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# HYDROGENATION, CRACKING AND HYDROGENOLYSIS OF BIBENZYL IN A HIGH-PRESSURE STIRRED AUTOCLAVE

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AND HYDROGENOLYSIS OF BIBENZYL
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ABSTRACT

The aromatic and hydroaromatic portions of coal are held together to a substantial extent by aliphatic bridges of the form $\{$--CH_2-$\}_n$, where $1 < n < 4$. When coal is liquefied, these bridging structures must be cleaved and hydrogen added to terminate the opened ends of the bridge. The extent to which coal liquefaction catalysts promote the cleavage of the aliphatic bridges has not been established and was the subject of this investigation. To pursue this problem, bibenzyl was chosen as a model to represent an ethyl bridge between two aromatic centers. The use of a model compound was adopted to facilitate the analysis of products and the interpretation of results.

An initial screening of catalysts was conducted in a magnetically stirred autoclave operated at 325° C and 3500 psig. It was found that cobalt molybdate on silica promoted alumina, tungsten disulfide, lithium

chloride   stannous chloride, stannous chloride promoted with ammonium chloride, zinc chloride, and antimony trichloride were all inactive as catalysts. Ferric chloride caused the bibenzyl to undergo a disproportion-ation reaction yielding benzene plus a tarry substance. Aluminum chloride brought about a complete conversion of the bibenzyl to benzene, toluene, and ethylbenzene as the primary products and lesser amounts of cyclohexane- and diphenyl-type derivatives, as well as a tarry substance. P-toluene sulfonic acid was found to decompose but did not cause the formation of products from bibenzyl.

Following the screening studies, more extensive experiments were per-formed with aluminum chloride. Investigations were performed to determine product yields and distributions as a function of temperature, hydrogen pressure, and catalyst concentration. The extent to which benzene, the solvent used for most of the runs, participated in these reactions was also investigated. The results showed that the bibenzyl conversion and the yields of toluene and ethylbenzene were a strong function of tempera-ture and catalyst concentration but not of hydrogen pressure. However, the yield of cyclohexane derivatives was found to increase with pressure. These results suggest that the hydrogen needed to form toluene and ethylbenzene is derived from the reactant or solvent but not from dissolved H_2. Conversely, the formation of cyclohexane derivatives does involve the consumption of dissolved H_2. Plausible mechanisms for the formation of the products are discussed.

CHAPTER 1

INTRODUCTION

I. THE IMPORTANCE OF COAL AND COAL DERIVED LIQUIDS.

Coal presently represents about 80 to 85 percent of the known fossil fuel energy reserves of the United States. These reserves are one of the most promising resource with which to attain energy self-sufficiency in the near future. The Department of the Interior (8) projects that with a scenario of business as usual and $11 oil, U.S. coal consumption will increase at an annual rate of 5 percent during the 1973-85 period. Further, coal consumption for electrical generation is projected to increase at an annual rate of 5.8 percent during the same period, while industrial consumption is expected to increase at an annual rate of 3 percent. In 1985, coal generating capacity is projected to be 35 percent of the total capacity of the electric utility industry.

In the first quarter of 1973, coal supplied 57 percent of the energy required for power stations. If oil from coal supplied the other 43 percent, then approximately 41 million barrels of natural oil per month and 214 billion cubic feet of natural gas would be available for other uses (22). Since reserves of natural gas and oil are being depleted rapidly and it is not anticipated that new reserves will be found in significant enough quantities to replace known reserves, synthetic fuels derived from coal will become increasingly important. As a result, the economic production of such fuels, and in particular synthetic crude oil, will become a task of major importance.

II. THE PURPOSE AND OBJECTIVES OF THIS INVESTIGATION

There are four major approaches to coal liquefaction:

1. Staged pyrolysis

2. Solvent refining

3. Fischer-Tropsch synthesis (i.e. coal gasification to produce a CO - H_2 mixture, followed by catalytic synthesis of hydrocarbons)

4. Direct pressure catalytic hydrogenation

Of these, the direct pressure catalytic hydrogenation route to coal liquefaction appears to be the most promising, because of its potential to yield large amounts of liquids instead of gases and char. While a number of approaches to catalytic hydrogenation have been developed (14), all require exceptionally high temperatures and pressures. Such severe operating conditions result in the need for expensive equipment and high operating costs. Thus, clearly there is an incentive to develop approaches which require less demanding reaction conditions.

To guide the rational search and development of catalysts capable of producing coal-derived liquids under mild reaction conditions, it is helpful to know as much as possible about the chemistry involved in coal liquefaction. A review of the liquefaction literature suggests that only broad generalizations can be drawn. Thus, it appears that liquefaction is initiated by a thermal depolymerization of the basic coal structure. Hydrogen must then be added to the free radical ends of the depolymerized units and to the interior of these units in order to produce a soluble liquid product. These later steps are accomplished catalytically. While the catalyst may play a role in facilitating depolymerization, it is not clear that the catalysts used to date serve that function.

One approach which should help to clarify the chemistry occurring during coal liquefaction is the study of what happens to model compounds when they are subjected to catalysts and reaction conditions similar to those which would be used with coal. By this means, it should be possible to follow specific reactions through the products that are formed. If model compounds are chosen which reflect different parts of the coal structure, it should be possible to establish how a given catalyst aids in activating reactions at specific structural sites. Such information would be of great help in the search for new liquefaction catalysts.

The present study represents the first of a series to investigate the effects of a given catalyst on the hydrogenation, cracking, and hydro-genolysis of specific model compounds. The model compound selected for the purpose of this study was bibenzyl since, as is discussed below, the aliphatic bridge present in this compound is representative of aliphatic bridges found in coal. Furthermore, the expected products should be small in number and easy to detect by routine analytical methods.

III. LITERATURE REVIEWS

A. The Molecular Structure of Bituminous Coal

Several models representing the molecular structure of bituminous coal have been reported (4, 21, 31, 51). Of these, the model proposed by Wiser (51) and shown in Figure 1-1 has become accepted as a reasonable rep-resentation of the structure of bituminous coal. As indicated by this model, about 70 to 75 percent of the carbon present is contained in aro-matic structures. Although six-membered aromatic rings predominate, a significant number of five-membered configurations also exist. About
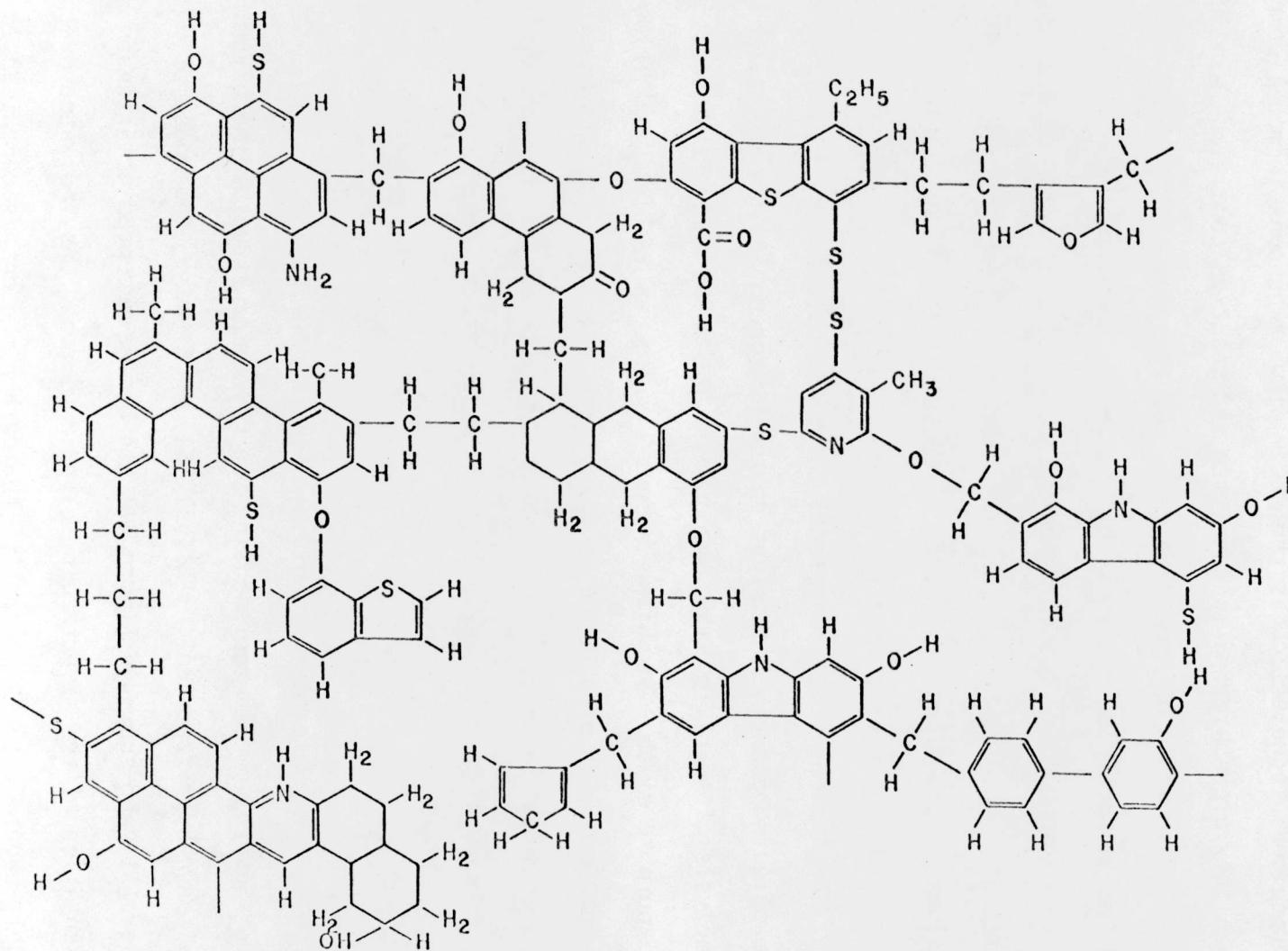
Figure 1-1: A Representation of the Structure of Bituminous Coal

Source: Ref. 51

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15 to 25 percent of the carbon is contained in hydroaromatic structures in which a part of the structure is saturated with respect to hydrogen. From x-ray and diamagnetic susceptibility studies (51), it has been concluded that the aromatic and hydroaromatic portions of the coal structure are present as fused rings containing an average of three rings per cluster.

In addition to carbon and hydrogen, coal also contains significant amounts of sulfur, nitrogen, and oxygen. Sulfur, nitrogen, and, to a lesser extent, oxygen are all contained in heterocyclic structures. Oxygen and to lesser extents sulfur and nitrogen are also found in side-chain structures. Both sulfur and oxygen are present to a considerable degree in bridging structures which link aromatic clusters. Typical types of organic sulfur structures present in coal are: thiophenes, sulfides, disulfides, and mercaptans. It should be noted, however, that inorganic (pyritic) sulfur is present in coal in amounts essentially equivalent to thsoe found in the organic matter. The nitrogen structures present in coal are: pyridines, quinolines, and amines (basic nitrogen structures) and pyrroles, carbazoles, etc. (non-basic nitrogen structures). Oxygen structures in coal consist of the following types: phenols, naphthols, ethers, ketones, quinones, carboxylics, and furan-type derivatives.

B. Coal Depolymerization.

Studies of the depolymerization of coal under mild reaction conditions have provided useful information relating to the identity of aromatic clusters present in coal and to the nature and number of aliphatic bridges which connect these clusters. Furthermore, these studies have served to identify the types of materials which can effect the

depolymerization of coal at temperatures well below those needed for thermal depolymerization.

The earliest work on coal depolymerization was performed by Heredy and Neuworth (18). Working on the assumption that the bridges between aromatic clusters were primarily aliphatic, these authors investigated the use of boron trifluoride and phenol to cleave the bridges. Prior to performing studies with coal, work was undertaken on two model compounds, whose structures are shown in Figure 1-2. Separate reactions of each compound in a phenol solution containing boron trifluoride at 100°C for 6 hours caused an aromatic interchange reaction to occur in which the catalyst cleaved the alphatic-aromatic carbon-carbon linkage and phenol was added to the aliphatic portion. The cleavage was observed to occur preferentially at the "a" linkage in the ethylene-bridge model compound. A similar selectivity was observed with the methylene-bridge model compound but to a much lesser extent.

For the studies of coal depolymerization, a high-volatile bituminous coal was reacted for 24 hours under the same conditions as were used for the model compounds. To better follow the extent of depolymerization, tagged phenol (1 - ^{14}C) was used. The reaction products were sequentially divided into fractions soluble in benzene, methanol, phenol, and pyridine. A large amount of benzene and phenol soluble extract was obtained and compared to that obtained under similar reaction conditions in the absence of boron trifluoride. This indicated that a considerable amount of depolymerization had taken place. Also, it was shown that about 90 percent of the phenols present in a low boiling fraction obtained from the benzene soluble fraction were derived by alkyl group transfer from the coal to

FIGURE 1 - 2

Model Compounds Used by Heredy and Neuworth

Source: Ref. 18

Methylene Model:

1 - (4 - hydroxy - 3,5 - dimethylbenzyl) - naphthalene
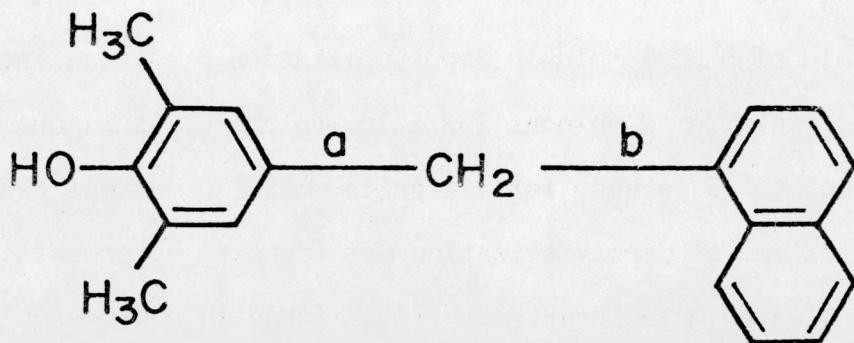
Ethylene Model:

1 - (β - (4 - hydroxy - 3,5 - dimethylphenyl) - ethyl) - naphthalene
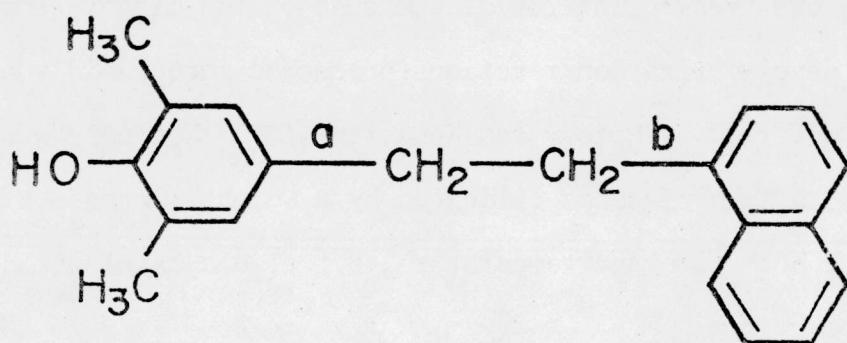
the phenol. The products expected from benzyl ether type linkages were not observed to a significant extent. From this evidence, the authors conclude that aliphatic linkages between aromatic groups definitely exist in bituminous coal.

