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Author

Taylor, N.D.

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ALIPHATIC AND ARYL-ARYL LINKAGES IN COAL

Newell D. Taylor and Alexis T. Bell

January 1980

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The Effects of Lewis Acid Catalysts on the Cleavage of
Aliphatic and Aryl-Aryl Linkages in Coal-Related Structures

by

Newell D. Taylor*

and

Alexis T. Bell

Materials and Molecular Research Division
Lawrence Berkeley Laboratory

and

Department of Chemical Engineering
University of California, Berkeley, CA 94720

ABSTRACT

The cleavage of aliphatic and aryl-aryl linkages between aromatic nuclei in coal-related structures have been studied using AlCl_3 and ZnCl_2 . It was observed that both catalysts promote the cleavage of aliphatic linkages but do not significantly catalyze the dissociation of aryl-aryl bonds. The former process was observed to occur via dissociation of an alkyl-aryl bond and was strongly affected by both the acidity of the Brønsted form of the catalyst [e.g., $\text{H}^+(\text{AlCl}_3\text{X})^-$ or $\text{H}^+(\text{ZnCl}_2\text{X})^-$] and the Brønsted basicity of the aromatic portions of the reactant. The composition of the final products depends upon whether the carbonium ion produced upon cleavage on alkyl-aryl bond reacts via electrophilic substitution or hydride abstraction.

* Present address: Upjohn Co.
1500-91-1
7000 Portage Road
Kalamazoo, Michigan 49001

INTRODUCTION

Studies of coal structure have shown that aliphatic groups play an important part in linking together aromatic or hydroaromatic clusters (1-8). Investigations by Heredy and Neuworth (1,2) and Heredy et al. (3) have suggested that methylene bridges comprise only a small fraction of the total number of aliphatic linkages. This conclusion has recently been confirmed by Deno et al. (5,6). Their work suggests that two- and three-carbon linkages occur much more frequently than one-carbon linkages. The fraction of carbon participating in aliphatic linkages is not well established, but studies by Huston et al. (7) suggest that it may be as high as 20%.

Since the cleavage of aliphatic linkages is expected to contribute significantly to the liquefaction of coal, it is important to establish the effects which catalysts may have on this process. The purpose of the present work was to investigate the role of Lewis acid catalysts in the cleavage of both aliphatic and aryl-aryl linkages. More specifically, we wished to determine the influence of organic structure on the ease of linkage cleavage, the relationship between the Lewis acid strength and catalytic activity, and the role of molecular hydrogen in the cleavage process. To facilitate product identification and the interpretation of reaction sequences, model compounds possessing structures similar to those present in coal were used. Three groups of compounds were selected: biphenyl and diphenylalkanes,

containing one to four aliphatic carbon atoms; hydroxylated analogs of biphenyl and diphenylmethane; and 1-phenyl- and 1-benzyl-naphthalene. Both ZnCl_2 and AlCl_3 were investigated as catalysts.

EXPERIMENTAL

Apparatus and Procedure

Reactions were carried out in a 300 cm³ stirred autoclave fitted with a glass liner to facilitate the introduction of reactants and the removal of products. The autoclave was heated by an external heater and could be brought up to temperature in about 20 min. Following reaction, the autoclave and its contents were quenched by removing the heater and replacing it with a water-cooled jacket. Using this procedure, the temperature within the autoclave could be reduced to room temperature in about 10 min.

A run was initiated by weighing out appropriate amounts of reactant, solvent, and catalyst into a dry glass liner placed inside a nitrogen-purged drybox. The filled liner was next transferred to the autoclave, which was quickly sealed and purged of air. The autoclave was then pressurized and heated. For all of the results reported here the reaction time was 90 min at a temperature of 325°C. At this temperature none of the substrates reacted in the absence of a catalyst, and consequently all of the products observed could be ascribed to catalyzed reactions.

Following reaction, the products were weighed and the solid and liquid components were separated by filtration. Quantitative analysis of the liquid products was carried out by gas chromatography, using a 1/8 in x 10 ft column packed with 5% OV-225 on Chromsorb P. Product identification was established with the aid of a Finnigan 4023 gas chromatograph/mass spectrometer.

Materials

The following compounds were used as reactants: biphenyl (Aldrich), diphenylmethane (Aldrich), bibenzyl (Aldrich), 1,3-diphenylpropane (Frinton Laboratories), 1,4-diphenylbutane (Frinton Laboratories), 2-phenylphenol (Aldrich), 4-phenylphenol (Aldrich), 2-hydroxydiphenylmethane (Aldrich), 4-hydroxydiphenylmethane (Aldrich), 1-phenylnaphthalene (Aldrich), and 1-benzyl-naphthalene (ICN Pharmaceuticals). All reactants, with the exception of the hydroxylated compounds, were used as received without further purification. Both isomers of hydroxydiphenylmethane and 2-phenylphenol were dried with anhydrous $MgSO_4$. Each compound was heated above its melting point for 24 hrs in a stoppered flask with $MgSO_4$ which previously had been dried in a vacuum oven at 110°C. The $MgSO_4$ was separated from the liquid substrate by vacuum filtration through a coarse glass frit. The dried compounds were subsequently stored and handled in a dry box under nitrogen. 4-Phenylphenol was not dried because of its relatively high melting point (169°C), but it was not hygroscopic.

Reagent grade benzene (Mallinckrodt) and cyclohexane (Aldrich) were dried by refluxing in a glass still under nitrogen and in the presence of a mixture of sodium metal and benzophenone. The solvent was collected in a previously dried glass bottle and stored under nitrogen until used.

