

## Hydrogenolysis of Dibenzyl Ether Using Zinc Chloride-Metal Cocatalyst Systems

The hydrogenolysis of dibenzyl ether was studied using zinc chloride together with either nickel, zinc, or magnesium. Reactions were carried out in cyclohexane solution at 225°C under hydrogen pressure. The presence of the metallic component, and in particular Raney nickel, was found to enhance the yields of toluene and reduce the formation of insoluble resin, observed when zinc chloride was used alone. It is proposed that the metal activates molecular  $H_2$  and promotes its reaction with benzylic carbonium ions formed through the action of zinc chloride on dibenzyl ether.

The cleavage of benzylic ether linkages is believed to be one of the processes which occurs during coal liquefaction in the presence of Lewis acids. We recently reported that  $ZnCl_2$  will readily promote the cleavage of various ethers under conditions where thermolysis of the ethers does not occur (1). The observed products indicate that  $ZnCl_2$  promotes the formation of benzylic carbonium ions. In an aromatic solvent these ions may react to form benzylation products and in an aliphatic solvent they initiate condensation of the ether to form an insoluble resin. In neither solvent, though, does the transfer of hydride ions from molecular hydrogen occur readily. An approach to facilitate this latter process is suggested by the fact that metallic palladium can be used in conjunction with Brønsted acids to promote the hydrogenolysis of benzylic ethers in the presence of molecular hydrogen, and a recent report indicating that a mixture of  $AlCl_3$  and palladium will promote the same reaction, with hydrogen transfer in this case occurring from cyclohexene (2, 3). We now wish to report that the use of  $ZnCl_2$  together with a metal capable of activating molecular hydrogen catalyzes the transfer of hydride ions to benzylic carbonium ions and inhibits the formation of condensation products.

The reactant used in these experiments was dibenzyl ether, which was dissolved in cyclohexane. Reactions were carried out in

a 300-cm<sup>3</sup> stirred, stainless-steel autoclave fitted with a glass liner. Products were identified with the aid of a gas chromatograph/mass spectrometer. Quantitative analyses were carried out by gas chromatography.

The results presented in Table 1 show that the addition of nickel, zinc, or magnesium to  $ZnCl_2$  causes a significant enhancement in the yield of toluene and a reduction in the yield of insoluble resin relative to that observed using  $ZnCl_2$  alone. The Ni/ $ZnCl_2$  cocatalyst system was found to be the most active. The use of a high-surface-area Raney nickel in place of powdered nickel permitted a reduction in the catalyst concentration, hydrogen pressure, and reaction time required for a given yield of toluene.

It should be noted that nickel alone produced a significant conversion of the ether to toluene and benzyl alcohol. This is not surprising since the activity of nickel for the hydrogenolysis of benzyl ethers is well established (4).

Working with the Ni/ $ZnCl_2$  system it was established that the hydrogenolysis of dibenzyl ether to toluene did not occur when the autoclave was pressurized with nitrogen instead of hydrogen. This result, together with the observed decrease in pressure during a run carried out with hydrogen, indicates that molecular hydrogen is the hydride source for hydrogenolysis of the ether. Use of methylcyclopent-

TABLE 1  
Products Obtained from the Catalytic Hydrogenolysis of Dibenzyl Ether<sup>a</sup>