In another study by the same authors (19), attempts were made to classify the extent of depolymerization observed with the rank of coal studied. It was found that the degree of depolymerization, as measured by the yield of phenol soluble depolymerization products, increased with decreasing rank from 9 percent for a low-volatile bituminous coal (91 percent carbon) to 73 percent for a lignite coal (70 percent carbon). Further, the extent of depolymerization was found to be proportional to the number of cleaved methylene-type bridges found in the benzene soluble fractions.

In a series of studies similar to those of Heredy and Neuworth (18), Ouchi et. al. (35) investigated the depolymerization of coal using p-toluene sulfonic acid dissolved in phenol. This system was refluxed at 185°C in a slow stream of nitrogen. Because of the higher temperature used, these depolymerization reactions proceeded more rapidly and completely than those performed by Heredy and Neuworth (18). Not only was depolymerization found to take place as evidenced by a weight increase of the reaction products with both time and temperature, but also a catalytic dehydration reaction of the form:
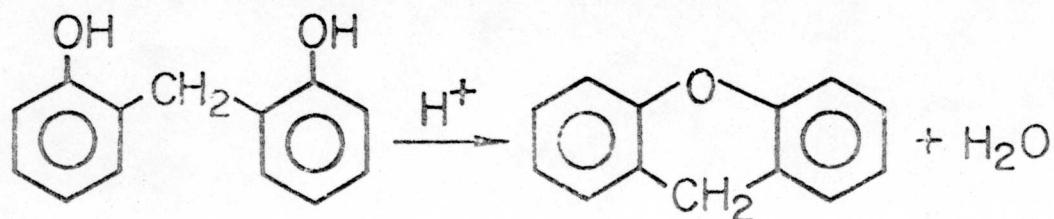
was noted. The depolymerization kinetics was analyzed, and the activation energy for the p-toluene sulfonic acid catalyzed cleavage reaction was found to be approximately 33 Kcal/mole which the authors noted is much lower than that obtained for carbon-carbon cleavage in thermal decomposition, viz. 40 to 50 Kcal/mole. In short, by means of a different catalyst system, these authors were also able to provide evidence for the existence of aliphatic bridges in coal.

The dependence of the extent of depolymerization on the rank of coal was also studied by Ouchi et al. (36). The products from most of the coals were almost entirely soluble in pyridine, and the extent of extraction with benzene-ethanol solutions decreased regularly with increasing rank from lignite to anthracite. The molecular weights of the products for coals of increasing rank in the range of 70 to 93 percent carbon content were found to increase from about 300 to 1100, respectively.

Other studies by Imuta and Ouchi (26) and Ouchi and Brooks (39) have concentrated on the isolation of certain compounds from the depolymerization of brown coals. Again, anhydrous p-toluene sulfonic acid and phenol were used as the depolymerization catalyst and solvent, respectively. The compounds confirmed, or very nearly confirmed, as existing in brown coals include 2-(2-hydroxy-phenyl)-benzofuran, 2-(4-hydroxy-phenyl)-benzofuran, 9-(2-hydroxy-phenyl)-xanthene, 9-(4-hydroxy-phenyl)-xanthene, 4, 4'-dihydroxydibenzyl, xanthone, and 2,2'-dihydroxy-diphenylmethane. These compounds indicate the presence of the following bridging structures in brown coals: -CH- , -CO- , and -CH = C (OH)-. This is the first evidence indicating that tertiary carbon atoms and carbonyl bridges connect aromatic nuclei in brown coals. However, it was admitted that some of the carboxylic

groups in the original coal could have formed carbonyl structures during depolymerization as a result of condensation reactions. On the basis of i.r. and u.v. analyses, Ouchi and Brooks (37) postulated that the unresolved products contain derivatives of benzene, naphthalene, diphenylmethane, bibenzyl, and phenanthrene.

In an attempt to rank catalysts according to their ability to depolymerize coal, Ouchi et al. (38) performed experiments on a bituminous coal using phenol as the solvent. Reaction times of 6 and 24 hours and temperatures of 95° C and 185° C were used. The ability of a catalyst to cause depolymerization was measured by the amount of pyridine and benzene-ethanol extracts derived from a dried portion of the reaction products relative to that derived from a similar reaction product obtained without the use of a catalyst. Their findings indicated that phosphoric acid, ferric chloride plus trichloroacetic acid, zinc chloride, aluminum chloride, ferric chloride, and the sodium salts of benzene sulfonic acid and p-toluene sulfonic acid were almost inactive in promoting depolymerization. On the other hand, benzene sulfonic acid, p-toluene sulfonic acid, and concentrated sulfuric acid proved to be very effective catalysts. Zinc chloride plus trichloroacetic acid, phosphorous pentoxide, and picric acid gave medium extraction yields. These seemingly surprising results might be explained in terms of a solvent effect in which the phenol-catalyst complex is often more effective than the use of the catalyst alone.

A somewhat different depolymerization procedure was used by Reggel et al.(39). The primary objective of their work was to determine the degree to which metal amine systems could catalytically reduce coal and certain model compounds. Here again, mild reaction conditions were used:

typically 100° C at atmospheric pressure.

A lithium-ethylenediamine catalyst system was found to be superior
to systems such as lithium-ethylamine, lithium-diethylenetriamine, and
sodium-ethylenediamine. The greatest addition of hydrogen with the lithium-
ethylenediamine system was found to be 55 atoms of hydrogen per 100 carbon
atoms for a coal containing 90 percent carbon (moisture and ash free basis).
In addition, the reduced coal was found to be more soluble in pyridine
than the starting material, the solubility increasing in one instance as
much as 35-fold.

Three types of interaction were reported to occur during the course
of the reaction, each being brought about by one of the following reagents:
lithium brought about the addition of hydrogen (alkali metals are known
to activate molecular hydrogen (31)) and cleavage of some of the carbon-
oxygen bonds (40,41); N-lithioethylenediamine, $H_2NCH_2CH_2NHLi$, brought
about the isomerization of olefins and the aromatization of some of the
cyclic dienes (42); and ethylenediamine (b.p. 117° C) brought about the
solubilization of coal in a manner that was not completely understood.

Although no depolymerization products were isolated by Reggel et al.
(39), several hydrocarbon model compounds were used to better understand
the reaction processes occurring with this system and coal. Benzene,
anthracene, and phenanthrene were reacted with the lithium-ethylenediamine
system for 2 to 3 hours at 100° C and hydrogen at pressures slightly above
atmospheric. Cyclohexane, dodecahydro- and tetradecahydro- anthracenes and
phenanthrenes were the respective reaction products. Cis- and trans-stilbene
were treated separately with N- lithioethylenediamine to yield bibenzyl,
toluene, bis-(-2 imidazolinyl)(a self condensation product of ethylene-
diamine) and a small amount of polymeric material. However, when bibenzyl

was treated with N-lithioethylenediamine, it was recovered unchanged, and
neither toluene nor bis-(-2 imidazolinyl) was found. Hence, the authors
conclude that the cleavage reaction leading to toluene does not take
place directly by way of stilbene, but instead through some other intermed-
iate.

Oxygen and sulfur containing hydrocarbons were also hydrogenated at
$100°C$ and slightly superatmospheric pressures with the lithium-ethylene-
diamine system. For example, dibenzofuran was reduced to chiefly
σ-cyclohexylphenol and dibenzyl ether primarily to phenol, benzene, and
cyclohexene. Similarly, dibenzothiophene was reduced largely to 1-cyclohexyl-
cyclohexene and σ-cyclohexylphenylmercaptan. Although lithium-ethylene-
diamine was generally active in catalyzing the saturation of aromatic
nuclei, it did not readily reduce the aromatic ring in phenol or phenolic
compounds.

In the experiments with coal, lithium-ethylenediamine was found to
decrease the sulfur content of the coal to a significant extent. In
addition, lithium metal was believed to be consumed via the reaction:
$$Ar + 2Li° + 2RNH_2 \rightarrow ArH_2 + 2Li^+ + 2RNH^- \text{ (31)}.$$

In summary, the findings presented up to this point indicate that
the major linkages between aromatic clusters in bituminous coal are:

1. short aliphatic groups, principally methylene, consisting of
    probably not more than four carbon atoms.

2. ether type linkages

3. sulfide and disulfide linkages

4. diphenyl type linkages

The extent and nature of the bridging structures is a function of

the rank of coal. The lower rank brown coals may contain tertiary carbon and carbonyl-type bridges in addition to the methylene-type bridging structures.

With regard to potential catalyst systems capable of reducing coal at mild reaction conditions, certain Lewis acid systems (i.e. BF_3-phenol, $ZnCl_2$-trichloroacetic acid-phenol), strong Bronsted proton acids (benzene sulfonic acid, p-toluene sulfonic acid, and concentrated sulfuric acid, all with phenol as the solvent), and certain metal amine systems (most notably, lithiumethylenediamine) have all proved to be effective.

C. Catalysts Used for the Liquefaction of Coal.

Unlike the depolymerization reactions just discussed, the catalytic liquefaction of coal employs severe operating conditions. Temperatures are typically in the range 400°C to 500°C and hydrogen pressures are typically 1500 to 4000 psig. Both heterogeneous and homogeneous catalysts have been used to effect the catalytic addition of hydrogen. In the review which follows, the effectiveness of both types of catalyst are summarized.

1. Heterogeneous Catalysts

Heterogeneous catalysts have been used both in pure and supported forms. Some of the carriers such as silica, diatomaceous earth, and bauxite are inert, while others such as silica-alumina, silica-magnesia, silica-titania, boric oxide-titania, etc. are active as cracking catalysts.

a. Metals

Metals are typically used in a finely divided form and are usually ball milled or dry mixed with coal. Powdered metals are not widely used for the liquefaction of coal due to the problem of achieving efficient

catalyst coal contacting. Hawk and Hiteshue (17), in an extensive review article on coal hydrogenation catalysts used by the Bureau of Mines, have indicated that both tin and zinc powders are superior to those of iron, nickel, and cobalt. It was also shown that the addition of small amounts of ammonium chloride or a hydrogen halide greatly enhanced the metal's catalytic activity. These halides by themselves showed no coal conversion capability with the exception of hydrogen iodide.

While metals can be used in the form of unsupported powders, these catalysts are more frequently supported on an acidic base such as silica-alumina. Nickel, iron and cobalt on silica alumina are examples (14).

b. Metal Oxides or Sulfides

Metal oxide and sulfide catalysts are not very soluble, if at all, in suitable impregnating solvents and are therefore seldom impregnated directly into coal.* More commonly, the metal oxide or sulfide is deposited on a support such as silica-alumina. One of the most effective coal lique-faction catalysts included in this category is cobalt-molybdate supported on silica promoted alumina (i.e. 3% CoO and 15% MoO_3). Another very effec-tive catalyst is unsupported tungsten disulfide. These two catalysts are well known for their ability to catalyze the removal of sulfur and nitro-gen from coal and coal tars.

In their review, Hawk and Hiteshue (17) have indicated that both stannous oxide and stannous sulfide are very effective coal conversion catalysts. Other commonly used oxides and sulfides are those of titanium,

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*This problem has been overcome as described in a recent patent (24) by impregnating metal halides (much more soluble in water, alcohols, and ethers than the metal sulfides) with subsequent in situ conversion to the sulfide by reaction with H_2S.

molybdenum, tungsten, iron, cobalt, nickel, and vanadium. Further compar-
isons of the effectiveness of metal oxides and sulfides for coal liquefac-
tion are given by Cox (5).

c. Metal Halides

Metal halide catalysts can easily be impregnated into coal and for
this reason are not very often deposited on a solid support. Stannous
chloride promoted with ammonium chloride has been found by Hawk and
Hiteshue (17) to be equivalent or superior in its performance to the best
metal, metal oxide, or metal sulfide catalysts described previously.
Gorin et al. (15, 16) have done extensive work towards the development of
molten zinc chloride as an effective coal liquefaction catalyst. Other
metal halides which are known to catalytically enhance coal liquefaction
are those of nickel, cobalt, molybdenum, iron, vanadium, and antimony (14).

In the temperature and pressure ranges mentioned earlier, namely
$400°C$ - $500°C$ and 1500 - 4000 psig, aluminum chloride in massive amounts
is capable of producing appreciable amounts of gaseous products with
essentially no liquid products (23). At lower temperatures, substantial
amounts of both oil and hydrocarbon gases are produced. For example, at
$250°C$, 4000 psi, and equal weights of coal and aluminum chloride, 19 weight
percent of the original m.a.f. coal was converted to a benzene soluble
oil whereas 27 weight percent of the coal was converted to hydrocarbon
gases.

Little work has been done to elucidate the effectiveness of metal
fluorides, bromides, or iodides. However, lead and ferrous bromides em-
ployed separately were shown to be moderately active in catalyzing the
conversion of coal into liquid products (17).

Again it seems that the addition of halides, typically a hydrogen halide or ammonium chloride, enhances the catalytic activity of a number of metal halides. Perhaps the active catalytic agent is a complex of the form $H^+MX_{n+1}^-$ where H^+ may represent a hydrogen or ammonium cation, M is the metal of oxidation state n, and X^- is the halide anion.

d. Miscellaneous Metal Compounds

Various metal oxalates and sulfates have also been used, although not as extensively as the metal oxides, sulfides, or halides, to successfully convert coal to liquid products (5, 17). Stannous oxalate, stannous sulfate, and ferrous sulfate are among the more active catalysts in this category.

2. Homogeneous Catalysts

Substantially less work has been done with regard to applying homogeneous catalysis to coal conversion. However, a few investigations reveal some encouraging prospects. Among the most promising homogeneous coal conversion catalysts are the metal carbonyls and metal naphthenates.

a. Metal Carbonyls

Metal carbonyls have been shown to be effective catalysts for the hydrogenation of polynuclear aromatic compounds as well as of coal. The most commonly used carbonyls are: dicobalt octacarbonyl, iron pentacarbonyl, and nickel tetracarbonyl.

Friedman et al. (13) have investigated the effects of dicobalt octacarbonyl on several polynuclear aromatic hydrocarbons. Their experiments were carried out at 150° C to 200° C in an equimolar mixture of carbon monoxide and hydrogen at 3000 psi. Isolated benzene rings were found to be stable in this system while naphthalenes were slowly reduced to tetralins, anthracene was readily hydrogenated at the meso position, more

highly condensed hydrocarbons were reduced to yield phenanthrene deriva-
tives and phenanthrene-type compounds were reduced very slowly to dihydro-
derivatives. At 200°C, coal itself was found to add both hydrogen and
carbon monoxide under the influence of dicobalt octacarbonyl.