Anhydrous AlCl_3 (Mallinckrodt) was used as received and was stored in a dry box under nitrogen to avoid contact with water vapor. Zinc chloride (Mallinckrodt) was dried in a vacuum oven at 110°C was also stored in the dry box until used.

RESULTS

The products obtained from the reactions of biphenyl and a series of diphenyl alkanes, catalyzed by AlCl_3 , are listed in Table I. Cyclohexane was used as the solvent in these experiments. To identify products obtained from the solvent, an experiment was performed with cyclohexane alone. As can be seen from the last column of Table I, the major product derived from cyclohexane is methylcyclopentane. Small amounts of light aliphatics and benzene are also observed. In the presence of a dissolved reactant, the isomerization of cyclohexane is strongly inhibited and, reactions of the substrate predominate. Most of the products obtained from the substrate are soluble in cyclohexane. However, the formation of an insoluble polymer, or tar, is noted in every case. The overall conversion of substrate to products, and the extent of tar formation, are indicated at the bottom of Table I.

Examination of Table I shows that the reactant structure influences both the reactant conversion and the distribution of products obtained. Biphenyl reacts to the lowest extent and forms principally heavy unknowns and tar. Cleavage of the aryl-aryl bond is limited since only a small amount of benzene is formed in excess of that derived from cyclohexane. By contrast, the diphenyl alkanes are much more reactive and undergo extensive cracking of the aliphatic bridge. In each case the principal product produced in the process is benzene. The counterproduct of bridge-cleavage depends on the length of the bridge. For diphenylmethane and bibenzyl the counterproducts are toluene and ethylbenzene, respectively, while for 1,3-diphenylpropane and 1,4-diphenylbutane the principal counterproducts are indan and tetralin. With the exception of 1,4-diphenylbutane, the concentration of the counterproduct is substantially lower than that of benzene. For the reactions of diphenylmethane and bibenzyl a part of the discrepancy can be accounted for by the dealkylation of toluene and ethylbenzene, reactions which were confirmed experimentally.

When the reaction of biphenyl and the diphenyl alkanes are conducted in benzene results qualitatively similar to those in cyclohexane are observed, as shown in Table II. The principal difference is that the reactant conversions are lower in benzene. This effect is particularly noticeable for biphenyl, bibenzyl, and 1,4-diphenylbutane.

The effects of gas composition on the products obtained from diphenylmethane and 1,3-diphenylpropane are indicated in Table III. When N_2 rather than H_2 is used to pressurize the autoclave, the reactant conversion is reduced by about 17 to 18% but the same distribution of products is obtained. These results indicate that while molecular H_2 is not required to obtain products, the presence of H_2 increases the conversion. The presence of H_2 also appears to enhance the yield of tar slightly.

Experiments similar to those reported in Table I were also carried out using $ZnCl_2$ as the catalyst. The only difference in these experiments was that the catalyst loading was roughly twenty-fold higher than that used with $AlCl_3$. In spite of this, products were not observed, indicating that $ZnCl_2$ is a significantly less active catalyst than $AlCl_3$.

The effects of phenolic hydroxyl groups on the cleavage of linkages between aromatic nuclei were studied using 2- and 4- phenylphenol and 2- and 4- hydroxydiphenylmethane. The reactions of these substrates were carried out in benzene solution since none of the reactants were soluble in cyclohexane. From the results shown in Table IV, it is apparent that 2-phenylphenol does not undergo cleavage of the aryl-aryl bond since phenol is not produced as one of the products. The only reaction observed to occur is isomerization to form 3-phenylphenol. Experiments conducted with 4-phenylphenol led to a

gelatinous mass insoluble in benzene. To analyze this material the solvent was first evaporated in a vacuum oven at 110°C. More than 97% of the original substrate weight was recovered by this means. Dissolution of this solid in pyridine and analysis by gas chromatography showed that the solid was almost entirely 4-phenylphenol. The only other product was a small amount of high molecular weight (200-250 MW) material. No evidence was found for either phenol or 3-phenylphenol.

Both 2- and 4- hydroxydiphenylmethane undergo substantial conversion in the presence of AlCl_3 . The conversion of 4-hydroxydiphenylmethane is identical to that for diphenylmethane (see Table II) but the conversion of 2-hydroxydiphenylmethane is 16% higher. The product distributions given in Table IV show large concentrations of phenol, indicating preferential cleavage of the alkyl-aryl bond between the hydroxyphenyl group and the methylene linkage. Some cleavage of the bond between the phenyl group and the methylene linkage also occurs, as evidenced by the formation of o- and p-cresol, but this process is much less extensive. The remaining products are principally diphenylmethane, toluene, and either the ortho or para isomer of the reactant, (e.g. 2-hydroxydiphenylmethane is converted to 4-hydroxydiphenylmethane). It is interesting to note that the amount of toluene produced from either isomer of hydroxydiphenylmethane is significantly less than that obtained from diphenylmethane (see Table II).

The reactions of hydroxydiphenylmethane were also investigated using ZnCl_2 as the catalyst. The results presented in Table V show that the substrate conversions are large and that 4-hydroxydiphenylmethane is more reactive than 2-hydroxydiphenylmethane. It is also evident that the activity of ZnCl_2 is substantially less than that of AlCl_3 , since nearly twenty times as much ZnCl_2 must be used to observe conversions on the same level as those obtained with AlCl_3 . Nevertheless, it is significant that hydroxydiphenylmethane reacts in the presence of ZnCl_2 while diphenylmethane is totally unreactive under comparable conditions. Both the nature and distribution of products obtained with ZnCl_2 are similar to those obtained with AlCl_3 . The only exception is the large concentration of isopropylbenzene obtained from 4-hydroxydiphenylmethane. The occurrence of this product in such high yield is unexpected and cannot be explained.

