Liquid-Phase Oxidation of Butadiene in Acetic Acid

Paul R. Stapp

Research and Development, Phillips Petroleum Company, Bartlesville, Oklahoma 74004

Received September 27, 1978

A method has been developed for the catalytic liquid-phase oxidation of butadiene in acetic acid with a catalyst system consisting of cupric acetate, lithium bromide, and 1,4-dibromo-2-butene. A 70% yield of a mixture of diacetates composed of 1,4-diacetoxy-2-butene (73%) and 3,4-diacetoxy-1-butene (27%) was obtained at 140 °C in acetic acid/acetic anhydride solvent. Carrying out the oxidation in pure acetic anhydride gave, in addition to 33% of the diacetate mixture, 27% of 4-vinyl-4-butyrolactone. Substitution of selenium or antimony compounds for cupric acetate also gave useful catalysts for the oxidation of butadiene in acetic acid when used in conjunction with lithium bromide and 1,4-dibromo-2-butene.

The halogenation of butadiene with cupric chloride[1] or cupric bromide[2] to produce mixtures of 1,4-dihalo- and 1,2-dihalobutenes has been previously reported by Baird and co-workers. Since the displacement of halide ion from 1,4-dihalobutenes with acetate ion in acetic acid is a known method for the preparation of 1,4-diacetoxybutenes,[3] the catalytic liquid-phase oxidation of butadiene in acetic acid to diacetoxybutenes via the indicated reaction sequence appeared to be feasible provided that lithium halide was present to aid in the reoxidation of the cuprous salts.[4]

$$CH_2{=}CHCH{=}CH_2 + 2CuX_2 \rightarrow XCH_2CH{=}CHCH_2X + 2CuX \quad (1)$$

$$XCH_2CH{=}CHCH_2X + Cu(OAc)_2 \rightarrow AcOCH_2CH{=}CHCH_2OAc + CuX_2 \quad (2)$$

$$2CuX + 2HOAc + {}^1/{}_2O_2 \rightarrow Cu(OAc)_2 + CuX_2 + H_2O \quad (3)$$

$$CH_2{=}CHCH{=}CH_2 + 2HOAc + {}^1/{}_2O_2 \rightarrow AcOCH_2CH{=}CHCH_2OAc + H_2O$$

Obviously, a mixture of 3,4-diacetoxy-1-butene and *cis*- and *trans*-1,4-diacetoxy-2-butene would be expected from this reaction scheme. The development of a catalytic process to carry out the desired transformation using cupric acetate, lithium halide, and either cupric halide or 1,4-dihalo-2-butene as co-catalyst is the subject of this paper. Similar liquid-phase oxidation systems based on selenium and antimony catalysts are also described.

Results and Discussion

A. Copper Catalysts. The oxidation of butadiene (174 mmol) in acetic acid (75 mL) containing 1,4-dichloro-2-butene (mixed cis and trans, 22.5 mmol), cupric acetate (48 mmol), and lithium chloride (75 mmol) with molecular oxygen at 65–90 psig and 120 °C led to a complex mixture of products. These were separated by preparative GLC and identified by NMR, mass, and infrared spectra. The resulting product distribution is show~~n in Table I~~. Thus, a total of 90.1 mmol of diacetates and hydroxy acetates (52% yield based on charged butadiene) was obtained.

Table I. Products from Oxidation of Butadiene in Acetic Acid

compd	wt % of total reaction product	mmol
$AcOCH_2CH(OH)CH{=}CH_2$ (1)	9.1	10.5
$ClCH_2CH{=}CHCH_2Cl$ (2)	2.0	2.5
$AcOCH_2CH(OAc)CH{=}CH_2$ (3)	26.2	23.0
$ClCH_2CH{=}CHCH_2OAc$ (4)	2.6	2.6
$HOCH_2CH(OAc)CH{=}CH_2$ (5)	13.9	16.2
unidentified (6)	0.5	
cis-$AcOCH_2CH{=}CHCH_2OAc$ (7)	2.0	1.7
trans-$AcOCH_2CH{=}CHCH_2OAc$ (8)	41.7	36.2
trans-$HOCH_2CH{=}CHCH_2OAc$ (9)	2.1	2.5