Interestingly, a comparative study was undertaken by Arco Chemical
Company (3) concerning the catalytic effects of dicobalt octacarbonyl and
a commercial cobalt molybdate catalyst. First, it was established that
among the carbonyls of cobalt, chromium, iron, molybdenum, rhodium, and
tungsten, that of cobalt possessed the highest overall degree of hydrogen-
ation activity. Further, it was found that dicobalt octacarbonyl is
active at lower temperatures than cobalt molybdate for the hydrogenation
of condensed aromatic hydrocarbons and that for a given degree of conver-
sion dicobalt octacarbonyl leads to products which contain less hydrogen
than those obtained when cobalt molybdate is used. It was also shown, how-
ever, that dicobalt octacarbonyl is not active for the hydrogenolysis of
heteroatom containing compounds such as carbazol, dibenzothiophene,
or acridine. Cobalt molybdate can, on the other hand, effect the removal
of these heteroatoms.

b. Metal Naphthenates

Metal naphthenates are typically obtained through a fusion of
naphthenic acids of the form $R(CH_2)_n COOH$, where R may be a polycyclic
nucleus whose basic unit is cyclopentane or cyclohexane, and a metal oxide,
hydroxide, or salt. Since metal naphthenates $(R(CH_2)_n COO)_x M$, where M is
the metal) are infinitely soluble in many hydrocarbon mixtures efficient
contacting of a coal catalyst slurry at elevated temperatures is not a
problem.

Hawk and Hiteshue (17) have presented evidence that molybdenum and nickel naphthenates are superior to the naphthenates of cobalt, chromium, copper, iron, tin, and zinc in their ability to liquefy coal. Typically, high yields were obtained with very small amounts of the catalyst (i.e. 0.01 to 1.00 percent by weight of the catalyst metal relative to the m.a.f. coal) at the following conditions: 500° C, zero time at temperature, initial (cold) pressure 3,000 psig hydrogen.

D. The Cracking, Hydrogenolysis, Hydrogenation, and Pyrolysis of Bibenzyl.

Table 1-1 provides a summary of studies performed on the cracking, hydrogenolysis, hydrogenation, and pyrolysis of bibenzyl.

1. The Catalytic Cracking of Bibenzyl

Catalytic cracking here implies bond breaking solely at temperatures below those required for pyrolysis. Entries 1-5 of Table 1-1 concern the use of $AlCl_3$ to catalytically crack bibenzyl. A transarylation reaction (a specific type of disproportionation) is proposed and described as taking place at the para positions of the aromatic rings with participation of the cleaved aliphatic bridges. The bibenzyl is thought to undergo two simultaneous processes: cleavage (solely unsymmetric) and condensation. The yield of distillable material is reported to increase upon increasing the catalyst concentration from 1.0 to 10.0 weight percent (6). This transarylation reaction can be described in terms of a disproportionation mechanism.

2. The Catalytic and Thermal Hydrogenolysis of Bibenzyl

Catalytic hydrogenolysis, sometimes called catalytic hydrocracking, implies bond breaking with the simultaneous or subsequent addition of

TABLE 1-1: REVIEW OF THE PRODUCTS OBTAINED FROM THE CRACKING
HYDROGENOLYSIS, HYDROGENATION, AND PYROLYSIS OF BIBENZYL

Number	Catalyst	T($^{\circ}$C)	Gas	P(psi)	Solvent	Reaction Time	Products	References
						CRACKING REACTIONS		
1.	$AlCl_3$/HCl	80-105	Inert	—	—	—	Bibenzyl and Al_2Cl_6 complex and react to form polymeric chains	28
2.	$AlCl_3$	130	N_2	14.7	None	5 hrs.	Yield: 61.2%; Benzene, 35.5%; Linear Polymer, 58.3%; Tridimensional Poly., 4.2%	29
3,	$AlCl_3$	—	—	—	—	—	Benzene plus a polymeric product	30
4.	$AlCl_3$	230-50 / 330-50	Inert	—	—	—	Benzene and a condensation prod. yielding Benzaldehyde and p-C_6H_4(COOH)$_2$ when oxidized	6
5.	$AlCl_3$	180-90	Inert	—	—	—	Benzene plus a resin	53
6.	Gumbrin Clay	170-90	Inert	—	—	40 hrs.	Yield: Benzene (up to 15% at 190°C in 26 hrs.); p-C_6H_4(CH_2CH_2Ph)$_2$ since oxidation gave p-C_6H_4(COOH)$_2$	7
						HYDROGENOLYSIS REACTIONS		
7.	$AlCl_3$	300-450	H_2	1425	—	—	Benzene, Toluene, Ethylbenzene, and Methyldiphenylethane	49
8. a.	Al_2O_3, MoO_3/Al_2O_3							
b.	MoO_3/SiO_2	300-450	H_2	1425	—	—	C_1 - C_8 Paraffins (at max. psig), C_5 - C_7 Cycloparaffins, and C_6 - C_{10} Aromatics	50
c.	MoO_3/SiO_2/Al_2O_3							
9.	CoMo/Al_2O_3	400$^+$	H_2	—	—	—	Ethylbenzene and other products (not listed)	10
10.	CoMo/Al_2O_3	440-80	H_2	—	—	—	Benzene, Toluene, Ethylbenzene, and Stilbene	11
11.	CoMo/Al_2O_3	430-93	H_2	—	—	—	Benzene, Toluene, Ethylbenzene, Stilbene, and traces of Styrene	12
12.	SiO_2/Al_2O_3	510-565	H_2	14.7	Toluene	1 sec. (Space Time)	At 550°C yields: Benzene, 12.7%; Styrene, 6.3%; Xylenes, 3.8%; remaining Bibenzyl, 77.2%	33
13. a.	I_2							
b.	CH_3I							
c.	CHI_3							
d.	Ni_2O_3	410	H_2	175	—	2 hrs.	Yield: 80% Toluene with I_2 vs. 17% without a catalyst; all oxide catalysts listed were found to be inferior to I_2, CH_3I, and CHI_3	54
e.	Fe_2O_3							
f.	CoO							
g.	Al_2O_3							
h.	MoO_3							
14. a.	Pumice	780	H_2	14.7	—	—	Yield: Toluene, 20-22%; Benzene, 5-14%; High Boiling, 7-10%; Residue (largely Stilbene), 33-40%	55
b.	Silica Gel	670	H_2	14.7	—	—	Yield: Toluene, 32%; very little Benzene	
15.	Adkins Cu-Cr Oxide	200	H_2	1895	Methylcyclohexane	6-8 hrs.	No reaction; Reactions did occur with more highly phenyl substituted ethanes	56
16.	None	475-650	H_2	—	—	—	Benzene, absence of Styrene, apparition of Phenanthrene	1
17.	None	505	H_2	700	Toluene	12 sec. (Space Time)	Conversion of Bibenzyl: 19.5%; selectivity to Ethylbenzene: 34.6%	9
						HYDROGENATION REACTIONS		
18.	Ni/Al_2O_3	300-450	H_2	1425	—	—	Primarily ring saturated products (See no. 8)	50
19.	Ni	175	H_2	1750	Methylcyclohexane	35 min.	1,2 - Dicyclohexylethane	56
20.	PtO_2	25-30	H_2	64	Acetic Acid	30 min.	1,2 - Dicyclohexylethane	43
						PYROLYSIS REACTION		
21.	None	710	N_2	very small bibenzyl partial pressures	—	1 sec.	Gaseous: H_2, CH_4, C_2's; Liquids: Benzene, 20 $\pm$ 5%; Ethylbenzene and Styrene, 25 $\pm$ 5% Toluene, 55 $\pm$ 10% Solid; Stilbene and Bibenzyl	25

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hydrogen to stabilize the free radicals formed. This may occur at temperatures below or above pyrolysis temperatures. Thermal hydrogenolysis, thermal hydrocracking, or uncatalyzed hydrogenolysis all imply the partial or total pyrolysis of the compound with the simultaneous or subsequent addition of hydrogen to the free radicals thus formed.

Entries 7-14 in Table 1-1 describe the products reported during the catalytic hydrogenolysis of bibenzyl by different catalysts. Entry 7 shows that $AlCl_3$ can also be used for the hydrogenolysis of bibenzyl. In reference 8, it is noted that methyl-substituted diphenylmethanes were easily hydrogenolyzed to yield low boiling compounds, but the same is not true for methyl-substituted bibenzyl derivatives. The most commonly used catalysts for the hydrogenolysis of bibenzyl are those usually employed by the petroleum refining industry. These include metal oxides used either by themselves or deposited on an acidic support, and acidic cracking catalysts such as silica-alumina. The catalytic activity of the catalysts listed in entry 14 (pumice and silica gel) is somewhat in doubt, since thermal hydrogenolysis may have played a significant role at the temperatures reported. It is interesting to note that entry 13 indicates the superiority of molecular iodine and iodo derivatives of methane over the oxides of nickel, iron, cobalt, aluminum, and molybdenum. Two possibilities may explain these findings: the in situ formation of hydrogen iodide may act as a catalyst promoter or more plausibly may even be the active catalytic species itself since it is acidic enough to participate in typical Friedel-Crafts reactions. Although entry 15 indicates that no reaction took place with bibenzyl, the copper chromium oxide catalyst was found active in causing hydrogenolysis of the ethane carbons in more

highly substituted phenyl derivatives such as 1,1,2 - triphenylethane, or 1,1,1,2 - tetraphenylethane.

Entries 16 and 17 describe studies of the uncatalyzed hydrogenolysis of bibenzyl. From these investigations the temperature at which bibenzyl starts to hydrocrack thermally can be estimated to be within the range 480°C to 500°C. A significant amount of thermal hydrogenolysis does not take place until temperatures of 550°C and above are reached.

3. The Catalytic Hydrogenation of Bibenzyl.

The catalytic hydrogenations discussed here refer to reactions whose primary result is the saturation of aromatic nuclei. Entry 18 in Table 1-1 shows that nickel deposited on alumina, when used under reaction conditions identical to those employed for the catalysts in entry 8, causes a preferential saturation of the aromatic nucleus. Furthermore, entry 19 indicates that unsupported nickel will cause hydrogenation without any carbon-carbon bond cleavage. Entry 20 indicates that platinum oxide at fairly mild reaction conditions can also be expected to give a ring-saturated product. Indeed, other investigations (32, 47) have used, in addition to platinum oxide, palladium and ruthenium oxides to selectively saturate the phenyl groups in benzyl ether without causing cleavage of the ether bridge between the phenyl groups.

4. The Pyrolysis of Bibenzyl.

By pyrolysis is meant the thermal cleavage of bonds in an inert atmosphere. The pyrolysis of bibenzyl (entry 21) at very low bibenzyl partial pressures yields toluene as the major liquid product. The authors of this study show that the process involves the dissociation of bibenzyl into benzyl radicals. This is in contrast to the cracking reactions

previously mentioned, where a transarylation-type disproportionation
mechanism is proposed. However, with regard to the hydrogenolysis reac-
tions, a mechanism involving bibenzyl radicals cannot be ruled out.

As part of the pyrolysis study (25), it was noted that the central
carbon-carbon bond distance in bibenzyl is shorter than the normal
carbon-carbon bond length by about 0.06A which results in the strength-
ening of this bond by about 13 kcal/mole. Since the resonance energy of
the bibenzyl radical is estimated to be 24.5 kcal/mole, the dissociation
energy of the central carbon-carbon bond in bibenzyl is predicted to be
47.1 kcal/mole. The Ph-C bond in bibenzyl is also noted to be about
0.04A shorter than the typical carbon-carbon bond length which again im-
plies appreciable strengthening of this bond.

CHAPTER 2

EXPERIMENTAL APPARATUS AND PROCEDURE

I. EXPERIMENTAL APPARATUS

The principal apparatus used in this work was a stirred autoclave which was housed in an explosion-proof bay. High-pressure gases could be fed to the autoclave, and the temperature and pressure within the autoclave could be monitored continuously on gauges and recorders located outside the explosion-proof bay. Figure 2-1 illustrates the autoclave, gas feed system, and instrumentation. A more detailed description of each of the components is given below.

A. The Autoclave.

The autoclave (Autoclave Engineers, Inc. Model ABP-300) was constructed of 316 stainless steel and was capable of operation up to 343° C and 5000 psig. The internal volume of the autoclave was 300 cm^3. Since glass liners were used to facilitate the introduction and removal of reactants and products, the working volume was reduced to 185 cm^3. The contents of the autoclave were stirred by a rotating propeller which was coupled magnetically to a DC motor (¼ hp, 2500 rpm maximum). The speed of the agitator shaft could be controlled by a rheostat and could be increased up to 1850 rpm. Heating was accomplished by a 600 watt heating mantle placed on the exterior wall of the autoclave. Power to the heater was controlled by means of an automatic temperature controller which acted in response to a signal from a thermocouple located inside the autoclave.

Attached to the cover of the autoclave was a dip tube for sampling the liquid contents and a cooling coil for cooling the contents at the end of a run. Water inlet and outlet connections were located on the side

1. Tachometer
2. Tachometer Pick-up Coil
3. Stirring Assembly
4. Variable Speed Motor
5. Motor Controls
6. Temperature Recorder
7. Temperature Controller
8. Autoclave Cover
9. Autoclave Body
10. Jacket Type Heater
11. Thermowell
12. Agitator Shaft and Impeller
13. Cooling Coil
14. Sampling Tube
15. Solenoid Valve
16. Gate Valve
17. Sampling Valve
18. Check Valve
19. Gas Inlet Shutoff Valve
20. Line Filter
21. Check Valves
22. Safety Head with Rupture Disc
23. Three Way Valve
24. Pressure Gauge
25. Pressure Transducer
26. Power Supply
27. Pressure (MV) Recorder

Inlet water

To drain

To sample

To vent

H_2 N_2

XBL7510-7707

Figure 2-1: Experimental Apparatus

of the cover. Also attached to the cover was a thermowell into which two thermocouples were inserted. One was used to control the heater and the other was used for temperature recording.

In addition to the entrances in the cover of the autoclave, there were three ports in the body of the autoclave. One of these was used as a gas inlet. The second was connected to a three-way valve (two ports open on pressure; see Figure 2-1). In normal operation the leg of the valve connected to the vent line was closed. When it was desired to vent the autoclave, this leg was opened. The second leg of this valve led to a pressure gauge and a pressure transducer. The third port in the autoclave body was connected to a safety head assembly containing an inconel rupture disc (5300 psig @ 72° F). The line leading from the rupture disc holder was teed into the vent line as shown in Figure 2-1.