The influence of the structure of the aromatic nucleus present at the end of an aryl-aryl or aliphatic linkage was also investigated. For this purpose the reactivities of 1-phenylnaphthalene and 1-benzyl-naphthalene were compared with those of biphenyl and diphenylmethane, respectively. Table VI lists the products obtained when AlCl_3 and ZnCl_2 are used to catalyze the reactions of 1-phenylnaphthalene and 1-benzyl-naphthalene.

In the presence of AlCl_3 , 1-phenylnaphthalene primarily undergoes isomerization to form 2-phenylnaphthalene. The appearance of a very small concentration of naphthalene in the products indicates that cleavage of the aryl-aryl bond occurs but only to a limited degree. When ZnCl_2 is used as the catalyst, the extent of isomerization is reduced and no cleavage of the aryl-aryl bond can be detected.

The reaction of 1-benzyl-naphthalene in the presence of AlCl_3 produces mainly naphthalene and benzene. Both products are indicative of cleavage of the aliphatic linkage between the naphthyl and phenyl groups. The principal counterproducts observed in this case are methyl-naphthalene and toluene. Some isomerization also occurs since 2-benzyl-naphthalene is found in the products. When ZnCl_2 is used as the catalyst instead of AlCl_3 similar products are obtained. The primary difference is that the substrate conversion is less with ZnCl_2 .

DISCUSSION

Structure of the Active Catalyst

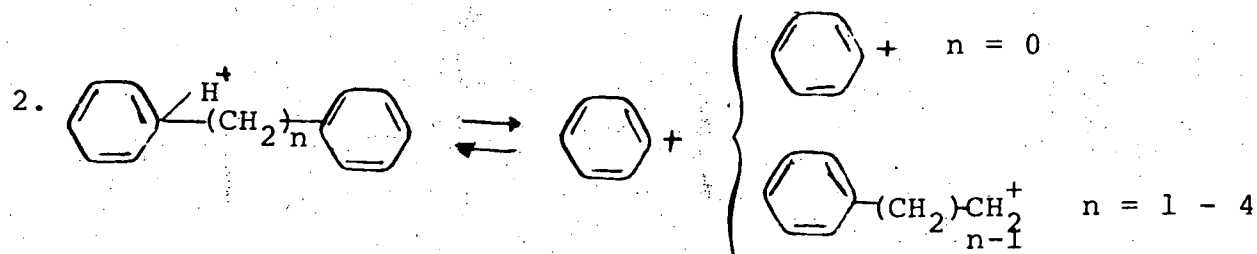
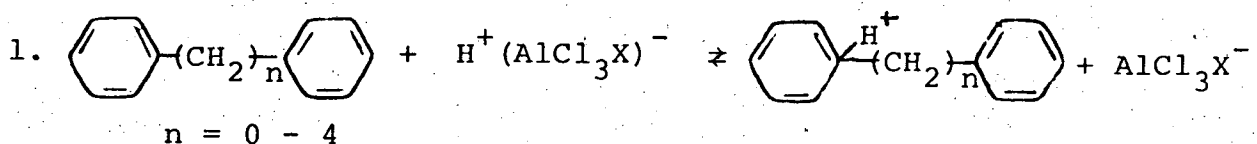
The active form of Lewis acid catalysts has been discussed extensively in the literature pertaining to hydrocarbon cracking and Friedel-Crafts chemistry (9-11). Evidence from many studies suggest that Lewis acids must first be converted to Brønsted acids, in order to be active. This conversion is envisioned to occur via a reaction of the Lewis acid with hydrogen halide, water, or an alcohol.

Consistent with this it is observed that anhydrous, freshly sublimed, AlCl_3 fails to initiate many Friedel-Crafts reactions without the addition of H_2O or HCl as promoters (9,11).

The exact nature of the Brønsted acids produced from AlCl_3 and ZnCl_2 are not known definitively and are a matter of debate. Several authors have suggested that the active form of AlCl_3 is $\text{H}^+\text{AlCl}_4^-$ while others suggest that the active species is $\text{H}^+(\text{AlCl}_3\text{OH})^-$ (8). In the case of ZnCl_2 , two active forms have been proposed $\text{H}^+(\text{ZnCl}_2\text{OH})^-$ (12) and $(\text{H}^+)_2[\text{ZnCl}_2(\text{OH})_2]^{2-}$ (10). In view of the uncertainty regarding the structure of the active catalyst, we have designated it as either $\text{H}^+(\text{AlCl}_3\text{X})^-$ or $\text{H}^+(\text{ZnCl}_2\text{X})^-$ for the purposes of subsequent discussion.

Cleavage of Aryl-Aryl and Alkyl-Aryl Bonds

The cleavage of aryl-aryl and alkyl-aryl bonds occurs via a two step process (13) as illustrated by reactions 1 and 2..