This is a 400% yield based on 1,4-dichloro-2-butene or 188% based on cupric acetate and verified that the oxidation was catalytic.[5] Similar reaction mixtures were obtained at 120 °C using cupric acetate/lithium bromide/cupric bromide or cupric acetate/lithium bromide/1,4-dibromo-2-butene catalyst systems in acetic acid, but cupric acetate/lithium iodide/1,4-diiodo-2-butene (prepared in situ from iodine and butadiene) gave a very slow oxidation and a complex reaction mixture containing little of the desired diacetoxybutenes. The chloride catalyst system was tested at varying temperatures; at 75 °C a very slow reaction was obtained but operation at 140 °C gave much more rapid oxidation and, surprisingly, higher selectivity (61% yield of diacetates and hydroxyacetates). In addition, at 75 °C the predominant diacetate was 3,4-diacetoxy-1-butene, while at 140 °C the 1,4-diacetate comprised 75% of the total. Several attempts were made to use lower catalyst levels with the chloride system, but reactions were slower and yields were much lower.

Verification of the assumption that 1,4-dihalo-2-butenes are intermediates in the process was provided by the reaction of *trans*-1,4-dibromo-2-butene with cupric acetate in refluxing acetic acid to give a mixture of 3,4-diacetoxy-1-butene (35–40%) and *cis-/trans*-1,4-diacetoxy-2-butene (60–65%) in over 90% yield providing that excess butadiene was present to prevent bromination of the product by the cupric bromide formed in the displacement. If the butadiene was omitted part of the product was

---

[1] W. C. Baird, Jr., and J. H. Surridge, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, **16** (1), B46 (1971); W. C. Baird, Jr., J. H. Surridge, and M. Buza, *J. Org. Chem.*, **36**, 3324 (1971).

[2] W. C. Baird, Jr., J. H. Surridge, and M. Buza, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, **16**, (3), B57 (1971).

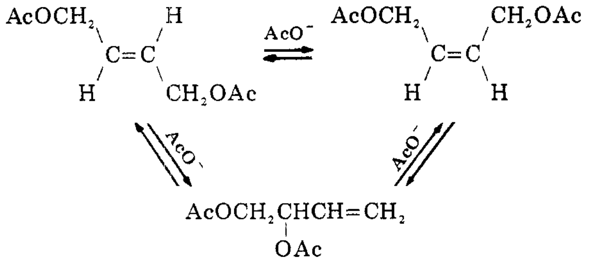
[3] (a) A. N. Podovik, *Zh. Obshch. Khim.*, **19**, 1179 (1949); (b) R. A. Raphael, *J. Chem. Soc.*, 401 (1952); (c) N. G. Vyunova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 467 (1964).

[4] P. M. Henry, *Inorg. Chem.*, **5**, 688 (1969).

[5] Since 1,4-dichloro-2-butene reacts with cupric acetate in acetic acid to give diacetoxybutenes (eq 2), the yield of diacetates would be somewhat lower if unrecovered 1,4-dichloro-2-butene is calculated as a reactant as well as a catalyst. For convenience in comparing experiments at varying dihalobutene levels, particularly those containing no dihalobutene, yields are based on the quantity of charged butadiene. The yield of diacetates and hydroxy acetates based on charged butadiene plus reacted 1,4-dichloro-2-butene would be 46% for the experiment shown in Table I or 310% based on 1,4-dichloro-2-butene and 145% based on cupric acetate.

0022-3263/79/1944-3216$01.00/0

Scheme I



brominated to give 1,4-diacetoxy-2,3-dibromobutane and yields were reduced considerably.

$$2BrCH_2CH{=}CHCH_2Br + 2Cu(OAc)_2 \rightarrow 2AcOCH_2CH{=}CHCH_2OAc + 2CuBr_2$$

$$2AcOCH_2CH{=}CHCH_2OAc + 2CuBr_2 \rightarrow AcOCH_2CH(Br)CH(Br)CH_2OAc + AcOCH_2CH{=}CHCH_2OAc + 2CuBr$$

Since S_N2' displacements of allylic halides are well known to give rearranged products, the production of mixtures of rearranged and nonrearranged products was not unexpected. Surprisingly however, in the preparation of *trans*-1,4-diacetoxy-2-butene by reaction of the same dibromide with anhydrous sodium acetate in acetic acid little rearrangement occurred; over 90% of the resulting diacetates were of the trans 1,4-configuration.