B. The Gas Inlet System

The gas inlet system was used to pressurize the autoclave with either hydrogen or nitrogen. An illustration of this system is shown in Figure 2-1. Each gas was supplied from a cylinder equipped with a high pressure regulator (Matheson type, delivery pressure 100-2500 psig). A check valve was placed in the line from each cylinder to prevent the flow of gas from one cylinder to the other if both cylinders were opened simultaneously. The separate gas lines were then teed into one line which contained a dual disc (5/10 μm) line filter in order to entrap any particulate matter originating in the gas cylinders. A high-pressure regulating type shut off valve was placed down stream from the line filter. The use of this valve is explained in Section II of this chapter. Finally, a third check valve was placed between the autoclave itself and the shuf off valve just

mentioned. This check valve served to confine the autoclave contents when the pressure in the autoclave rose above that in the gas inlet system.

C. Instrumentation and Controls.

1. Agitator Shaft Speed Controls

As stated previously, the stirring assembly was driven by a DC motor powered by an AC/DC converter. During autoclave operations, a stator assembly was fitted over the top cylindrical portion of the magnetic drive assembly. This stator assembly acts as the pick-up coil for a tachometer. By this means, a direct readout of the stirrer speed could be obtained. By controlling the power to the motor, the stirrer speed could be altered. A maximum speed of 1850 rpm could be obtained.

2. Cooling-Water Controls

A solenoid valve connected to an on-off switch was used to turn on and off the flow of cooling water. The upstream side of the solenoid valve was connected to a water line which contained a gate valve. This valve was always left in the open position since the solenoid valve was normally closed when no current was being supplied.

3. Temperature Controlling and Recording System

The temperature controlling and recording systems were independent of one another. An iron-constantan thermocouple inserted into the thermo-well of the autoclave provided a signal for a Honeywell Pyrovane tempera-ture controller. This instrument controlled the current supplied to the heating jacket surrounding the autoclave.

A Leads and Northrup Speedomax Type G temperature recorder was used in conjunction with a copper-constantan thermocouple, also located in the thermowell of the autoclave, in order to obtain a recording of the

temperature of the autoclave contents versus time. This recorder was calibrated to register temperatures up to 350°C.

4. Pressure Recording System

The pressure in the autoclave was recorded versus time through the use of a Honeywell pressure tranducer connected to a Leads and Northrup Speedomax recorder. Voltage (42±2 VDC) for the transducer was supplied by a DC power supply. Calibration of the transducer was accomplished by means of comparing the transducer output with the reading of a bourdon type pressure gauge attached directly to the autoclave. This subsystem is illustrated as part of Figure 2-1.

II. OPERATING PROCEDURE

A. Catalyst Preparation.

The catalysts used, their source, purity, and the form in which they were charged are presented in Table 2-1. No further purification of any of the catalysts was undertaken. The cobalt molybdate on alumina was obtained as 1/8 inch extruded pellets and was ball milled to pass a 270 Tyler mesh screen (0.053 mm openings). The aluminum chloride was used initially in its original crystalline form but subsequently in a powdered form. The powder was obtained by ball milling and screening a portion of the crystalline aluminum chloride to pass a 100 Tyler mesh screen (0.147 mm openings). Both operations were conducted in a dry box under an atmosphere of nitrogen.

B. Experimental Procedure During the Run

The experimental work was divided into two phases. During the first, all of the catalysts listed in Table 2-1 were screened to determine their activity for catalyzing reactions of bibenzyl. During the second phase of

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Table 2-1: Catalysts Used

Catalyst	Source	Purity	Typical Form Charged To The Autoclave
$CoMo/Al_2O_3$ ($3\%CoO$, $15\%MoO_3$)	Harshaw Chemical Company	---	< 270 Mesh Powder
WS	Research Organic/ Inorganic Chemical Co.	94.8%	1-2 Micron Powder
LiCl	Research Organic/ Inorganic Chemical Co.	99.7%	Granular
NH_4Cl *	Baker & Adamson Prod., Div. Allied Chemical Corp.	99.8%	Granular
$SnCl_2$	Research Organic/ Inorganic Chemical Co.	99%	Powder
$ZnCl_2$	Mallinokroot, Inc.	97% (min.)	Granular
$SbCl_3$	Research Organic/ Inorganic Chemical Co.	99%	Granular
$FeCl_3$	Research Organic/ Inorganic Chemical Co.	99%	Powder
$AlCl_3$	Research Organic/ Inorganic Chemical Co.	99%	< 100 Mesh Powder and Crystalline
PTS $p\text{-}CH_3C_6H_4SO_3H\cdot H_2O$	Fisher Scientific Co.	99.9%	Crystalline

* used as a promotor with $SnCl_2$.

the work, aluminum chloride, the catalyst found to be most active under conditions obtainable in the autoclave, was used under a variety of reaction conditions. The operating procedures used during both phases of the work were nearly identical.

In keeping with the fact that most catalytic coal conversion schemes either slurry or dissolve the coal in a solvent, a suitable solvent for bibenzyl was sought. The desirability of good solubility for bibenzyl as well as for the expected hydrogenolysis products led to the choice of benzene. Therefore, all runs, unless otherwise stated, used 50 ml. of benzene, 10 grams of bibenzyl, and 5 grams of the catalyst to be tested. The run with both catalyst and promotor used 5 grams of stannous chloride and 2.5 grams of ammonium chloride, respectively. Each run was initiated by placing these amounts of catalyst, bibenzyl, and benzene in a glass "liner" vessel which was then placed inside the autoclave. The cover was then attached to the autoclave body and the air trapped in the autoclave was displaced first with nitrogen and then with hydrogen. The procedure for the subsequent pressurization of the autoclave depended upon whether or not the reaction was to be run at pressures above or below that of the hydrogen in the gas cylinder.

For the screening studies, it was desired to use pressures of about 3500 psig. To achieve this pressure, the autoclave was pressurized while cold with hydrogen to 1800 psig, the cylinder pressure. The gas inlet line shut-off valve was then closed and the power to the heating jacket and stirrer was turned on. The gas inlet line shut-off valve was then closed and the power to the heating jacket and stirrer was turned on. The stirring speed was always maintained constant at 1250 rpm. The d esired pressure was achieved

by raising the temperature to 325°C. This step required about 60 minutes. Once the final temperature was reached, the reaction was allowed to proceed for an additional 90 minutes. At the end of the constant temperature period, the heater power was shut off and the cooling water was turned on. Once room temperature was regained (in about 65 to 80 minutes), the stirrer was turned off and the autoclave was depressured by venting the gases in the head space. A purge of nitrogen was then used to displace any remaining traces of hydrogen and gases formed during the reaction. At this point the autoclave was opened and the glass vessel was removed.

During the second phase of the work, a constant pressure was maintained by using the hydrogen cylinder as a gas reservoir. For these runs, (performed solely with aluminum chloride as the catalyst) the start-up procedure was similar to that just described. After the purging steps, the autoclave was pressurized to a value set on the delivery side of the gas regulator, and the gas inlet line shut-off valve was closed. Then, by means of the vent valve (the three-way valve), the initial cold pressure (calculated on the basis of the head space volume and the final temperature and pressure) was set. At this point, the heater and stirrer (again maintained at 1250 rpm) were turned on and the autoclave was allowed to come up to temperature. Once the desired temperature and the set pressure had been reached, the gas inlet line shut-off valve was opened thereby allowing additional hydrogen to flow into the autoclave to replace any which might have been consumed by reaction. At the end of the 90-minute constant-temperature and pressure reaction period, the gas inlet line shut-off valve was again closed. The autoclave was then cooled down and depressurized using the procedures described previously.

C.   Preparations and Analysis of Reaction Products.

The principal method used to analyze the liquid reaction products was gas chromatography. Some nmr spectra were also recorded, but these were used only for qualitative analysis. The gas chromatograph used was a Varian Associates Model 1420-10 which was equipped for linear temperature programming. The sample and reference columns used were both 1/8 inch in o.d. and 6.5 ft. long and were packed with 15% Carbowax 20M on Chromosorb W (80/100 mesh). The output from the chromatograph was displayed on a Linear Instrument Model 252A recorder equipped with an electronic integrator.

Prior to being analyzed, the liquid products from each experiment were filtered to remove the catalyst and any tarry residue. In some instances, settling was required to remove the catalyst-tar sludge. Typically, 0.25 μl. of the filtrate was injected into the chromatograph. The initial column temperature was 90°C. After injection, the temperature was increased at a linear rate of 12°C/min up to 250°C. The final temperature was maintained until the last peak of the chromatogram was obtained.

A typical chromatogram of the liquid product is shown in Figure 2-2 and the peak identities, elution times, and the relative concentration of the components present are given in Table 2-2. A few of the minor peaks could not be unabmiguously identified. Thermal conductivity detector response factors were obtained for the majority of the peaks identified positively. These response factors are given in Table 2-3. The relative amounts of those components of the liquid which were not positively identified were estimated by using an average detector response factor obtained from known components eluted on either side of the unknown.

No attempt was made to identify any of the gaseous products produced

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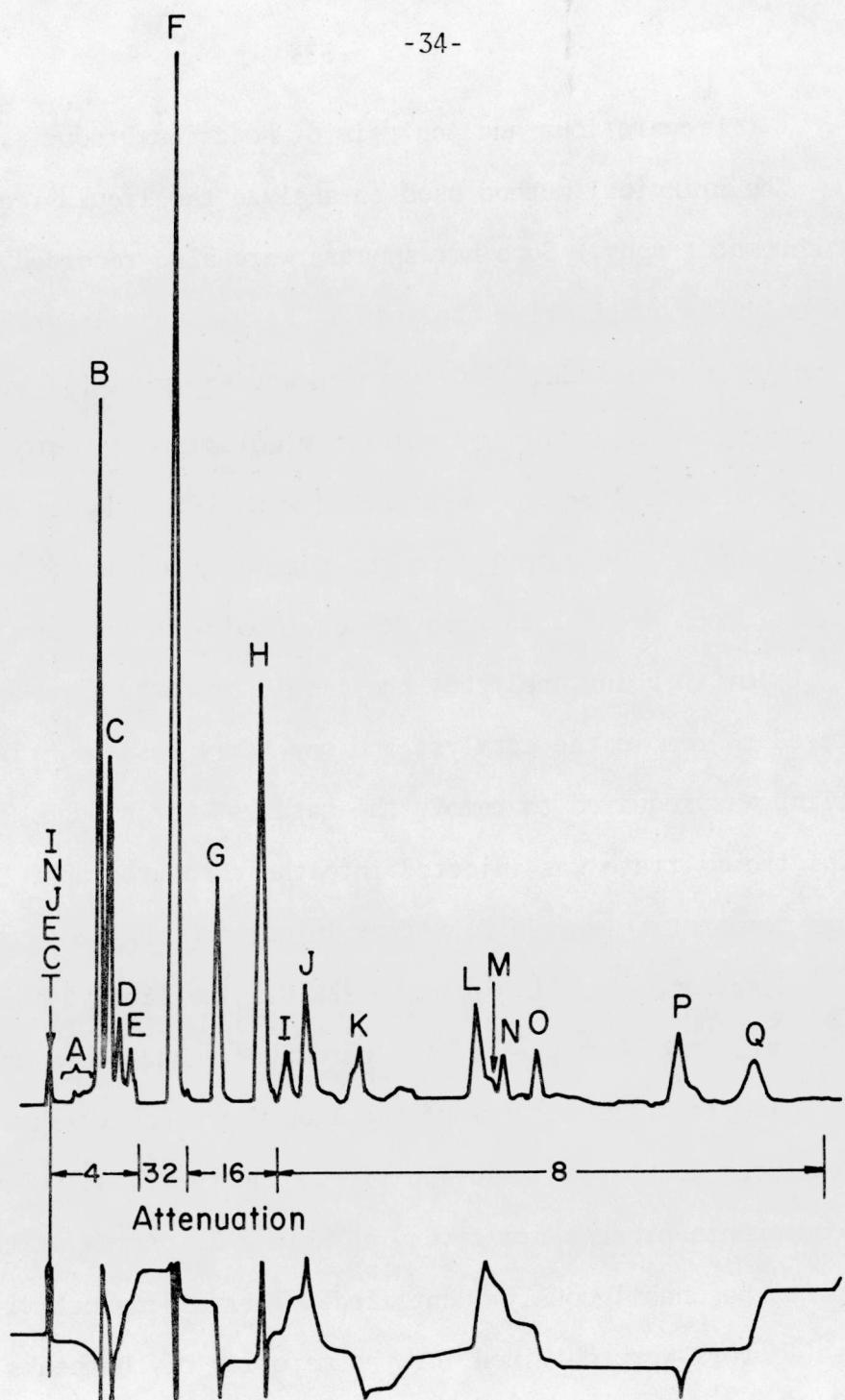
Figure 2-2: A Typical Gas Chromatograph of the Liquid
Reaction Product Obtained When AlCl$_3$ Is
Used as the Catalyst

XBL7510-7706

Table 2-2: Analysis of a Typical Liquid Reaction Product Obtained When
AlCl$_3$ Is Used as the Catalyst

Peak	Identity	Retention Time In Minutes	Relative Weight Percent Present
A	Alkanes	0.47 - 1.15	Tr
B	Cyclohexane	1.35	2.88
C	Methylcyclohexane	1.64	1.83
D	Ethylcyclohexane	1.88	0.52
E	Propylcyclohexane*	2.23	0.44
F	Benzene	3.28	58.74
G	Toluene	4.45	6.72
H	Ethylbenzene	5.63	15.28
I	Cumene	6.27	0.87
J	Propylbenzene	6.91	2.95
K	n-Butylbenzene*	8.20	1.39
L	Cyclohexylcyclohexane*	11.37	2.78
M	Unknown	11.84	Tr
N	1,2-Dicyclohexylethane*	12.13	0.87
O	Phenylcyclohexane	13.13	0.87
P	Diphenyl	16.88	2.12
Q	Bibenzyl	18.87	1.74
			100.00

*Not Positively Identified

Table 2-3: Thermal Conductivity Detector Response Factors

Compound	Response Factor $\left(\dfrac{\mu gm.}{mv\text{-}sec}\right)$
Cyclohexane	8.366
Methylcyclohexane	8.371
Benzene	8.080
Toluene	8.038
Ethylbenzene	8.313
Styrene	8.234
Phenylcyclohexane	9.901
Diphenyl	9.752
Diphenylmethane	9.491
Bibenzyl	9.230

during a run. Likewise, analyses were not performed on the tarry materials separated from the liquid products.