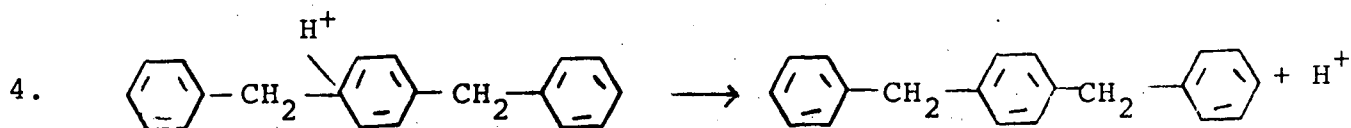
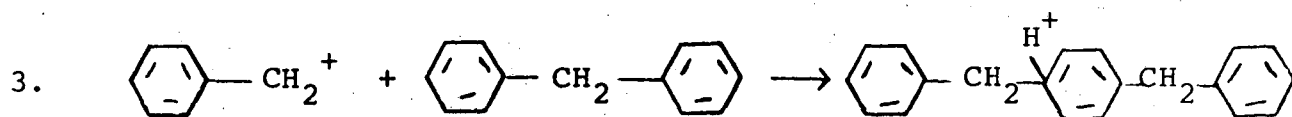
The rate limiting step in the overall process is protonation of the substrate (reaction 1) to form a benzenium ion (13,14). The extent to which reaction 1 proceeds to the right depends upon the Brønsted acidity of the active catalyst, as well as the Brønsted basicity of the reactant. The first of these effects is demonstrated by the relative activities of AlCl_3 and ZnCl_2 . Aluminum chloride forms a strong Brønsted acid and actively promotes the cleavage of alkyl-aryl bonds in diphenyl alkanes. On the other hand, ZnCl_2 forms a weaker Brønsted acid and is not active. By increasing the basicity of the substrate, the transfer of a proton from the catalyst to the substrate is enhanced. This effect will be discussed in greater detail below.

The stability of the carbonium ion formed in reaction 2 strongly influences the extent to which cleavage of the linkage between two aryl groups occurs. In the case of biphenyl, cleavage of the aryl-aryl bond must result in the formation of a phenyl carbonium ion. This cation is highly unstable because of the difficulty in delocalizing the positive charge. As a result, the reverse of reaction 2 occurs very rapidly and cleavage of the aryl-aryl bond takes place to only a limited extent. By contrast, cleavage of an alkyl-aryl bond produces a phenylalkyl carbonium which can be stabilized by distribution of the positive charge around the phenyl ring (15). The resulting resonance structures formed are illustrated in Fig. 1.

The phenylalkyl carbonium ions generated by the cleavage of alkyl-aryl bonds can react further by either electrophilic substitution or hydride abstraction. The first of these processes involves the attack of the carbonium ion on an aromatic nucleus and the subsequent release of a proton. One example of such a sequence is the reverse of reactions 1 and 2. In this instance, benzene acts as the aromatic nucleus, and the final product is the original reactant. The occurrence of this reaction sequence would explain the lower substrate conversions observed for the reactions of diphenylalkanes in benzene as opposed to cyclohexane solution (compare Tables I and II).

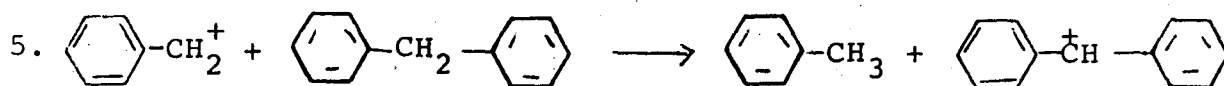
The formation of indan and teralin from diphenylpropane and diphenylbutane can also be explained by an electrophilic substitution reaction of a phenylalkyl carbonium ion. The alkyl portion of both the phenylpropyl and phenylbutyl carbonium ions is flexible enough for the free end of the alkyl group to approach the phenyl ring. When this occurs, an intramolecular reaction can take place which produces the resonance structures shown in Fig. 1. Subsequent deprotonation of these structures yields the final hydroaromatic products.

A third example of electrophilic substitution is given by reactions 3 and 4. In this instance the aromatic center being attacked is that of the reactant itself and the product formed has a higher molecular weight than the reactant.



The product produced in reaction 4 can react with additional ions to produce a yet higher molecular weight product. Continued repetition of steps 3 and 4 can lead to the formation of a polymer or tar.

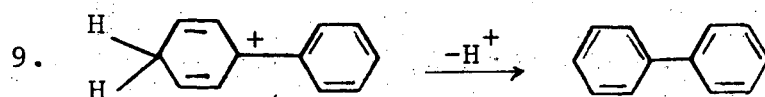
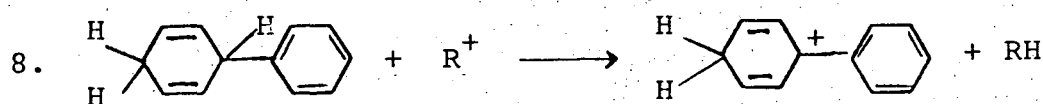
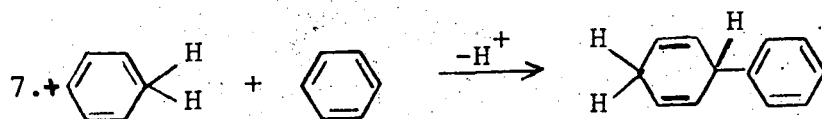
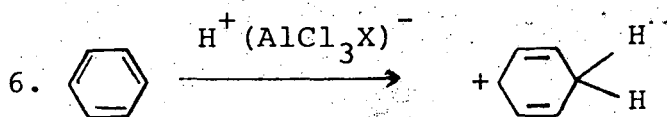
Hydride abstraction is envisioned to occur in parallel to electrophilic substitution and may involve as many as three sources of hydride ions. The first of these is the reactant itself. Reaction 5 exemplifies this process.



The diphenylmethyl carbonium ion produced in reaction 5 may in turn react via electrophilic substitution, thereby contributing to tar formation, or be restored to diphenyl methane by further hydride abstraction.

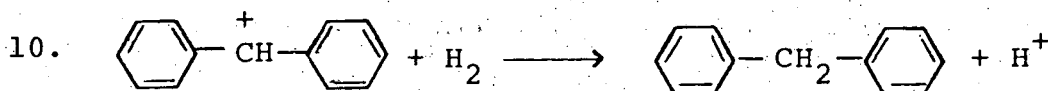
Products formed through Scholl condensations (9,10) can provide a second source of hydride ions. This process may involve any of the aromatic compounds present in solution and proceeds via the following mechanism (10), shown here

for the condensation of benzene. Hydride abstraction



occurs in reaction 8 and involves the adduct formed in reaction 7.