Reversible isomerization of *cis-/trans*-1,4-diacetoxy-2-butene to 3,4-diacetoxy-1-butene is readily accomplished with a number of catalysts including palladium acetate, cupric acetate–sodium acetate, or cupric acetate–lithium acetate combinations in refluxing acetic acid. Cupric acetate alone can also be used, but the isomerization is considerably slower. Equilibrium distributions, obtained from each of the isomers individually, contained 35% of 3,4-diacetoxy-1-butene, 9% of *cis*-1,4-diacetoxy-2-butene, and 56% of *trans*-1,4-diacetoxy-2-butene (Scheme I). Obviously product distribution in the oxidation experiments is kinetically controlled.

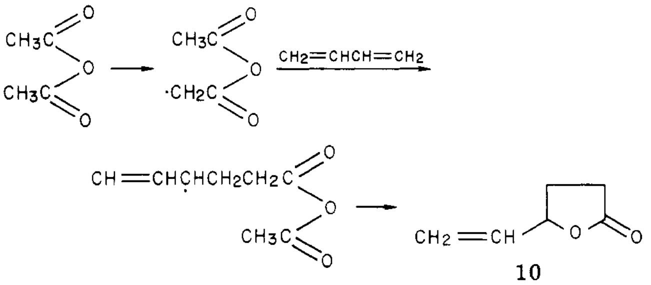
Because the presence of hydroxy acetates complicated analysis of the reaction mixtures, addition of sufficient acetic anhydride to maintain water-free conditions in the acetic acid used as solvent and co-reactant was tested. Oxidation of butadiene (203.7 mmol) in the presence of cupric acetate (48 mmol), lithium bromide (75 mmol), and 1,4-dibromo-2-butene (21.5 mmol) in a mixed solvent containing 50 mL of acetic acid and 25 mL of acetic anhydride gave a rapid oxygen uptake at 140 °C. *Only three* volatile products were found in larger than trace quantities: 3,4-diacetoxy-1-butene (**3**, 27%), *cis*-1,4-diacetoxy-2-butene (**7**, 7%), and *trans*-1,4-diacetoxy-2-butene (**8**, 66%). The yield of diacetates based on charged butadiene was 70%, or 680% based on dibromobutene and 305% based on cupric acetate. In addition to the volatile butenyl diacetates, there was also some heavy liquid amounting to about 15% of the total product, which by high temperature GLC was a complex mixture. In this system, in contrast to the chloride-containing catalysts, a significant reduction in catalyst level was possible; at catalyst concentrations of 12 mmol of cupric acetate, 37.5 mmol of lithium bromide, and 5.6 mmol of 1,4-dibromo-2-butene, a completely homogeneous system was obtained, oxidation was still quite rapid, and a 65% yield of butenyl diacetates having essentially the same isomer distribution was found.

Substitution of an equivalent quantity of cupric bromide for the 1,4-dibromo-2-butene catalyst components gave results indistinguishable from those shown above; bromination of butadiene by cupric bromide undoubtedly occurs by the time the reaction mixture is heated to reaction temperature. It would be expected that, in acetic acid solution, some anion exchange would occur between cupric acetate and lithium halides.

$$Cu(OAc)_2 + 2LiBr \rightleftarrows CuBr_2 + 2LiOAc$$

Accordingly, it would be expected that the catalytic oxidation of butadiene could be carried out without using added cupric bromide and/or 1,4-dibromo-2-butene, e.g., the sole catalyst components necessary should be cupric acetate and lithium bromide. However, oxidations carried out without cupric bromide or dibromobutene catalyst gave long induction periods and reduced yields. Throughout this work, it was also found that bromide or chloride ion was a necessary co-catalyst; oxidation was found to occur with cupric acetate–lithium acetate catalyst combinations with no halide ion present but yields of diacetates were generally under 20% and the major products were tars.