Catalyst	Catalyst loading (mole)	Reaction time (min)	Reaction pressure (MPa)	Products	Percentage yield	Percentage conversion of ether <sup>b</sup>
None	—	60	13.8	Toluene Bibenzyl + <i>o</i> -, <i>m</i> -, and <i>p</i> -benzyl toluenes	1.4 0.1	3.8
ZnCl <sub>2</sub>	5.0 × 10 <sup>-3</sup>	60	13.6	Toluene Bibenzyl + <i>o</i> -, <i>m</i> -, and <i>p</i> -benzyl toluenes Insoluble resin <sup>c</sup>	3.9 2.5 97	100
Ni <sup>d</sup>	2.0 × 10 <sup>-1</sup>	60	13.8	Toluene Benzyl alcohol Bibenzyl + <i>o</i> -, <i>m</i> -, and <i>p</i> -benzyl toluenes Insoluble resin <sup>c</sup>	19.5 5.7 2.3 2.5	38.2
Ni <sup>d</sup> ZnCl <sub>2</sub>	2.0 × 10 <sup>-1</sup> 5.0 × 10 <sup>-3</sup>	60	13.7	Toluene Bibenzyl + <i>o</i> -, <i>m</i> -, and <i>p</i> -benzyl toluenes Insoluble resin <sup>e</sup>	39.6 12.3 35	100
Ni <sup>d</sup> ZnCl <sub>2</sub>	2.0 × 10 <sup>-1</sup> 1.0 × 10 <sup>-3</sup>	60	13.7	Methylcyclohexane Toluene Bibenzyl + <i>o</i> -, <i>m</i> -, and <i>p</i> -benzyl toluenes Insoluble resin <sup>e</sup>	0.5 65.6 8.2 6.0	96.5
Raney Ni <sup>e</sup>	2.0 × 10 <sup>-3</sup>	30	3.14	Methylcyclohexane Toluene Bibenzyl + <i>o</i> -, <i>m</i> -, and <i>p</i> -benzyl toluenes	2.3 21.2 2.4	23.7
Raney Ni <sup>e</sup> ZnCl <sub>2</sub>	2.0 × 10 <sup>-3</sup> 1.0 × 10 <sup>-3</sup>	30	3.21	Toluene Diphenylmethane Bibenzyl + <i>o</i> -, <i>m</i> -, and <i>p</i> -benzyl toluenes Insoluble resin <sup>c</sup>	60.2 0.2 7.1 22	97.4
Zn <sup>c</sup>	2.0 × 10 <sup>-1</sup>	60	13.8	Toluene Bibenzyl + <i>o</i> -, <i>m</i> -, and <i>p</i> -benzyl toluenes	0.5 0.5	2.1
Zn <sup>d</sup> ZnCl <sub>2</sub>	2.0 × 10 <sup>-1</sup> 5.0 × 10 <sup>-3</sup>	60	13.7	Toluene Bibenzyl + <i>o</i> -, <i>m</i> -, and <i>p</i> -benzyl toluenes Insoluble resin <sup>c</sup>	7.4 1.8 29	28.8
Mg <sup>d</sup> ZnCl <sub>2</sub>	2.0 × 10 <sup>-1</sup> 5.0 × 10 <sup>-3</sup>	60	14.0	Toluene Benzyl alcohol Bibenzyl + <i>o</i> -, <i>m</i> -, and <i>p</i> -benzyl toluenes Insoluble resin <sup>c</sup>	7.1 0.7 2.3 56	69.7

<sup>a</sup> Reactions at 225°C of 2.0 × 10<sup>-2</sup> mole dibenzyl ether in 50 ml of cyclohexane under hydrogen pressure.

<sup>b</sup> In addition to experimental error, the total percentage yield may be less than the percentage conversion due to the presence of soluble, but undetected, resins, or the incorporation of solvent into insoluble resins.

<sup>c</sup> The result of cationic polymerization of dibenzyl ether.

<sup>d</sup> Powdered metal; nickel: -200 mesh, zinc: dust, Mallinckrodt reagent, pretreated with dilute HCl wash to remove oxide, magnesium: 40 mesh.

<sup>e</sup> Prepared by the method of L. F. Fieser and M. Fieser ("Reagents for Organic Syntheses," Vol. 1, p. 723, Wiley, New York, 1967), but stored under cyclohexane after ethanol wash.

tane, a potential tertiary hydride donor which could be formed by isomerization of cyclohexane, as the solvent had no significant effect on the reaction products or yields obtained. This result confirms that it is the nickel which activates the hydrogen and promotes its subsequent reaction. The possibility that  $\text{NiCl}_2$ , formed through the interaction of Ni and  $\text{ZnCl}_2$ , might be an active component can be discounted since  $\text{NiCl}_2$  was found to be inactive for hydrogenolysis of dibenzyl ether.

The present observations suggest that the enhanced yields of toluene and the reduced formation of insoluble resin obtained when a metal is used in conjunction with  $\text{ZnCl}_2$  can be ascribed to the cooperative actions of the two catalyst functions. In our previous studies we suggested that  $\text{ZnCl}_2$  is active as a Brønsted acid [e.g.,  $\text{H}^+(\text{ZnCl}_2\text{OH})^-$ ] and that it is the interaction of this form of the catalyst with dibenzyl ether which leads to the formation of benzyl carbonium ions (1). In view of the low dielectric coefficient of cyclohexane, these ions are likely to be present in the form of a soluble but undissociated salt [e.g.,  $(\text{C}_6\text{H}_5\text{CH}_2)^+(\text{ZnCl}_2\text{OH})^-$ ]. The reaction of such a salt with a pair of hydrogen atoms,

formed on the surface of the metal, could lead to the formation of toluene and the regeneration of the Brønsted acid form of  $\text{ZnCl}_2$ .

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