The third source of hydride ions is molecular H_2 , which can react with a carbonium ion in the manner illustrated by reaction 10.



The extent to which hydride abstraction from H_2 occurs depends on the structure of the carbonium ion. Thus, tertiary carbonium ions will react more readily than secondary carbonium ions, which in turn will react more readily than primary carbonium ions. By combining reaction 10 with reaction 5, one sees that a hydride shuttle can be set up.

Similar reaction pairs have been proposed to explain the ability of superacids to catalyze the hydrogenation of benzene in the presence of a tertiary hydride donor (16,17).

The results of the present experiments do not unambiguously establish the source of hydride ions required to form alkyl-benzene products. However, the fact that the presence or absence of H_2 has only a modest effect on the conversion of substrate to products (see Table III) indicates that only a part of the required hydride ions are supplied by H_2 and, hence, it must be concluded that the principle sources of hydride ions are the substrate itself and the tar or polymer formed by Scholl condensation.

It is apparent from the preceding discussion that the composition of final products is strongly influenced by the reactions of the carbonium ion generated upon cleavage of an alkyl-aryl bond in a diphenyl alkane. If as in the case of the phenylpropyl and phenylbutyl carbonium ions ring closure can be achieved through an intramolecular electrophilic substitution reaction, then a stable product is produced which is not readily cracked (18,19). For the shorter benzyl and phenylethyl carbonium ions ring closure is not possible and these ions react to form alkylbenzenes via hydride abstraction or tar via electrophilic substitution. The alkyl-benzene formed in the first of these processes is not stable and can dealkylate to produce benzene and a gaseous product (viz.

methane or ethylene) (9,10). As a result of these processes, only a fraction of the originally generated carbonium ions can be recovered as alkylbenzenes. This could explain why the concentrations of toluene and ethylbenzene observed in Table I are significantly smaller than the concentration of benzene.

Effects of Aromatic Substituents on the Cleavage of Aryl-Aryl and Alkyl-Aryl Bonds

The results presented in Tables IV and V clearly demonstrate that the substitution of a phenolic hydroxyl group on one of the phenyl rings of diphenylmethane facilitates the cleavage of the alkyl-aryl bond nearest to the substituted ring. These observations are in good agreement with the work of Tsuge and Tashiro (20) who studied the cleavage of a series of alkyl-substituted diphenylmethanes under the influence of AlCl_3 . It was observed that the reactant conversion was increased by the addition of alkyl groups to one of the phenyl rings, and that as the relative basicity of the alkyl group increased so did the ease of cleavage. The facilitation of alkyl-aryl bond cleavage, which results from either a hydroxyl or an alkyl substituent on the phenyl ring, can be ascribed to a stabilization of the benzenium ion formed upon protonation of the substrate (reaction 1). Such stabilization is enhanced by the presence of a nucleophilic group on the phenyl ring, which promotes the transfer of electronic charge to compensate for the positive charge introduced by the proton.

A further consequence of the more basic character of a hydroxyphenyl group is its ability to accept a proton from weaker acids. Thus, the observation that $ZnCl_2$ will catalyze the cleavage of hydroxydiphenylmethane but not diphenyl can be ascribed to the higher basicity of the former reactant.

The reactions of hydroxydiphenylmethane, following protonation, are envisioned to be very similar to those of diphenylmethane. In each case the benzenium ion dissociates to form a benzyl carbonium ion and phenol. The benzyl carbonium ion may then form toluene and diphenylmethane, if benzene is used as the solvent. In addition, isomers of the original substrate can be formed by reaction of the carbonium ion with phenol.

The absence of phenol from the products formed from either 2- or 4-phenylphenol indicates that phenolic hydroxyl groups do not promote the cleavage of an aryl-aryl bond. This observation suggests that the observed isomerization of 2-phenylphenol to 3-phenylphenol occurs via an intramolecular reaction, a conclusion which is in agreement with the results of previous investigations (21,22). It should also be noted that the failure of 4-phenylphenol to undergo isomerization is in agreement with the work of Hay (21).

Substitution of a phenyl group by a naphthyl group also enhances the cleavage of alkyl-aryl bonds. Comparison of Tables I and VI shows that when $AlCl_3$ is used as the catalyst the conversion of 1-benzyl-naphthalene is higher

than that of diphenylmethane. Table VI shows further that $ZnCl_2$ will also catalyze the reaction of 1-benzyl-naphthalene. Both of these observations can be explained by the fact that the naphthyl group is more basic than the phenyl group and hence will protonate more easily. Consistent with this we note that in the presence of $ZnCl_2$ the concentration of naphthalene in the products is nearly fourfold higher than that of benzene.

It is interesting to see that while the substitution of a phenyl group by a hydroxyphenyl group did not promote cleavage of an aryl-aryl bond, the substitution by a naphthyl group apparently does. Thus Table VI shows a small concentration of naphthalene following the reaction of 1-phenyl-naphthalene. This product could only arise through a cleavage of the phenyl-naphthyl bond. Nevertheless it is quite clear that the extent of this reaction is small. The isomerization of 1-phenyl-naphthalene to 2-phenyl-naphthalene does not constitute further evidence for aryl-aryl bond cleavage since a number of previous studies (22-24) have shown that this reaction proceeds via an intramolecular process.