When the relative proportions of acetic anhydride to acetic acid solvent were varied from 1:2 to 2:1 no changes in reaction rates, yields, or isomer distributions were noted, but carrying out the oxidation of butadiene in acetic anhydride alone gave, in addition to 75% of butenyl diacetate, 10% of 4-vinyl-4-butyrolactone (**10**). The lactone probably arises via free-radical oxidation of the solvent.



10

Similar free-radical oxidations of acetic acid in the presence of olefins to form lactones have been described by Heiba.[6] In the present case, the free radical type oxidation becomes even more pronounced as the solvent polarity is decreased, i.e., the acetic acid concentration is decreased even further. Since the cupric acetate was charged as the monohydrate, 96 mmol of acetic acid would be generated by drying the catalyst. The use of anhydrous cupric acetate in the catalyst recipe with pure acetic anhydride as solvent altered the product distribution from the butadiene oxidation to give 27% of 4-vinyl-4-butyrolactone and only 33% of the diacetate mixture. Oxidation of butadiene with a catalyst from anhydrous manganese(II) acetate and lithium bromide in acetic anhydride, however, gave only traces of lactone; the major reaction product was butenyl diacetate.[7]

B. Selenium and Antimony Catalysts. Concurrent with the study of the cupric acetate based catalysts for the liquid-phase oxidation of butadiene in acetic acid–acetic anhydride, a wide variety of other catalyst systems was evaluated in an attempt to develop higher yields of diacetoxybutenes, particularly the 1,4-isomer. Of these catalysts, selenium and antimony derived materials appeared to be the most promising.

For the initial experiments with the selenium-based systems, a catalyst recipe similar to that which gave the best results with the copper acetate system was tested. Thus, butadiene (198.1 mmol) was oxidized with molecular

---

[6] E. I. Heiba, R. M. Dessau, and P. G. Rodewald, *J. Am. Chem. Soc.*, **96**, 7977 (1974).

[7] This oxidation was carried out to determine whether manganese(II) acetate would be oxidized to manganese(III) acetate under the usual reaction conditions and provide a catalytic route to the lactones.[6]

Table II. Effect of Lithium Bromide Concentration on Yield

mmol of butadiene charged	LiBr concn, M	% yield of diacetate
198.1	1.0	81
218.5	1.5	82
203.7	2.0	78
233.3	0.5	58
216.6	0	22

Table III. Effect of Catalyst Concentrations on Yield of Diacetates

mmol of butadiene	mmol of SeO_2	mmol of $C_4H_6Br_2$	% yield of diacetates
231.5	20	21.5	84
229.6	20	10.7	78
209.2	20	0	69
227.8	10	10.7	73

oxygen in the presence of selenium dioxide (20 mmol), lithium bromide (75 mmol), and 1,4-dibromo-2-butene (21.5 mmol) in a mixed solvent containing 50 mL of acetic acid and 25 mL of acetic anhydride at 140 °C. A homogeneous system resulted and a rapid oxygen uptake was observed. Over three identical experiments an average yield of 81% of butenyl diacetates based on charged butadiene was obtained. The diacetate mixture was composed of about 20% 3,4-diacetoxy-1-butene and 80% 1,4-diacetoxy-2-butene.

$$CH_2{=}CHCH{=}CH_2 + 2HOAc + \tfrac{1}{2}O_2 \xrightarrow[C_4H_6Br_2]{\substack{SeO_2\\LiBr}} AcOCH_2CH{=}CHCH_2OAc + AcOCH_2CH(OAc)CH{=}CH_2$$

The reaction product was not so clean as that obtained using the cupric acetate catalyst system under the same conditions; in each run 5–8% 4-vinyl-4-butyrolactone was also found. In addition, diacetates purified by fractionation contained trace quantities of volatile organoselenium compounds (detectable by odor but not by GLC) as did the recovered acetic acid–acetic anhydride solvent mixture.

The effect of lithium bromide concentration on yield of diacetates was tested under otherwise comparable conditions. Results are summarized in Table II. There appears to be a critical minimum level of bromide ion concentration at about 1 M for acceptable yields but no advantage is apparent in going to higher concentrations. The experiments at 1.5 and 2.0 M lithium bromide gave thicker reaction mixtures which were difficult to stir. The run with no lithium bromide[8] is worthy of comment because smooth, rapid oxygen uptake was observed and complete butadiene conversion was obtained in the same time period as with the bromide system. The major product, however, was an acetone-soluble tar.