CHAPTER 3

RESULTS AND DISCUSSION

I. SCREENING EXPERIMENTS

Table 3-1 summarizes the effectiveness of the various catalysts
screened to promote the reactions of bibenzyl. All of the experiments
listed were conducted at a temperature of 325°C and all but one at this
temperature reached a final total pressure of 3500 psig. In all of these
experiments, the autoclave was initially pressurized at room temperature
with hydrogen to 1800 psig. Under the reaction conditions used, all of
the benzene and about 50 mole percent of the bibenzyl are predicted to be
in the vapor phase. The anticipated phase of the majority of each cata-
lyst is indicated in Table 3-1 together with a qualitative indication of
the degree of contacting of the catalyst with the reaction medium. As
noted in Table 3-1, cobalt molybdate on silica promoted alumina, tungsten
disulfide, lithium chloride, stannous chloride, stannous chloride promoted
with ammonium chloride, zinc chloride, antimony trichloride, and
p-toluene sulfonic acid were not effective in promoting the reaction of
bibenzyl. Of the catalysts tested, only ferric chloride and aluminum
chloride led to observable products. With ferric chloride, the products
were benzene and a small amount of tar; the extent of bibenzyl conversion,
as measured by its diappearance from the liquid product, was found to be
15.5%. When aluminum chloride was used, cyclohexane, benzene, toluene,
ethylbenzene, and propylbenzene were observed as the major products, to-
gether with a tarry residue. The relative amount of tarry substance compared
to the liquid product was difficult to determine accurately, but is esti-
mated to be approximately 0.15 to 1.00 on a weight basis. The extent of

TABLE 3-1: Effectiveness of the Catalyst Used

Catalyst Used	Catalyst Phase at Reaction Conditions	Degree of Contacting	Catalytic Activity
$CoMo/Al_2O_3$	Solid	Good-Excellent	No Reaction
WS_2	Solid	Good-Excellent	No Reaction
LiCl	Solid	Good	No Reaction
$SnCl_2$	Liquid	Good-Excellent	No Reaction
$SnCl_2/NH_4Cl$	Liquid/Solid	Good	No Reaction
$ZnCl_2$	Liquid	Good-Excellent	No Reaction
$SbCl_3$	Vapor	Excellent	No Reaction
$FeCl_3$	Liquid	Good-Excellent	15.5% Conversion of Bibenzyl
$AlCl_3$	Vapor	Excellent	100% Conversion of Bibenzyl
PTS	-----	---------	Catalyst Decomposed

bibenzyl conversion in this instance was essentially 100%.

The superior catalytic activity of aluminum chloride was also noted by its effect on the gas pressure in the autoclave. As mentioned earlier, in all of the runs the autoclave was initially pressurized with hydrogen to 1800 psig at room temperature. When heated to 325°C, the pressure in all of the runs except that conducted with aluminum chloride rose to 3500 psig. When aluminum chloride was used, the final pressure obtained was only 3000 psig. After reaction, cooling of the autoclave contents to room temperature caused the gas pressure to fall to 1600 psig, indicating that at least 0.333 moles of hydrogen had been consumed. It is of some interest to note that if the hydrogen had only been used to completely convert bibenzyl to benzene and ethylbenzene, 0.055 moles of hydrogen would have been consumed. Since a larger amount of hydrogen was consumed, this could indicate that a substantial amount of hydrogen is being taken up in the saturation of aromatic rings and possibly for the hydrocracking of these rings.

Since only aluminum chloride showed substantial activity under the most severe operating conditions attainable in the present apparatus, this catalyst was selected for further study. The following section details the results obtained as a function of reaction conditions using this catalyst.

II. EXPERIMENTS WITH ALUMINUM CHLORIDE

A. The Effect of Varying the Reaction Conditions.

In the course of the experiments with aluminum chloride, it was discovered that this catalyst also promoted a substantial reaction of the

solvent, benzene. A host of investigators (48) have shown that,depending upon the reaction conditions used, benzene in the presence of aluminum chloride can be converted to a miscellany of products not unlike those that appear as products in this study. As a result of this, most of the subsequent experiments were conducted both with and without bibenzyl present in the initial charge under identical reaction conditions. In addition, a few runs were performed without the presence of the solvent.

The effects of reaction temperature at a fixed pressure are presented in Table 3-2. Listed are the weight percentages of each product and the extent of bibenzyl conversion to products, regardless of their final phase. The latter figure is computed on the assumption that all of the unreacted bibenzyl remains dissolved in the liquid product at the end of each run. Table 3-2 reveals that the distribution of products obtained from benzene is comparable to that obtained from the solution of bibenzyl in benzene. In fact, the yield of products from benzene alone is so high that it was not possible to separate the source of products when bibenzyl and benzene were reacted together, as had been originally intended. Both in the presence and absence of bibenzyl, the primary products were toluene and ethylbenzene. Significantly smaller amounts of cyclohexanes, other alkylated benzenes and condensation products were also observed. Putting the liquid product analyses on a bibenzyl-free basis, for the runs where less than 100% bibenzyl conversion occurred, allows one to conclude that benzene is also a major reaction product.

In the runs conducted with bibenzyl initially present in the charge, the extent of bibenzyl conversion is a strong function of the reaction temperature. A plot of the bibenzyl conversion versus reaction temperature is shown in Figure 3-1. The conversion increases linearly up to

Table 3-2: Weight Percents of Components Found in the Liquid Product as a Function of Reaction Temperature

Reaction Conditions

Feed: 50 ml. Benzene, 5 gm AlCl , with (w) and without (w/o) 10 gm Bibenzyl

Pressure: 1000 psig total

| COMPONENT	155°C		205°C		235°C		260°C		310°C	
	w	w/o	w	w/o	w	w/o	w	w/o	w	w/o
Alkanes	——	——	——	——	——	——	Tr	Tr	0.28	0.81
Cyclohexane	——	0.94	1.13	4.15	1.08	2.89	0.31	1.37	0.87	1.45
Methylcyclohexane	Tr	1.41	0.78	2.79	0.59	1.58	0.16	0.76	Tr	0.64
Ethylcyclohexane	1.88	Tr	Tr	Tr	0.14	0.10	0.16	0.38	Tr	0.58
Propylcyclohexane*	Tr	——	——	Tr	Tr	Tr	Tr	0.23	Tr	0.37
Benzene	80.97	93.01	84.06	80.57	80.95	80.06	76.28	78.09	72.54	62.72
Toluene	0.06	0.64	1.73	3.12	4.03	4.54	7.17	5.05	7.55	11.63
Ethylbenzene	0.18	2.60	2.98	5.55	7.55	8.31	14.27	9.40	14.12	15.46
Cumene	Tr	Tr	Tr	0.22	Tr	0.32	Tr	0.38	1.01	1.18
Propylbenzene	0.28	0.33	Tr	0.52	0.72	0.86	1.17	1.14	2.60	3.09
n-Butylbenzene*	Tr	0.33	Tr	0.82	0.14	0.36	0.40	0.61	0.83	1.18
Cyclohexylcyclohexane*	Tr	0.13	0.81	0.45	1.04	0.36	Tr+	0.53	Tr	0.61
M	Tr	——	——	——	——	——	——	——	——	——
1,2-Dicyclohexylethane*	Tr	0.07	Tr	0.22	Tr	0.11	Tr	0.11	Tr+	0.17
Phenylcyclohexane	0.92	0.53	Tr+	0.75	Tr+	0.18	Tr+	0.11	Tr+	——
Diphenyl	Tr	Tr	Tr+	0.42	0.19	0.18	Tr+	0.93	Tr	0.11
Bibenzyl	15.71	Tr	8.51	0.42	3.57	0.16	0.08	0.46	0.20	——
Mole Ratio of Ethylbenzene To Toluene	——	——	1.49	1.54	1.63	1.59	1.73	1.48	1.62	1.15
Bibenzyl Conversion (%)	17.8		55.5		81.3		~100		~100	

*Not positively identified.
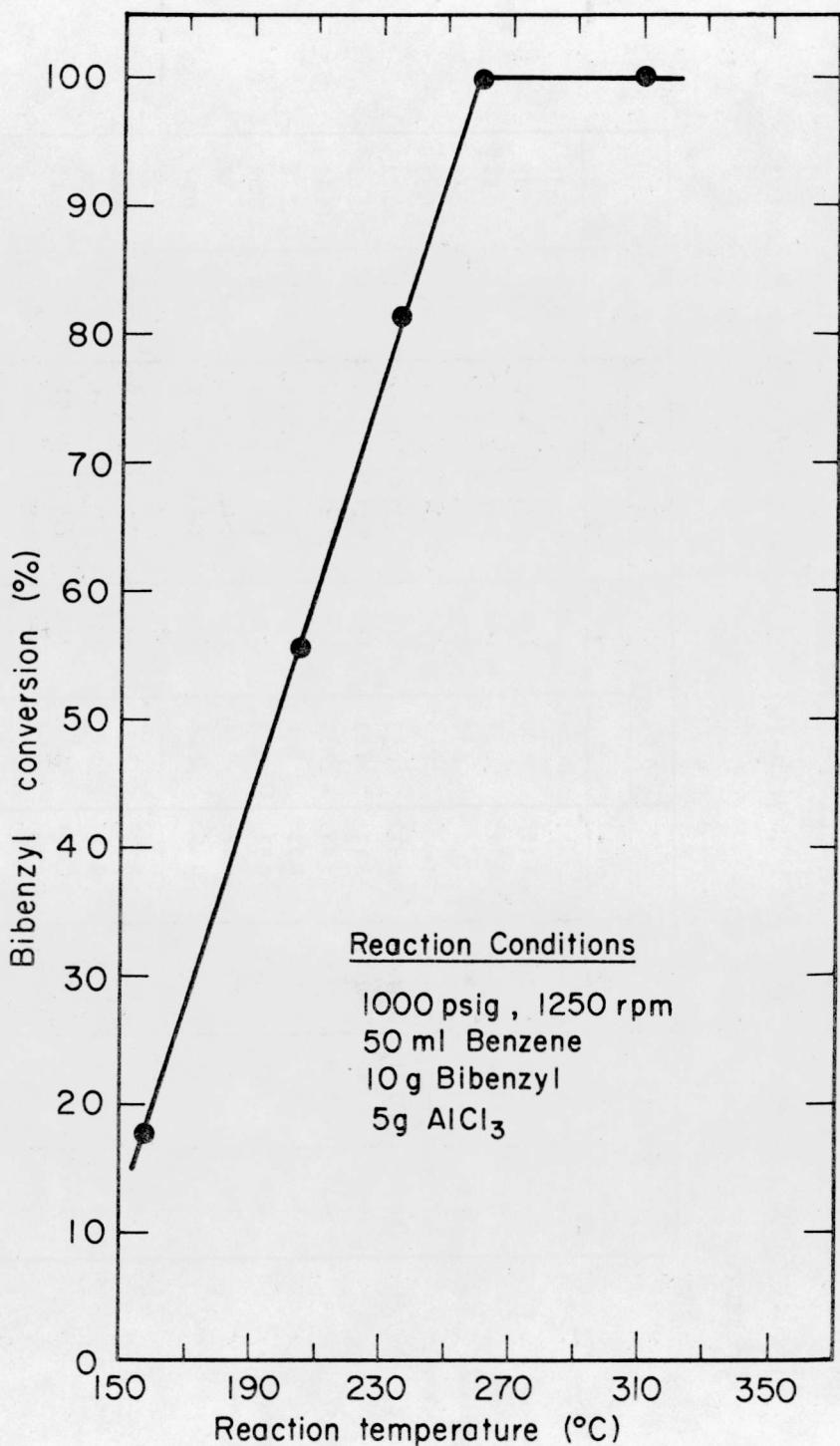
Figure 3-1:   Bibenzyl Conversion as a Function of Reaction Temperature
(90 min. at reaction temperature)

260° C at which point essentially all of the bibenzyl has been consumed. Regardless of whether or not bibenzyl is initially present in the charge the amount of tarry substance is also a strong function of temperature. Very little tarry material is observed at 155° C, whereas a substantial amount is present at 310° C.

The mole ratio of ethylbenzene to toluene in the liquid product is also a strong function of temperature. To emphasize this point, the data given in Table 3-2 have been plotted in Figure 3-2. Since the absolute amounts of ethylbenzene and toluene were so low when the reaction temperature was 155° C, any error in measuring these small amounts would be magnified in their ratio, and for this reason they were not included in the plot. As the temperature is increased, the ratio increases and then passes through a maximum. The position of the maximum depends on whether or not bibenzyl is present in the starting mixture. Furthermore, it is observed that at high temperatures, the ethylbenzene to toluene mole ratio is significantly larger for those runs conducted with bibenzyl than for those done with benzene alone.

Table 3-3 shows the effects of increasing the total pressure (by means of increasing the hydrogen partial pressure) on the distribution of reaction products in the liquid phase and the extent of bibenzyl conversion. From this table it is evident that between 500 and 1850 psig total, the extent of bibenzyl conversion and the final concentration of the major components of the liquid reaction products, namely toluene and ethylbenzene, are essentially independent of the total gas pressure and equally independent, therefore, of the hydrogen partial pressure. The amount of tarry residue formed in these runs was also observed to be relatively
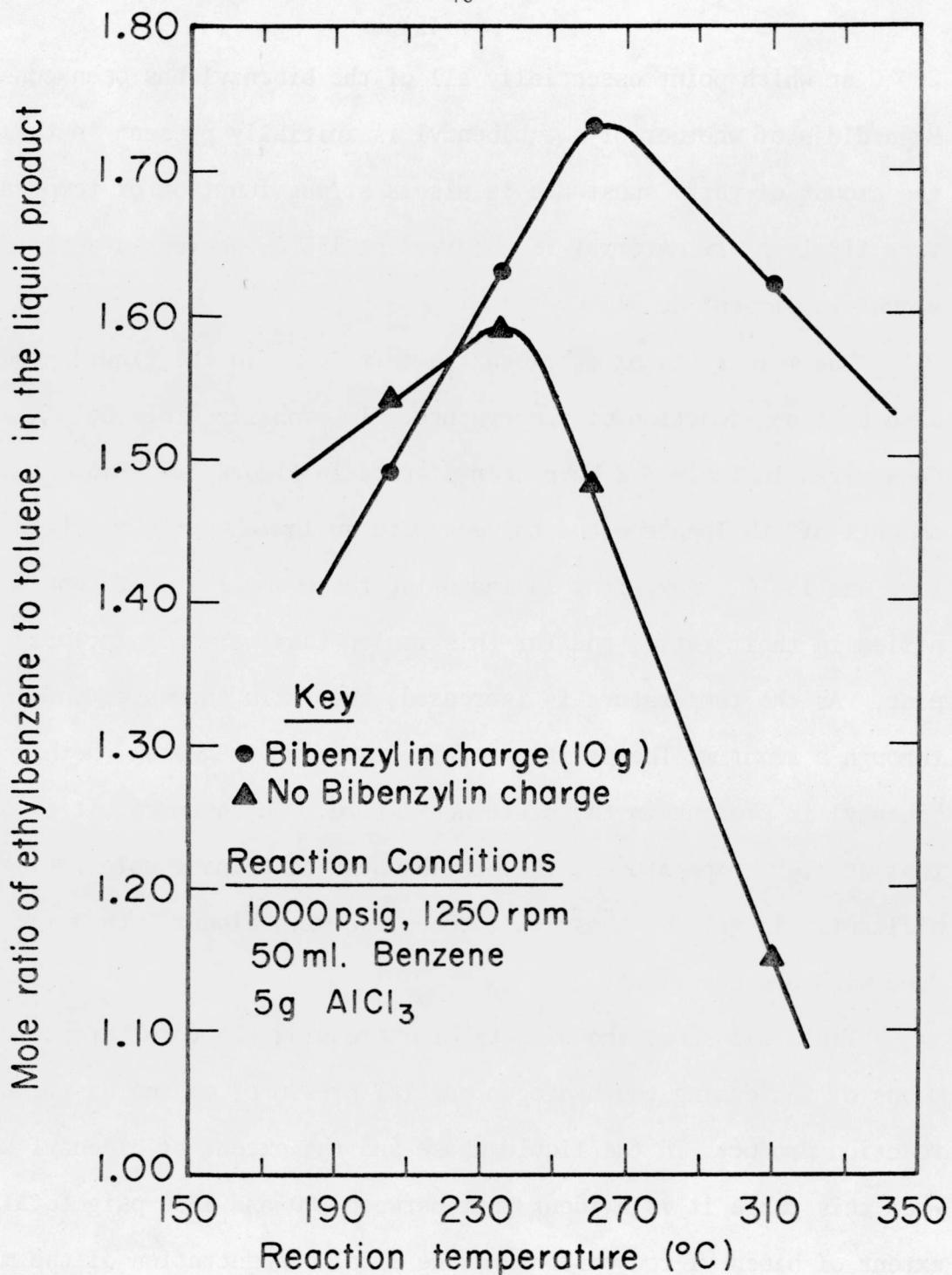
Figure 3-2: Mole Ratio of Ethylbenzene to Toluene as a Function of
Reaction Temperature (90 min. at reaction temperature)