CONCLUSIONS

The present studies have demonstrated that $ZnCl_2$ and $AlCl_3$ will catalyze the cleavage of aliphatic linkages between aromatic nuclei but will not significantly promote the cleavage of direct aryl-aryl bonds between such nuclei. Cleavage of aliphatic linkages always occurs at an alkyl-

aryl bond, and the rate of this process depends on the Brønsted acidity of the active catalyst [e.g. $H^+(ZnCl_2X)^-$ or $H^+(AlCl_3X)^-$] and the Brønsted basicity of the aromatic portions of the reactant. Thus, $AlCl_3$ is significantly more active than $ZnCl_2$, and reactants containing hydroxyphenyl or naphthyl groups are more reactive than those containing phenyl groups.

The distribution of final products is strongly affected by the reactions of the aryl-alkyl carbonium ion formed upon cleavage of an alkyl-aryl bond. If the alkyl portion of the carbonium ion contains three or more carbon atoms, the ion preferentially undergoes an intramolecular reaction to form a hydroaromatic product. When only one or two carbon atoms are present in the alkyl portion of the carbonium ion, the ion reacts via either hydride abstraction or electrophilic substitution. The first of these processes produces alkyl-aromatic product, which may in turn undergo dealkylation. The reactant and products produced by Scholl condensation act as the principal sources of hydride ions. Molecular H_2 also contributes hydride ions but to a lesser extent. The reaction of carbonium ions by electrophilic substitution leads either to the regeneration of the initial reactant or to the formation of high molecular weight tars.

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LITERATURE REFERENCES

1. L. A. Heredy and M. B. Neuworth, *Fuel* 41, 221 (1962).
2. L. A. Heredy, A. E. Kostyo, and M. B. Neuworth, *Fuel* 44, 125 (1965).
3. L. A. Heredy, A. E. Kostyo, and M. B. Neuworth, *Adv. in Chem. Ser.* 55, 493 (1966).
4. J. A. Franz, J. R. Morey, G. L. Tingey, W. E. Skievs, R. J. Pugmire and D. M. Grant, *Fuel* 56, 366 (1977).
5. N. C. Deno, B. A. Greigger, L. A. Messer, M. D. Meyer, and S. G. Stroud, *Tetrahedron Lett.*, 1703 (1977).
6. N. C. Deno, B. A. Greigger, S. G. Stroud, *Fuel* 57, 455 (1978).
7. J. L. Huston, R. G. Scott, and M. H. Studier, *Fuel* 55, 281 (1976).
8. R. Hayatsu, R. G. Scott, L. R. Moore, and M. H. Studier, *Nature* 257, 378 (1975).
9. C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry", Reinhold Publishing Corp., New York, 1941.
10. G. A. Olah, "Friedel-Crafts Chemistry", John Wiley & Sons, New York, 1973.
11. G. A. Olah, ed., "Friedel-Crafts and Related Reactions", Vol. 1, John Wiley & Sons, New York, 1963.
12. C. W. Zielke, R. T. Struck, J. M. Evans, C. P. Constanza,

- and E. Gorin, I&EC Proc. Des. and Dev. 5, 151 (1966).
13. R. T. Morrison and R. N. Boyd, "Organic Chemistry", 3rd ed., Allyn and Bacon, Boston, 1973.
 14. G. A. Olah, J. S. Staral, G. Asencio, G. Liang, D. A. Forsyth, G. D. Mateescu, J.A.C.S. 100, 6299 (1978).
 15. J. March, "Advanced Organic Chemistry: Reaction, Mechanisms, and Structure", McGraw Hill, New York, 1968.
 16. M. Siskin, J.A.C.S. 95, 3641 (1974).
 17. J. Wristers, J.A.C.S. 97, 4312 (1975).
 18. V. V. Korshak and G. S. Kolesnikov, Doklady. Akad. Nauk SSSR 76, 69 (1951).
 19. S. S. Salim and A. T. Bell, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, CA, unpublished results.
 20. O. Tsuge and M. Tashiro, Bull. Chem. Soc. Japan 38, 184 (1965).
 21. A. S. Hay, J. Org. Chem. 30, 3577 (1965).
 22. G. A. Olah and M. W. Meyer, J. Org. Chem. 27, 3682 (1962).
 23. O. M. Nefedov and M. Shih, Neftekhimiya 3, 48 (1963).
 24. G. A. Olah and J. A. Olah, J. A. C. S. 98, 1839 (1976).

TABLE I

Cleavage of Aliphatic Bridges between Phenyl RingsReaction Conditions

T = 325°C
 P = 1000 psig H₂ @ 325°C
 t = 90 min. @ 325°C
 ω = 1250 RPM

Substrate = 0.0768 mole (Runs 48, 49, 50, 51)
 = 0.0095 mole (Run 41)
 Cyclohexane = 61.5 gm. (0.787 mole)
 AlCl₃ = 0.70 gm. (Runs 48,49,50,51,B-19)
 = 0.09 gm. (Run 41)

Run No.	48	49	50	51	41	B-19
Substrate	Biphenyl	Diphenylmethane	Bibenzyl	1,3-Diphenylpropane	1,4-Diphenylbutane	No Substrate
Substrate/AlCl ₃ Mole Ratio	14.1	14.7	14.7	14.7	12.7	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Light Aliphatics	4.28	0.14	0.45	0.39	Trace	3.60
Methylcyclopentane	33.76	1.41	9.52	8.17	0.44	34.62
Cyclohexane	51.59	86.34	80.62	77.60	97.83	58.98
Methylcyclohexane	1.49	---	0.13	0.15	---	1.88
Benzene	0.86	8.33	5.74	7.31	0.66	0.29
Ethylcyclohexane	0.14	---	---	---	---	0.23
Toluene	0.17	1.75	0.25	0.14	---	---
Ethylbenzene	0.16	0.16	1.14	0.18	---	---
Isopropylbenzene	---	0.06	Trace	Trace	---	---
n-Propylbenzene	---	---	Trace	0.09	---	---
n-Butylbenzene	---	---	0.03	---	---	---
Indan	---	---	---	4.70	---	---
Tetralin	---	---	---	---	0.70	---
Dicyclohexyl	---	0.02	Trace	0.05	---	---
Dicyclohexylmethane	---	0.17	Trace	---	---	---
Cyclohexylbenzene	---	0.11	Trace	---	---	---
Biphenyl	6.89	---	---	---	---	---
Diphenylmethane	---	1.37	---	---	---	---
Bibenzyl	---	---	1.80	---	---	---
1,3-Diphenylpropane	---	---	---	1.14	---	---
1,4-Diphenylbutane	---	---	---	---	0.37	---
Heavy Unknowns	0.77	0.14	0.33	---	---	0.41
Reactant Conversion (%)	32	82	76	83	68	---
Tar (wt %)	13	16	11	5	0	---