The effect of variations in catalyst levels was also tested. Table III summarizes the effect of a number of experiments at 1.0 M lithium bromide concentration with varying catalyst composition at 140 °C. When the oxidation temperature was lowered to 120 °C the yield of butenyl diacetate decreased from 78 to 64% under otherwise identical conditions. Selenous acid can be substituted for selenium dioxide in the catalyst, but no advantage is observed. It is also of interest that neither *trans*-2-butene nor 1-hexene underwent oxidation under the same conditions that gave smooth oxidation of butadiene. This is particularly surprising in view of the well-known allylic oxidation of olefins using stoichiometric quantities of selenium dioxide in acetic acid or acetic anhydride.[9]

In contrast with the copper acetate catalyzed oxidation, lithium chloride/1,4-dichloro-2-butene were not effective co-catalysts with selenium dioxide nor was lithium iodide/1,4-diiodo-2-butene. In both cases, oxidation failed to initiate. In addition, oxidation of butadiene in pure acetic anhydride as solvent (which improved yields with copper) gave only 31% of butenyl diacetates and a rather messy reaction mixture.

Antimony based catalysts gave results similar to copper acetate based catalysts in the liquid-phase oxidation of butadiene in acetic acid–acetic anhydride mixtures at 140 °C. Antimony pentachloride (20 mmol) and antimony(III) oxide (10 mmol) in combination with lithium bromide (1 M) and 1,4-dibromo-2-butene (22.5 mmol) gave systems which smoothly oxidized butadiene to butenyl diacetates (72 and 75% yield, respectively) with less than 5% of byproduct 4-vinyl-4-butyrolactone. This isomer distribution was about 30% 3,4-diacetoxy-1-butene, 15% *cis*-1,4-diacetoxy-2-butene, and 55% *trans*-1,4-diacetoxy-2-butene. Antimony triacetate also gave an effective catalyst but carrying out the oxidation in pure acetic anhydride gave no improvement with any of the antimony derived catalysts.

In summary, a study of the liquid-phase oxidation of butadiene in acetic acid–acetic anhydride solvent to produce mixtures of 3,4-diacetoxy-1-butene, bp 78–80 °C (11 mm), and *cis-/trans*-1,4-diacetoxy-2-butene, bp 108–111 °C (11 mm), has been conducted. Useful catalyst systems are based on cupric acetate, selenium dioxide, or antimony compounds.

Experimental Section

Oxidations were carried out in Fisher–Porter aerosol compatibility bottles fitted with a magnetic stirrer, a pressure gauge, and a $^1/_8$-in. stainless steel line for introduction of oxygen. Catalyst components were weighed into the vessel, solvent was charged, and butadiene was charged vapor phase from tared cylinders. The bottle was placed in a stirred silicone oil bath on a magnetic hot plate, pressured to 30 psig with oxygen, and heated to the desired temperature. When the oxygen pressure at reaction temperature fell to 60–70 psig, the bottle was repressured to 120 psig. This process was repeated until no further oxygen uptake was observed. All oxidations were carried out behind a double shield; i.e., an explosion shield and the hood doors. Oxygen was introduced from an external needle valve. Although no explosions were ever observed in this work butadiene and oxygen form explosive mixtures and due caution should be observed.

The following reference compounds were prepared as indicated: 1,4-diacetoxy-*trans*-2-butene was obtained from the reaction of sodium acetate with 1,4-dibromo-*trans*-2-butene in acetic acid,[3] 1,4-diacetoxy-*cis*-2-butene was prepared by reaction of the commercially available *cis*-2-butene-1,4-diol with acetyl chloride in triethylamine, and 3,4-diacetoxy-1-butene was prepared by solvolysis of butadiene monoepoxide in acetic acid and acetylation of the resulting hydroxyacetate with acetyl chloride and triethylamine.

A representative example of the oxidation procedure is shown below.

