that bond cleavage is necessary for solubilization; simple incorporation of alkyl groups is not sufficient. The reasonable agreement between the two counting techniques suggests that colloidal material is not present in the soluble fractions.

Table IV. Incorporation Expressed as Groups per 100 Carbon Atoms of Illinois No. 6 Coal

fraction no.	naphthalene	THF	ethyl
1	5.3	0.2	5.1
2	6.8	0.1	1.2
3	5.2	0.4	6.2
4	0.2	1.0	11.0
5	0.1	0.2	9.7
6	0.1	0.2	9.9

The reductive alkylation is quite complex. The use of silica gel chromatography does separate cleanly very complex products containing only ~50% coal from products which can be accurately described as being "solubilized coal". If the first fractions are ignored, one can work with the solubilized coals confident that results will not be adversely affected by significant amounts of solvent incorporation. These results should hold for coals similar to Illinois No. 6; extrapolation to coals of quite different rank is not encouraged.

Experimental Section

Alkali metals, mossy zinc, naphthalene, ethyl iodide, carbon disulfide, aluminum chloride, benzene, toluene, and hexanes were all high purity commercial materials and were used without further purification. THF was treated with solid cuprous chloride to destroy peroxides, dried over sodium wire for 48 h, and distilled from $LiAlH_4$ in a dry N_2 atmosphere. Labeled compounds were obtained from New England Nuclear. The silica gel used was 60–200 mesh, grade 62, from Matheson Coleman and Bell. Using a 1.5 in. i.d. column, ~5 in. of column length per gram of coal product was used. The dried Illinois No. 6 coal (Burning Star mine) used had the following analysis: C, 75.46; H, 4.83; N, 1.75; S, 1.95; ash, 5.54. It was ground under dry N_2 to pass 200 mesh. It was stored under dry N_2 and dried in vacuo at 70–80 °C for 6–10 h before use.

Liquid scintillation counting was done on a Beckman LS 8100 instrument using program no. 8. Toluene–Liquifluor cocktails in glass vials, both obtained from New England Nuclear, were used to count the dissolved coal fractions. The combusted samples were counted with Oxisorb-CO_2 and Oxyprep-CO_2. NMR spectra were obtained with a Varian T-60A.

[^{14}C]Naphthalene. Naphthalene labeled with ^{14}C was prepared from [1,4-^{14}C]succinic anhydride (50 μCi) using the Haworth synthesis as outlined in Scheme II.[30] The overall yield was 55% and naphthalene with an activity of 4.26×10^6 cpm/g was obtained.

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[^{14}C]THF. This material was synthesized by the two methods shown in Schemes III and IV.

Scheme III. Labeled [2,3-^{14}C]succinic acid (0.17 mg in 0.5 mL of 9:1 ethanol–water) was reduced with a slight excess of $LiAlH_4$ in THF. The resulting labeled 1,4-butanediol was diluted to the desired activity by adding unlabeled 1,4-butanediol and the mixture was added dropwise to hot diethyl phosphite.[31] The THF was distilled off as it formed. It was redistilled from $LiAlH_4$ to remove ethanol. Yields ranged between 60 and 70% and material having an activity of 2.2×10^5 cpm/mL was obtained.

Scheme IV. A mixture of labeled [1,4-^{14}C]succinic anhydride diluted to the desired activity with unlabeled succinic anhydride was refluxed with ethanol to form the half-ester. This ester was reduced with an excess of $LiAlH_4$ in ether using standard procedures. The labeled 1,4-butanediol was converted to THF as outlined in Scheme III.

[^{14}C]Ethyl Iodide. Material purchased from New England Nuclear was used without further purification.

Chromatographic Separation of Coal Products. The procedure developed by Burk and Sun was used.[32] Chromatography in 60–200 mesh, grade 62 MC/B silica gel was used. For a 6-g sample 1300 mL of hexanes, 2000 mL of benzene–hexanes (1:1 vol), and 1100 mL of THF were used followed by dissolving the column in concentrated aqueous NaOH and the liberated organics were dissolved in benzene. About 400 mL of solution was collected in fraction 2 as a transition between hexanes and the benzene–hexane fractions. Fraction 6 was material insoluble in THF and was not chromatographed.