TABLE II

Cleavage of Aliphatic Bridges between Phen-1 RingsReaction Conditions

T = 325°C
 P = 1000 psig H₂ @ 325°C
 t = 90 min. @ 325°C
 ω = 1250 RPM

Reactant = 0.0768 mole (Runs 34, 31, 27, 35)
 = 0.00951 mole (Run 42)
 Benzene = 61.5 gm. (0.787 mole)
 AlCl₃ = 0.70 gm (Runs 34, 31, 27, 35, B-20)
 = 0.09 gm. (Run 42)

Run No.	48	31	27	35	42	B-20
Substrate	Biphenyl	Diphenylmethane	Bibenzyl	1,3-Diphenylpropane	1,4-Diphenylbutane	No Substrate
Substrate/AlCl ₃ Mole Ratio	13.7	13.7	14.5	14.7	14.7	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Methylcyclopentane	---	Trace	0.08	Trace	---	Trace
Cyclohexane	Trace	Trace	0.27	---	0.04	Trace
Benzene	90.25	95.84	92.56	91.99	98.90	99.41
Toluene	---	2.14	0.86	0.31	---	0.19
Ethylbenzene	0.05	0.12	2.72	0.55	---	0.23
Isopropylbenzene	0.13	0.03	0.10	0.26	---	0.08
n-Propylbenzene	0.05	Trace	0.07	0.20	---	0.10
n-Butylbenzene	0.04	Trace	0.01	---	---	---
Indan	---	---	---	4.62	---	---
Tetralin	---	---	---	---	0.10	---
Dicyclohexyl	---	Trace	0.05	0.06	---	---
Cyclohexylbenzene	---	Trace	0.01	---	---	---
Biphenyl	9.48	---	Trace	---	---	Trace
Diphenylmethane	---	1.85	0.08	0.08	---	---
Bibenzyl	---	---	3.02	0.07	---	Trace
1,3-Diphenylpropane	---	---	---	1.81	---	---
1,4-Diphenylbutane	---	---	---	---	0.97	---
Heavy Unknowns	---	0.02	0.17	0.06	---	---
Reactant Conversion (%)	4	74	58	73	17	---
Tar (wt %)	0	17	13	3	0	---

Table III

Cleavage of Aliphatic Bridges between Phenyl Rings Under N₂ AtmosphereReaction Conditions

T = 325°C
 P = 1000 psig H₂ or N₂ @ 325°C
 t = 90 min. @ 325°C
 ω = 1250 RPM

Reactant = 0.0768 mole
 Benzene = 61.5 gm (0.787 mole)
 AlCl₃ = 0.70 gm (0.0052 mole)

Run No	54	31	56	35
Substrate	Diphenylmethane	Diphenylmethane	1,3-Diphenylpropane	1,3-Diphenylpropane
Atmosphere	Nitrogen	Hydrogen	Nitrogen	Hydrogen
Substrate/AlCl ₃ Mole Ratio	14.3	13.7	14.7	14.7
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Cyclohexane	Trace	Trace	Trace	---
Benzene	94.68	95.84	92.11	91.99
Toluene	1.62	2.14	0.15	0.31
Ethylbenzene	0.08	0.12	0.29	0.55
Isopropylbenzene	0.20	0.03	0.13	0.26
n-Propylbenzene	---	Trace	0.12	0.20
Indan	---	---	3.98	4.62
Phenol	---	---	---	---
o-Cresol	---	---	---	---
p-Cresol	---	---	---	---
Diphenylmethane	3.22	1.85	0.05	0.08
Bibenzene	0.02	---	0.04	0.07
1,3-Diphenylpropane	---	---	3.10	1.81
2-Hydroxydiphenylmethane	---	---	---	---
4-Hydroxydiphenylmethane	---	---	---	---
Heavy Unknowns	---	0.02	0.05	0.06
Reactant Conversion (%)	57	74	55	73
Tar (wt %)	12	17	2	3

Table IV

Cleavage of Hydroxylated Diphenylmethane CompoundsReaction Conditions

T = 325°C
 P = 1000 psig H₂ @ 325°C
 t = 90 min. @ 325°C
 ω = 1250 RPM

Reactant = 0.0768 mole
 Benzene = 61.5 gm. (0.787 mole)
 AlCl₃ = 0.70 gm. (0.0052 mole)

Run No.	39	44	30	40
Substrate	2-Phenylphenol	4-Phenylphenol	2-Hydroxy- diphenylmethane	4-Hydroxy- diphenylmethane
Substrate/AlCl ₃ Mole Ratio	14.7	14.7	14.7	14.5
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Benzene	93.19	Reaction	94.30	93.35
Toluene	---	Products	0.12	0.16
Ethylbenzene	---	Not	---	---
Isopropylbenzene	---	Soluble	---	---
Phenol	---	in	3.27	3.07
o-Cresol	---	Benzene	0.23	Trace
p-Cresol	---		0.05	0.10
Diphenylmethane	---		0.73	0.58
Bibenzyl	---		0.02	---
2-Phenylphenol	5.43		---	---
3-Phenylphenol	1.39		---	---
4-Phenylphenol	Trace		---	---
2-Hydroxydiphenylmethane	---		0.83	0.81
4-Hydroxydiphenylmethane	---		0.44	1.93
Heavy Unknown	---		---	---
Reactant Conversion (%)	38	---	90	74