Oxidation of Butadiene. A 6-oz. aerosol compatibility bottle equipped with a $^1/_8$-in. stainless steel inlet and a pressure gauge and containing a Teflon coated magnetic stirring bar was charged with 4.6 g (21.5 mmol) of 1,4-dibromo-2-butene, 6.5 g (75 mmol) of lithium bromide, 9.6 g (48 mmol) of cupric acetate monohydrate, 25 mL of acetic anhydride, and 50 mL of acetic acid. Then 11.0 g (203.7 mmol) of butadiene was charged vapor phase from a tared cylinder. The bottle was placed in an oil bath, pressured to 30 psig with oxygen, and heated to 140 °C. The initial pressure was 112 psig at 140 °C. When the pressure fell to 80–90 psig the bottle was repressured to 120 psig, a total of 13 times over 3.7 h. The

---

(8) This run also contained no 1,4-dibromo-2-butene.

(9) N. Rabjohn, *Org. React.*, **5**, 331 (1949).

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

John W. Larsen* and Ludvik O. Urban

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

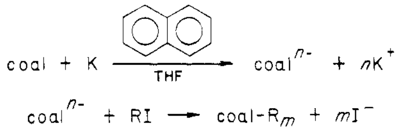
Received April 10, 1979

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.

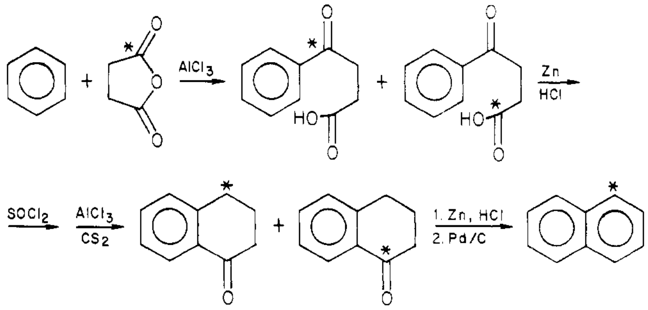
Coals are solid, insoluble, complex mixtures of polymeric organics and minerals.[1] Most organic spectroscopic techniques do not work well on solids, so one major thrust of coal research has been to solubilize coals by carrying out known, selective chemical reactions. Perhaps the reaction most used for 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



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

---

[1] D. W. van Krevelen, "Coal", Elsevier, New York, N.Y., 1961.

[2] H. W. Sternberg and C. L. Delle Donne, *Fuel*, **53**, 172 (1974).

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

[4] J. W. Larsen and E. W. Kuemmerle, *Fuel*, **55**, 162 (1976).

[5] L. B. Alemany, S. R. King, and L. M. Stock, *Fuel*, **57**, 738 (1978).

[6] D. H. Eargle, Jr., *J. Org. Chem.*, **28**, 1703 (1963).

[7] C. G. Screttos, *J. Chem. Soc., Chem. Commun.*, 869 (1972).

[8] J. J. Eisch, *J. Org. Chem.*, **28**, 707 (1963).

[9] Ch. Elschenbroich, F. Gerson, and J. A. Reiss, *J. Am. Chem. Soc.*, **99**, 60 (1977).

[10] A. Lagendijk and M. Szwarc, *J. Am. Chem. Soc.*, **93**, 5359 (1971).

[11] H. Gilman and B. J. Gaj, *J. Org. Chem.*, **28**, 1725 (1963).

[12] H. O. House and V. Kramar, *J. Org. Chem.*, **27**, 4146 (1962).

[13] F. Beguin and R. Setton, *Carbon*, **10**, 539 (1972).

[14] M. A. Kamha, N. M. Katkova, T. V. Leshina, R. Z. Sagdeev, and S. M. Shein, *Tetrahedron Lett.*, 1313 (1977).

[15] M. Malissard, J. P. Mazaleyrat, and Z. Welvart, *J. Am. Chem. Soc.*, **99**, 6933 (1977), and references cited therein.

[16] S. Bank and D. A. Juckett, *J. Am. Chem. Soc.*, **97**, 567 (1975).

[17] R. Rabideau and E. G. Burkholder, *J. Org. Chem.*, **43**, 4283 (1978).

0022-3263/79/1944-3219$01.00/0 © 1979 American Chemical Society