Table 3-3: Weight Percents of Components Found in the Liquid Product as a Function of Reaction Pressure

Reaction Conditions

Feed: 50 ml. Benzene, 10gm. Bibenzyl, and 5gm. $AlCl_3$
Temperature: 235°C

Component	Total Pressure, Psig		
	500	1000	1850
Alkanes	----	----	----
Cyclohexane	0.60	1.08	4.09
Methylcyclohexane	Tr	0.59	2.68
Ethylcyclohexane	Tr	0.14	0.35
Phenylcyclohexane*	Tr	Tr	Tr
Benzene	83.17	80.95	74.69
Toluene	3.89	4.03	4.09
Ethylbenzene	7.09	7.55	7.25
Cumene	Tr	Tr	Tr
Propylbenzene	0.69	0.78	0.91
n-Butylbenzene*	Tr	0.14	0.43
Cyclohexylcyclohexane*	0.76	1.04	1.49
Unknown (M)	----	----	----
1,2-Dicyclohexylethane*	Tr	Tr	Tr
Phenylcyclohexane	Tr	Tr	Tr
Diphenyl	0.33	0.19	1.06
Bibenzyl	3.45	3.57	3.03
Bibenzyl Conv. (%)	82.0	81.3	84.1

*Not positively identified

independent of the pressure employed. It should be noted that the concentrations of cyclohexane and its derivatives, as well as those of the condensation products such as diphenyl, both increase with increasing total pressure and therefore with increasing hydrogen partial pressure.

These results suggest that the formation of toluene, ethylbenzene, and the other alkylated benzenes may not involve the consumption of molecular hydrogen but instead occurs through a redistribution of the hydrogen present in the starting bibenzyl and benzene. To test this hypothesis, runs were conducted using nitrogen instead of hydrogen to pressure the autoclave. The results given in Table 3-4 show that the product concentrations of toluene, ethylbenzene, and the other alkylated benzene products are nearly the same when nitrogen or hydrogen is used. Closer inspection shows a slight increase in the concentrations of the alkylated benzene products with the use of nitrogen. A possible explanation for the latter observation may be contained in the recognition (27) that hydrogen inhibits aluminum chloride's ability to catalyze autodestructive alkylation. Table 3-4 also indicates that the concentrations of cyclohexane and its derivatives are significantly higher (without an accompanying increase in the concentrations of the condensation products) when hydrogen is used than when nitrogen is used. These findings tend to substantiate the aforementioned hypothesis, and further indicate that the hydrogen used to form cyclohexane and its derivatives is derived from the gaseous hydrogen used to pressurize the autoclave.

The effects of catalyst concentration are illustrated in Table 3-5. Here the results are compared for runs in which the catalyst concentration was 5% and 50% by weight of the bibenzyl charged to the autoclave. For the

Table 3-4: Weight Percent of Components Found in the Liquid Product When Autoclave Was Pressurized With Nitrogen Instead of Hydrogen
Reaction Conditions
Feed: 50ml. Benzene, 5gm. AlCl₃, With (W) and Without (W/O) 10gm. Bibenzyl
Temperature: 235° C

Pressure: 1000 psig

Component	Without Bibenzyl		With Bibenzyl	
	N₂	H₂	N₂	H₂
Alkanes	Tr	--	--	--
Cyclohexane	0.16	2.89	0.36	1.08
Methylcyclohexane	Tr	1.58	Tr	0.59
Ethycyclohexane	0.61	0.10	Tr	0.14
Propylcyclohexane*	--	Tr	Tr	Tr
Benzene	81.39	80.06	76.46	80.95
Toluene	6.21	4.54	5.62	4.03
Ethylbenzene	8.19	8.31	9.50	7.55
Cumene	0.69	0.32	0.78	Tr
Propylbenzene	1.20	0.86	1.42	0.72
n-Butylbenzene*	0.31	0.36	0.50	0.14
Cyclohexylcyclohexane*	0.25	0.36	0.85	1.04
Unknown (M)	--	--	--	Tr
1,2-Dicyclohexylethane*	0.28	0.11	0.35	Tr
Phenylcyclohexane	--	0.18	--	Tr
Diphenyl	0.84	0.18	1.89	0.19
Bibenzyl	0.24	0.16	2.28	3.57
Bibenzyl Conv. (%)			88.1	81.3

*Not positively identified

Table 3-5: Weight Percents of the Components Found in the Liquid Product as a Function of Catalyst Loading

Reaction Conditions

Feed: 50ml. Benzene, with (W) and without (W/O) 10gm. Bibenzyl, and 0.5 or 5gm. $AlCl_3$

Temperature: 235° C

Pressure: 1000 psig

Component	0.05gm. AlCl /gm. Bibenzyl		0.5gm. AlCl /gm. Bibenzyl	
	W	W/O	W	W/O
Alkanes	--	--	--	--
Cyclohexane	--	--	1.08	2.89
Methylcyclohexane	--	--	0.59	1.58
Ethylcyclohexane	0.07	0.34	0.14	0.10
Propylcyclohexane*	--	Tr	Tr	Tr
Benzene	84.97	99.45	80.95	80.06
Toluene	0.11	--	4.03	4.54
Ehtylbenzene	0.55	--	7.55	8.31
Cumene	--	--	Tr	0.32
Propylbenzene	--	--	0.72	0.86
n-Butylbenzene*	--	--	0.14	0.36
Cyclohexylcyclohexane*	--	--	1.04	0.36
Unknown (M)	--	--	--	--
1,2-Dicyclohexylethane*	--	--	Tr	0.11
Phenylcyclohexane	--	--	Tr	0.18
Diphenyl	0.06	0.21	0.19	0.18
Bibenzyl	14.23	--	3.57	0.16
Bibenzyl Conv (%)	25.5		81.3	

*Not positively identified

lower catalyst loading, the concentration of products was less than 1% by weight, and no toluene or ethylbenzene was observed when the reaction was run in the absence of bibenzyl. In the presence of bibenzyl, however, the primary products were toluene and ethylbenzene and the bibenzyl conversion was about 25%. For the higher catalyst loading, the concentrations of toluene, ethylbenzene, and the other alkylated benzenes were essentially the same in the presence and absence of bibenzyl. As indicated previously, the bibenzyl conversion at the conditions given in the table for the higher catalyst loading was 100%. These results suggest that at low catalyst loadings bibenzyl is more readily activated than benzene, but that with a significant increase in catalyst loading the activation of bibenzyl and of benzene are more nearly comparable. In addition, it is worth noting that hardly any tarry substance was observed in the runs using the lower catalyst loading, whereas approximately 15% by weight of the initial charge was converted to tar in those runs using the higher catalyst loading.

Table 3-6 presents the results obtained when bibenzyl was reacted in the absence of benzene. In this case, the number of products observed is greater than when the reaction is run with benzene. Unfortunately, most of the additional products observed could not be readily identified. Numbers are used to indicate the presence of new unidentifiable components. It is clearly evident, however, that the primary reaction products are benzene, toluene, and ethylbenzene. Of these products, benzene must be considered as an intermediate since (as shown in discussing Table 3-2) toluene and ethylbenzene can be formed from benzene under these conditions. Further support of this conclusion is given by the observation that the mole ratios of ethylbenzene and toluene to benzene are larger at the higher

Table 3-6: Weight Percents of Components Found in the Liquid Product When No Solvent Was Used

Reaction Conditions
Feed: 30gm. Bibenzyl and 1.5 or 15gm. $AlCl_3$
Temperature: 235° C
Pressure: 1000 psig

Component	0.05gm. $AlCl_3$/gm. Bibenzyl	0.5gm. $AlCl_3$/gm. Bibenzyl
Alkanes	Tr	2.40
Cyclohexane	Tr	3.83
Methylcyclohexane	Tr	4.70
Ethylcyclohexane	Tr	6.52
Propylcyclohexane*	0.47	4.12
1	11.62	2.68
2		1.73
Benzene	54.46	31.75
3	Tr	0.64
Toluene	8.07	12.71
Ethylbenzene	8.74	13.33
Cumene	Tr	2.19
Propylbenzene	0.94	4.76
n-Butylbenzene*	Tr	1.14
4	Tr	1.90
5	Tr	0.38
Cyclohexylcyclohexane*	1.40	2.19
Unknown (M)	--	0.86
1,2-Dicyclohexylethane*	--	0.57
Phenylcyclohexane	--	0.53
6	--	0.53
Diphenyl	Tr	0.21
Bibenzyl	12.91	0.32
7	0.78	--
8	0.61	--
Bibenzyl Conv. (%)	32.4	100.

*Not positively identified

catalyst loading. At the lower catalyst loading the total bibenzyl conversion is 32.4% with little if any discernible tarry substance. At the higher catalyst loading the bibenzyl conversion is essentially 100% and about 85% by weight of the initial charge is present as tarry products. Since it was observed that the extent of tar formation was substantially less when benzene was present, it would appear that benzene can in some way reduce the formation of tar.

B.   Possible Reaction Paths

The complexity of the present reaction system and the nature of the available experimental data make it impossible to establish unambiguous reaction mechanisms. Nevertheless, it is possible to propose plausible reaction paths to explain the occurrence of the major reaction products.

As noted here and in the literature reviewed in Chapter 1 (see Table 1-1, Cracking Reactions) a tarry substance is always formed when bibenzyl reacts in the presence of aluminum chloride at moderate reaction conditions. Mechanisms for the formation of a tar can be proposed which involve either bibenzyl or benzene and possibly both. The first of these mechanisms, solely involving bibenzyl, is referred to as a disproportionation mechanism. The exact form of the mechanism is still subject to discussion. However, the most recent studies by Streitwieser (44,45) indicate that an initial oxidation is followed by carbonium-ion chain reactions similar to those exhibited in Friedel-Crafts reactions. This mechanism does not involve a simple S_N2 type reaction as postulated by Brown and Smoot (2). A Streitwieser type mechanism of bibenzyl disproportionation is shown below (46):

$PhCH_2CH_2Ph \xrightarrow{H^+}$

$PhCH_2CH_2 \text{---} \overset{+}{\bigcirc}\text{---} CH_2CH_2Ph + H^+$

(p-di(phenylethyl)benzene)
+ σ-di(phenylethyl)benzene
+ m-di(phenylethyl)benzene

$PhCH_2CH_2Ph$
etc.

$n \left(\bigcirc \right)$

$+ PhCH_2CH_2\text{---}\left[\bigcirc \text{---}CH_2CH_2\text{---} \right]_n \bigcirc \text{---}CH_2CH_2Ph$
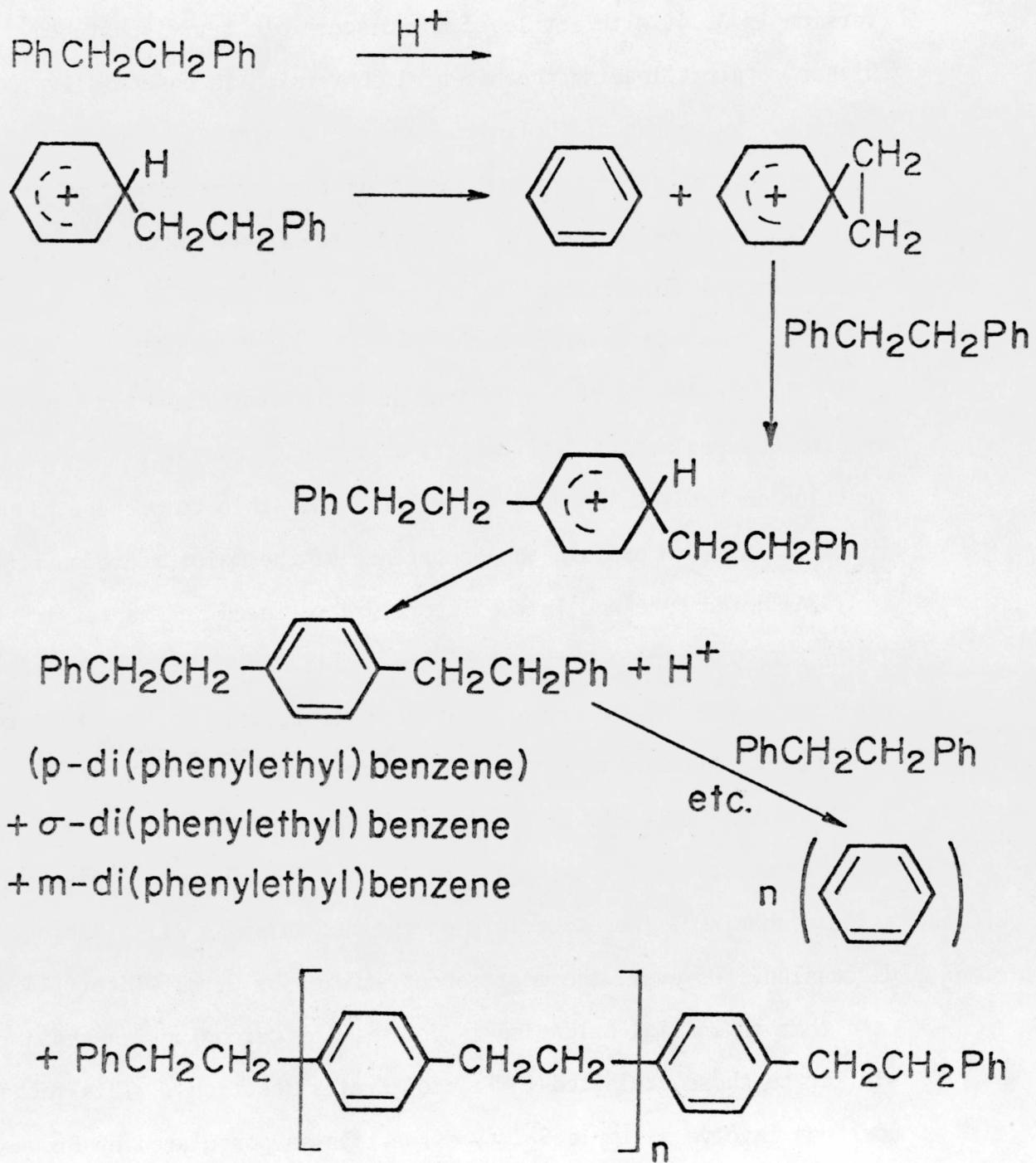
Direct evidence of the occurrence of a disproportionation reaction was found in at least one experiment. A mixture of bibenzyl and aluminum chloride was prepared and allowed to stand for 24 hours at room temperature and pressure. At the end of this period, it was found that the solid mixture had changed to a reddish brown liquid (most likely an $AlCl_3$/aromatic complex) on which floated a clear liquid. Gas chromatographic analysis of the clear liquid showed that it contained only benzene.