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Table V

Cleavage of Hydroxylated Diphenylmethane CompoundsReaction Conditions

T = 325°C

P = 1000 psig H₂ @ 325°C

t = 90 min. @ 325°C

ω = 1250 RPM

Reactant = 0.0275 mole

Benzene = 61.5 gm. (0.787 mole), Runs 46, 54, B-22

Cyclohexane = 54.5 gm. (0.648 mole), Run 45

ZnCl₂ = 5.14 gm. (0.0377 mole)

Run No	46	53
Substrate	2-Hydroxy- diphenylmethane	4-Hydroxy- diphenylmethane
Substrate/ZnCl ₂ Mole Ratio	0.75	0.75
<u>Product</u>		
Cyclohexane	Trace	Trace
Benzene	97.72	96.55
Toluene	0.11	0.11
Ethylbenzene	0.03	---
Isopropylbenzene	---	0.52
n-Propylbenzene	---	0.04
Phenol	0.69	1.35
p-Cresol	---	0.05
Diphenylmethane	0.22	0.70
2-Hydroxydiphenylmethane	1.23	0.29
4-Hydroxydiphenylmethane	---	0.39
Reactant Conversion (%)	63	86

Table VI

Cleavage of Aliphatic Bridges Between Naphthyl-Phenyl Nuclei - Comparison of CatalystsReaction Conditions

T = 325°C
 P = 1000 psig H₂ @ 325°C
 t = 90 min. @ 325°C
 ω = 1250 RPM

Reactant = 0.0149 mole (Runs 43, 52)
 = 0.0201 mole (Run 60)
 = 0.0276 mole (Run 61)
 Cyclohexane = 0.787 mole (Runs 43, 52)
 = 0.470 mole (Run 60)
 = 0.648 mole (Run 61)
 AlCl₃ = 0.0011 mole (Runs 43, 52)
 ZnCl₂ = 0.028 mole (Runs 60, 61)
 = 0.041 mole (Run 61)

Run No.	43	61	52	60
Substrate	1-Phenylnaphthalene	1-Phenylnaphthalene	1-Benzylnaphthalene	1-Benxylnaphthalene
Catalyst	AlCl ₃	ZnCl ₂	AlCl ₃	ZnCl ₂
Substrate/Catalyst Mole Ratio	12.7	0.73	12.7	0.73
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Light Aliphatics	Trace	0.10	0.04	0.20
Methylcyclopentane	0.80	0.18	0.19	0.41
Cyclohexane	98.14	96.15	97.97	96.80
Benzene	0.07	---	0.55	0.15
Toluene	---	---	0.99	0.11
Naphthalene	0.01	---	0.82	0.38
2-Methylnaphthalene	---	---	0.07	Trace
1-Methylnaphthalene	---	---	0.01	Trace
Diphenylmethane	---	---	0.12	Trace
1-Phenylnaphthalene	0.10	3.06	---	---
Unknown	0.03	0.04	---	---
2-Phenylnaphthalene	0.83	0.48	---	---
1-Benzylnaphthalene	---	---	0.01	1.63
2-Benzylnaphthalene	---	---	0.13	0.32
Heavy Unknowns	---	---	---	---
Reactant Conversion (%)	94	20	99	41

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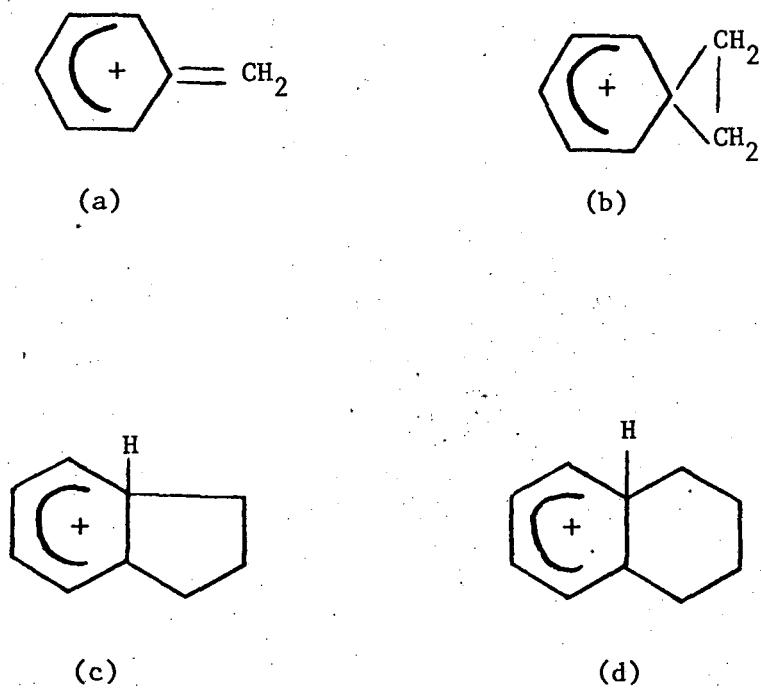


Fig. 1 Resonance stabilized structures of carbonium ions formed from (a) diphenylmethane, (b) bibenzyl, (c) 1,4-diphenylpropane, and (d) 1,4-diphenylbutane.

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TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720