Liquid Scintillation Counting. In LSC, the radiation emitted by the decaying nucleus interacts with dyes in the solution producing fluorescence which is detected by the instrument. In counting the coal-derived materials, several possible sources of error exist. If some of the coal-derived materials form colloidal species, the emitted particle may not escape from the colloid and thus will not be counted. The colored materials formed from the coal may absorb some of the fluorescent radiation preventing its detection. Molecules derived from the coal may quench the fluorescence. Finally, materials derived from the coal may fluoresce themselves. The last three of these difficulties can be circumvented using an internal standard. Toluene labeled with ^{14}C was used as an internal standard in all of the solutions containing coal-derived materials and was used to determine the counting efficiency of these solutions. This would not correct for any errors introduced due to the presence of colloidal materials. Solutions were normally run at the highest dilutions possible compatible with good counting statistics. This minimizes the effects of the colored materials. Also, all solutions were allowed to stand for 24 h before counting to minimize problems with chemiluminescence. The LS 8100 instrument used permits the counting of fluorescence of specific energies and this was done. This also will minimize the effect of chemiluminescent materials.

Because of the possibility of the presence of colloidal materials, all samples were burned using the procedure of Davidson[28] and the CO_2 was absorbed by Oxysorb-CO_2 and counted using standard techniques. The agreement in most cases between the two methods is reasonable. With proper care, direct liquid scintillation studies of coal-derived materials can be done with reasonable accuracy. However the combustion technique is the more reliable.

Acknowledgment. We are grateful to the Fossil Fuel Division at the Department of Energy for support of this work. The comments and criticisms of Lee Stock were very helpful and are gratefully acknowledged. Without the excellent advice of Dr. Arthur Jungreis on LSC techniques we would still be doing experiments and we thank him for his generous contribution of time and counsel. The encouragement and experimental directions provided by Emmet Burk are acknowledged with thanks.

Registry No. [1-^{14}C]Naphthalene, 16341-53-0; [2-^{14}C]succinic anhydride, 70969-12-9; [2-^{14}C]THF, 70969-13-0; [2-^{14}C]succinic acid, 70969-14-1; [2-^{14}C]-1,4-butanediol, 70969-15-2; ethyl iodide, 75-03-6.

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Conformational Analysis of Pinanols[†]

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Empirical nonbonded atom interaction potentials are used in a Monte Carlo computational procedure to generate minimum conformational energy geometries for *trans*- and *cis*-2-pinanol, isopinocampheol, and neoisopinocampheol. The calculated dihedral angles of the cyclobutyl rings are in quantitative agreement with those determined by X-ray diffraction for a C_3-substituted pinane. The preferred conformations of *trans*- and *cis*-2-pinanol, respectively, are chair and boat, and both of the pinocampheols studied also favor the boat conformation. These three boat conformations are not "full boats" and are more accurately described as skewed, semiboats.

Little is conclusively known about the preferred conformations of pinanols,[1] although these conformations govern the direction of certain reactions[2-5] and modulate the circular dichroism of the far-ultraviolet hydroxyl-centered $\sigma^*/3s\leftarrow n$ transitions[6] reported by Kirk et al.[7] We propose to study (cf. Figure 1) the conformational stability of the methylnopinols I and II, isopinocampheol (III), and neoisopinocampheol (IV). The study of these species should lead to conclusions concerning the effects of configurational isomerizations of the C_{10} methyl group about C_2 and of the hydroxyl group about C_3.

Boat, chair, and nearly planar conformations for the six-membered ring have been observed in or predicted for a variety of ketone derivatives[8] of pinane, and a similar range of conformations has been assigned to the pinanols.

[†] Supported in part by National Science Foundation Grant PCM77-21220.

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