The benzene formed from the disproportionation of bibenzyl or added as a solvent for the bibenzyl can also undergo reactions leading to tar formation. An example for such a sequence, involving only benzene, is shown below and follows the pattern of a Scholl condensation (34).

(p-polyphenyl)
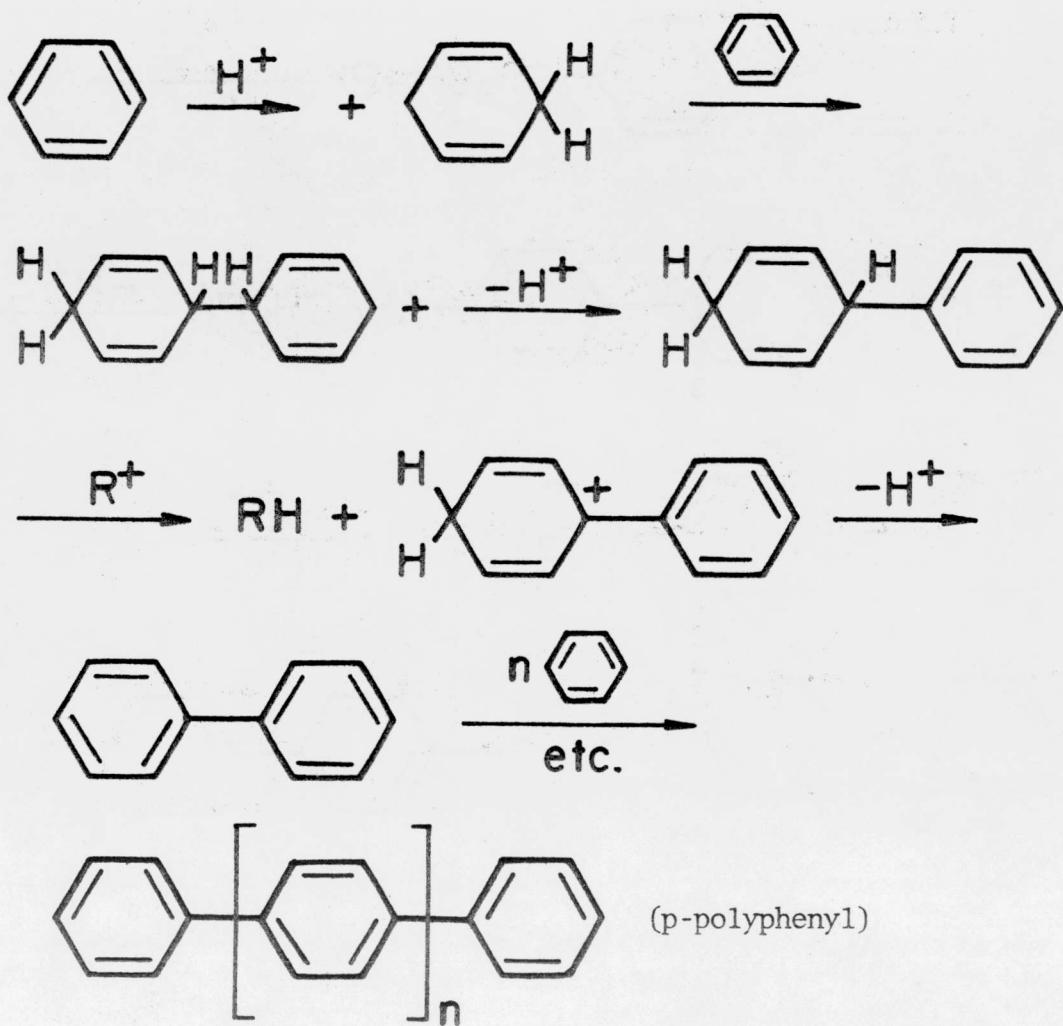
Other reaction sequences can be proposed in which both bibenzyl and benzene
are involved in the formation of tar. An example of such a sequence is
shown below.
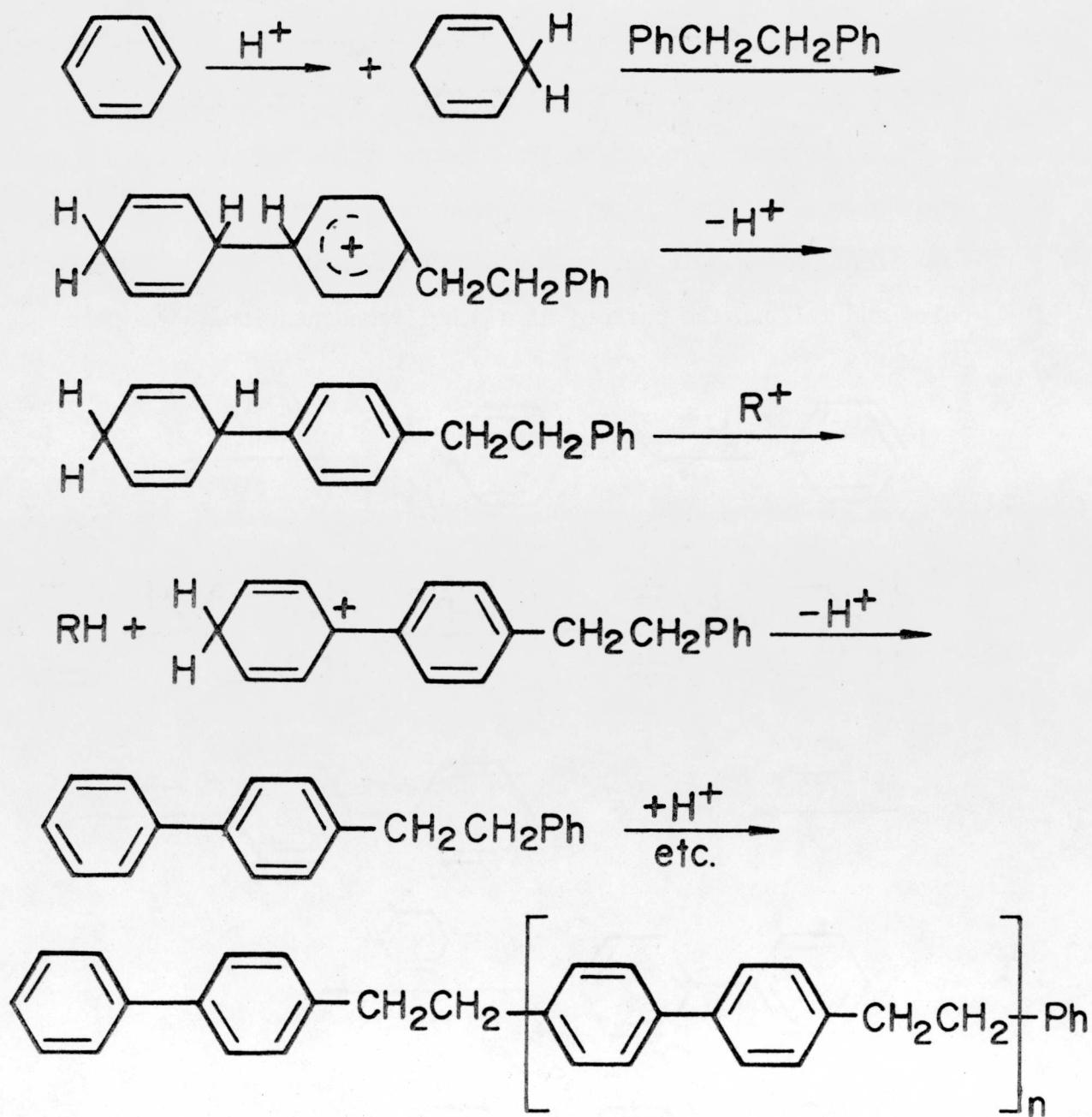
As illustrated by the experimental results reported here, toluene
and ethylbenzene are formed both in the presence and absence of bibenzyl
in benzene with aluminum chloride. Thus mechanisms must be proposed to
account for both of these products. The presence of the stable
intermediate
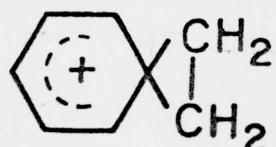
formed by protonation of bibenzyl suggests a mechanism for the appearance
of ethylbenzene from bibenzyl.

$$PhCH_2CH_2Ph \quad + \quad$$ $$\longrightarrow$$

$$PhCH_2CH_3 \quad + \quad Ph\overset{+}{C}H CH_2 Ph$$
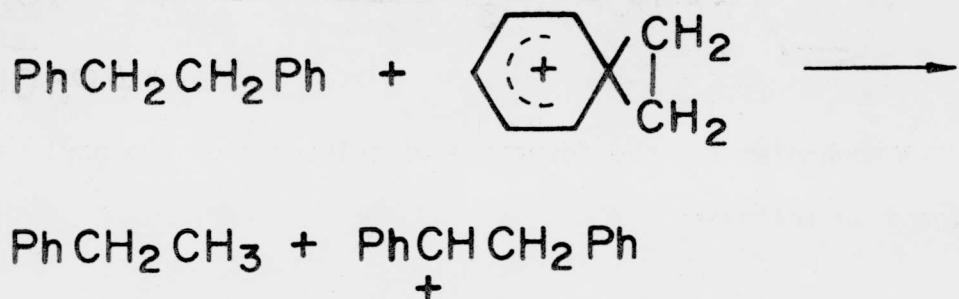
The carbonium ion formed as a product of this reaction can also be
envisioned as participating in reaction leading to ethylbenzene
directly from bibenzyl.

-58-

$$PhCHCH_2Ph \longrightarrow Ph-\overset{+}{C}-CH_3$$
$$\overset{+}{} \qquad\qquad\qquad \underset{Ph}{|}$$

$$\downarrow PhCH_2CH_2Ph$$

$$Ph-CH-CH_3 \overset{H^+}{\longleftarrow} Ph-\underset{Ph}{CH} CH_3 + Ph\overset{+}{C}HCH_2Ph$$
$$\underset{H}{|}$$

$$\bigcirc + Ph\overset{+}{C}HCH_3 \xrightarrow{PhCH_2CH_2Ph} PhCH_2CH_3$$
$$\overset{+}{} $$
$$+ Ph\overset{+}{C}HCH_2Ph$$
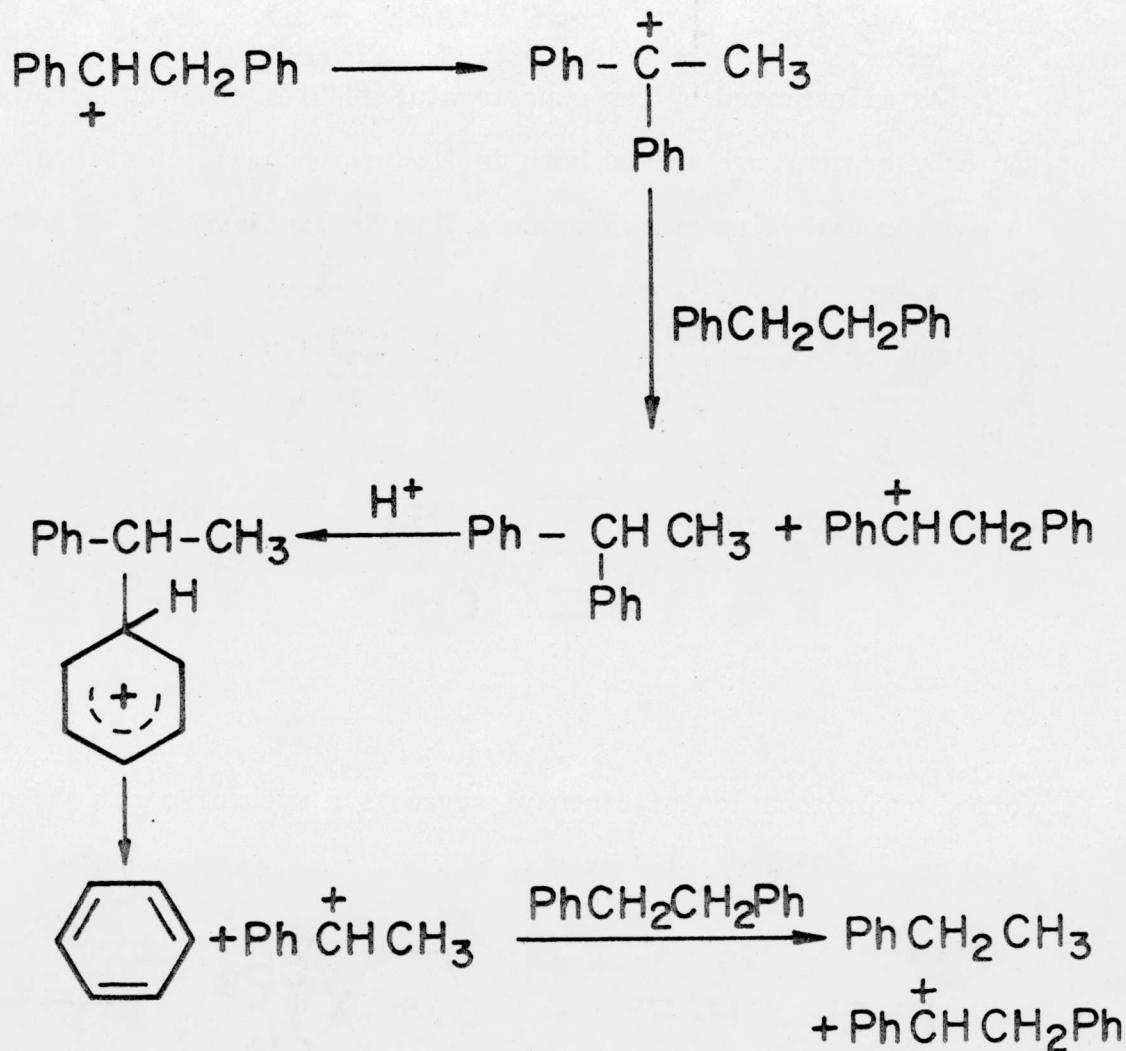
A mechanism for the formation of toluene from bibenzyl can be envisioned as follows:

$$PhCH_2CH_2Ph \xrightarrow{H^+} PhCH_2CH_2-\bigcirc\overset{H}{\underset{H}{+}} \longrightarrow$$

$$\longrightarrow \text{Ph }\overset{+}{\text{C}}\text{H}_2 \ + \ \text{CH}_2 =$$

PhCH$_2$CH$_2$Ph

Ph CH$_3$

$+$Ph $\underset{+}{\text{C}}$H CH$_2$ Ph

PhCH$_3$
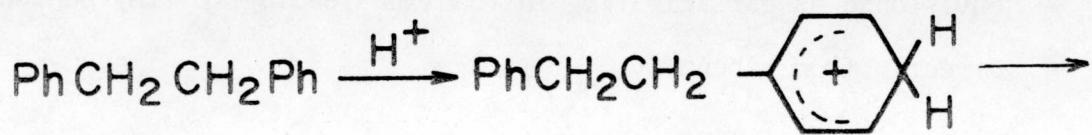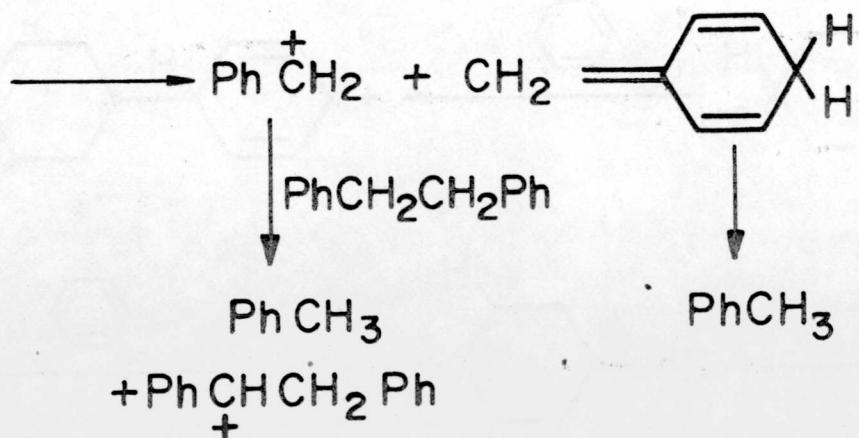
While the formation of toluene and ethylbenzene from benzene is known to occur, the mechanisms for forming these products cannot be envisioned readily. It appears likely that the first step in the mechanism involves cracking or hydrocracking of benzene to produce a series of olefins. These products could act as alkylating agents to form toluene, ethylbenzene, and the other alkylated benzene products by conventional Friedel-Crafts mechanisms. A second source of aklylating agents may occur from benzene which is first saturated to cyclohexane and then hydro cracked to form a lower molecular weight alkane and olefin (eg. $CH_2=CH_2$ + $CH_3CH_2CH_2CH_3$). In addition, alternative pathways can be envisioned in which the cracking of a benzene condensation product is involved. A way in which this might happen is given below:

$$\text{Ph}-\text{Ph}+\tfrac{1}{2}\text{H}_2 \longrightarrow \qquad \xrightarrow{\ \text{H}^+\ }$$
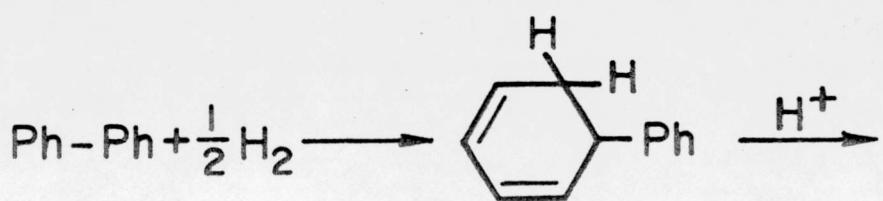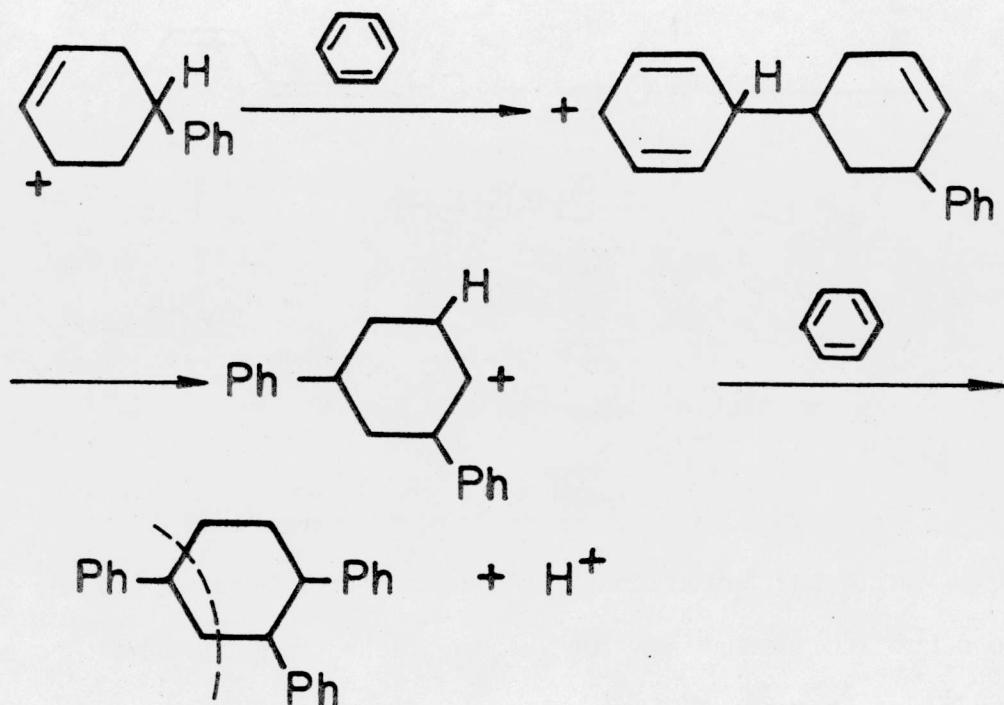
If the last product shown is then able to crack in the manner indicated by the dotted line, then one of the products formed will be ethylbenzene. In a similar fashion, other mechanisms can be proposed to explain the presence of a host of alkylated benzenes.

If an excess of benzene were present, as was the case in all the experiments performed except those where bibenzyl was run by itself, then the occurrence of disproportionation reactions should be obscured, since the benzene could exchange with the phenyl group of a particular aromatic compound, and the net result would be identical to the starting materials. For example:

$$^*C_6H_5-\underset{+}{C}H-CH_3 + C_6H_6 \longrightarrow C_6H_5-\underset{^*C_6H_5}{\overset{|}{C}}H-CH_3$$

$$C_6H_5-\underset{^*C_6H_5}{\overset{|}{C}}H-CH_3 \longrightarrow C_6H_6 + {}^*C_6H_5-\underset{+}{C}H-CH_3$$

$$\longrightarrow {}^*C_6H_6 + C_6H_5-\underset{+}{C}H-CH_3$$

$$C_6H_5-\underset{+}{C}H-CH_3 + {}^*C_6H_5-CH_2-CH_3 \longrightarrow$$
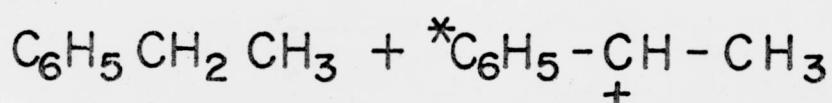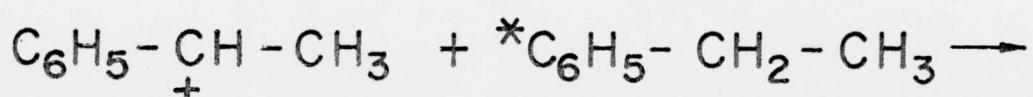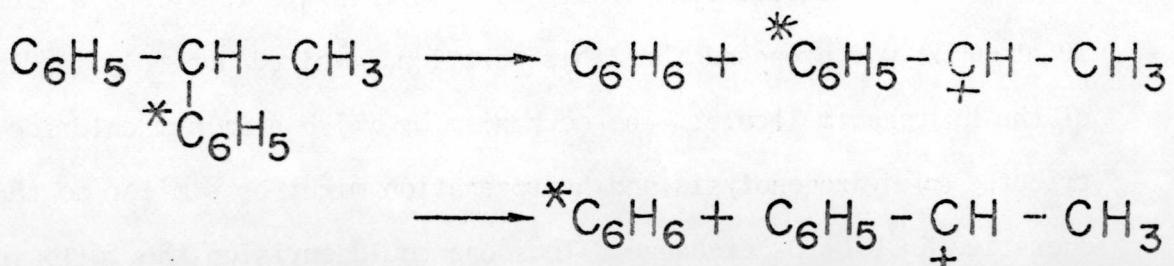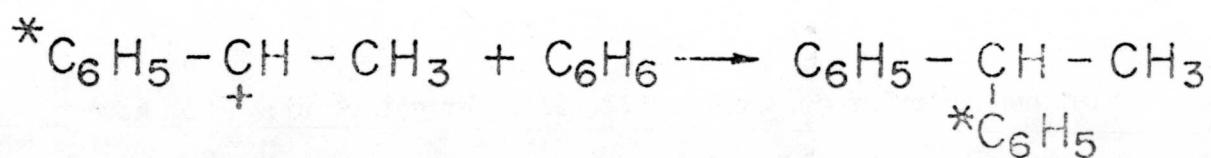
$$C_6H_5CH_2CH_3 + {}^*C_6H_5-\underset{+}{C}H-CH_3 \qquad \text{(Source: ref. 45)}$$

Such mechanisms might explain why no disproportionation products of toluene and ethylbenzene (xylenes and diethylbenzenes) were observed in the liquid products of runs performed in the presence of an excess of benzene. Conversely, in the absence of an excess of benzene, disproportionation of the initial reaction products could take place and might account for the unidentified products observed in Table 3-6.

In most of the mechanisms proposed the first step involves a protonation. The actual source of this proton is the complex $H^+AlCl_4^-$. Although the aluminum chloride used in these experiments was "anhydrous," traces of moisture were present in the air and in the benzene (0.02 -0.03% water). The water from these sources can react with the aluminum chloride to give hydrogen chloride which can then complex with the remaining aluminum chloride in the manner indicated above.

Thus far no discussion has been given concerning the molecular hydrogen charged to the autoclave. The mechanisms postulated to this point have involved cracking reactions in which a rearrangement of the hydrogen already present in the organic compounds takes place accompanied by bond cleavage and formation. Evidence for the activation of molecular hydrogen by

aluminum chloride does exist (27, 52). Wright et al. (52) have observed

that aluminum chloride can promote H_2 - D_2 exchange reactions at $200°C$ and

10 atm. It was proposed that this reaction involved heterolytic cleavage

of the hydrogen molecule. The mechanism by which aluminum chloride con-

tributes to hydrogenolysis and hydrogenation might be similar to that

operative in H_2 - D_2 exchange. Thus one could envision the following reac-

tion to occur:

$$H^+ : H^- + (R)^+ (AlCl_3X)^- \rightleftharpoons$$
$$RH + H^+ (AlCl_3X)^-$$
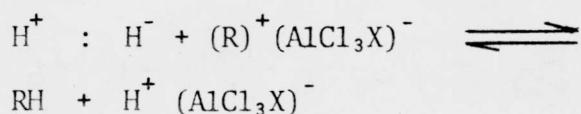
where R^+ is a carbonium ion and X^- a hydroxyl, chloride, or hydride ion.

From the data obtained in this study, it is difficult to determine whether

this mechanism is operating in conjunction with the various cracking mech-

anisms or not. It is evident (see Table 3-4), however, that the molecular

hydrogen charged to the autoclave is definietly participating in aromatic-

ring saturation reactions. The reaction mechanism may be of the type

indicated above with R^+ being:
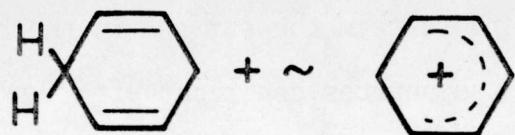
CHAPTER 4

CONCLUSIONS

The present work has shown that cobalt molybdate on silica promoted
alumina, tungsten disulfide, lithium chloride, stannous chloride promoted
with ammonium chloride, stannous chloride, zinc chloride, antimony tri-
chloride, and p-toluene sulfonic acid are all inactive for promoting the
hydrogenolysis or hydrogenation of bibenzyl at 325°C and 3500 psig. Under
the same conditions, ferric chloride caused the bibenzyl to undergo a dis-
proportionation reaction. Only aluminum chloride, a strong Lewis acid, was
found to bring about both hydrogenolysis and hydrogenation of bibenzyl.

More extensive investigation of the catalytic properties of aluminum
chloride revealed that it caused not only the reactions of bibenzyl but also
those involving benzene, the solvent used in most of the experiments. The
reaction products were found to contain primarily benzene, ethylbenzene,
toluene, and a tarry substance. Lesser amounts of cyclohexanes, other
alkylbenzenes, and diphenyl were also found. Similar products were pro-
duced by reacting benzene in the absence of bibenzyl. However, careful
examination of the results showed that both toluene and ethylbenzene were
formed directly from bibenzyl, and that bibenzyl appears to inhibit the
reactions involving benzene. From a study of the effects of hydrogen
pressure, it was established that the conversion of bibenzyl and the
yields of toluene and ethylbenzene do not depend on the pressure of gaseous
hydrogen. The formation of these products can in fact be achieved without
gaseous hydrogen using only the hydrogen available in the organic materials.
By contrast, the yields of cyclohexane derivatives are strongly affected by
the hydrogen pressure, leading to the conclusion that gaseous hydrogen is

involved in the formation of these products.

Studies with different catalyst-to-bibenzyl ratios revealed that the extent of bibenzyl conversion is reduced when smaller amounts of catalyst are used. Furthermore, low catalyst loadings appear to reduce significantly the extent to which benzene is reacted and the tarry substance is formed. These results suggest that future work should be done with low loadings of catalyst to avoid the interfering effects of solvent reaction.

Finally, mechanisms have been proposed to explain the formation of the tarry substance as well as toluene and ethylbenzene, the major reaction products. A key step in all of these mechanisms is the protonation of the bibenzyl which subsequently leads to either a symmetric or unsymmetric cleavage of the aliphatic bridge between the phenyl groups.

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