A New Reaction That Occurs in the Hydrocracking of Certain Aromatic Hydrocarbons

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The hydrocracking of hexamethylbenzene over a nickel sulfide on silica–alumina catalyst results in an unusual product distribution. Principal products are lower molecular weight methylbenzenes and light isoparaffins, particularly isobutane. A reaction occurs that, in its apparent effect, peels or pares methyl groups from the aromatic ring and eliminates them as isoparaffins with essentially no loss of rings. This reaction has been named the paring reaction. A mechanism is proposed that involves changes in ring size by isomerization to produce side chain growth. The larger alkyl side chains are then selectively eliminated by cracking to produce isoparaffins.

Introduction

The cracking of alkyl aromatics at 400° to 550° over solid acidic cracking catalysts, such as silica–alumina, has been reported previously.[1,2] Aromatic hydrocarbons with alkyl substituents of three or more carbon atoms react rapidly by simple dealkylation. Those containing only methyl and ethyl side chains react much more slowly, but again the principal mode of cracking is reported to be simple dealkylation.

When methylbenzenes containing four or more methyl groups are hydrocracked at 300° to 350° over a nickel sulfide on silica–alumina catalyst, an unexpected product distribution is obtained, and an unusual, new reaction is observed. This paper presents the results obtained with hexamethylbenzene and outlines a proposed mechanism for the new reaction.

Additional papers on the behavior of other types of hydrocarbons under these hydrocracking conditions will be published later.

Experimental

Equipment and Chemicals.—The experiments were performed in a continuous flow, fixed bed, microcatalytic unit. The 6 ml. of catalyst was supported inside a 0.79-cm. i.d. stainless steel tube 85 cm. in length, which was surrounded by a heavy-walled steel block inside an electrically heated oven. Catalyst temperatures were measured by a chromel-alumel thermocouple located on the reactor wall at the central portion of the catalyst bed. A Celectray controller was used to control the temperature.

Hydrocarbon feed rates were measured by a means of a Microfeeder pump (Proportioneers, Inc.). The hydrogen rate was measured by oil displacement in a reservoir.

The hexamethylbenzene used was Eastman Kodak white label without further purification. No impurities were detectable by gas chromatography. The hydrogen used was more than 99.5 mole per cent. pure.

The catalyst consisted of nickel sulfide (3.6% Ni) on commercial silica–alumina (10% alumina). It was prepared by impregnating the support with a solution of nickel nitrate, drying the impregnated support for 10 hours at 120°, followed by 10 hours at 540°. The nickel oxide in the catalyst was then reduced with hydrogen at 300°. The nickel was then sulfided by treating the catalyst with 7% H_2S in hydrogen.

Analysis.—Liquid products were analyzed by gas chromatography using a Perkin–Elmer model 154-B with either a dioctyl terephthalate or a silicone column. The accuracy of the method was confirmed by analysis of known mixtures of pure hydrocarbons. The gaseous portion of the product was analyzed by mass spectrometry.

The aromatic product was separated from the paraffin-naphthene portion on a silica gel column; the separated fractions were analyzed by gas chromatography. In addition, the paraffin-naphthene portion was examined in the mass spectrometer to obtain paraffin-to-naphthene ratios

and the amount of naphthenes of each carbon number. Each reported analysis is a composite of all analyses obtained.

Results

With Nickel Sulfide on Silica–Alumina.—The hydrocracking of hexamethylbenzene with nickel sulfide on silica–alumina results in a most unusual product distribution. Figure 1 shows the moles of aromatics, naphthenes and paraffins of each carbon number in the product from 100 moles of hexamethylbenzene in a typical experiment. Table I presents the conditions and product analyses for four runs with hexamethylbenzene.

The product distribution is unusual in that: 1. Each type of compound is produced in a narrow molecular weight distribution with the maximum amount for each type of compound at a different carbon number. The paraffins have a much lower molecular weight than the hexamethylbenzene, with butanes being by far the predominant species. Naphthenes are concentrated in the C_7–C_9 range, and aromatics are principally C_{10} and C_{11}. 2. Very little ring rupture occurs. The yield of cyclic compounds in the product is in excess of 90 mole per cent. of the hexamethylbenzene reacting. 3. The small amount of methane and the significant yield of light isoparaffins in the product indicate that the production of lower molecular weight methylbenzenes and naphthenes is not a simple process of demethanation.

A reaction occurs that, in its apparent effect, peels or pares methyl groups from aromatic and naphthenic rings and eliminates them as light isoparaffins, mainly isobutane, in such a way as to conserve rings. For convenience, we have named this the *paring reaction*. The magnitude of this reaction is illustrated graphically in Fig. 2, in which the number of moles of carbon found in the paraffinic products for each 100 moles of hexamethylbenzene is compared with the number available from the hexamethylbenzene that reacted by ring cleavage. In each case, there are many more moles of carbon in the paraffinic product than can be accounted for by ring cleavage. The remaining paraffins (namely those not accounted for by ring cleavage) must have been formed from methyl groups removed from the ring compounds that remain. In all four experiments shown in Fig. 2, some of these methyl groups appear in paraffins as large as the pentanes, even if it is assumed that the highest molecular weight paraffins were formed by ring cleavage. In two of the runs, the methyl groups removed by the paring reaction appear in paraffins having at least six carbons. The ex-

(1) B. S. Greensfelder, H. H. Voge and G. M. Good, *Ind. Eng. Chem.*, **37**, 1168 (1945); **41**, 2573 (1949).

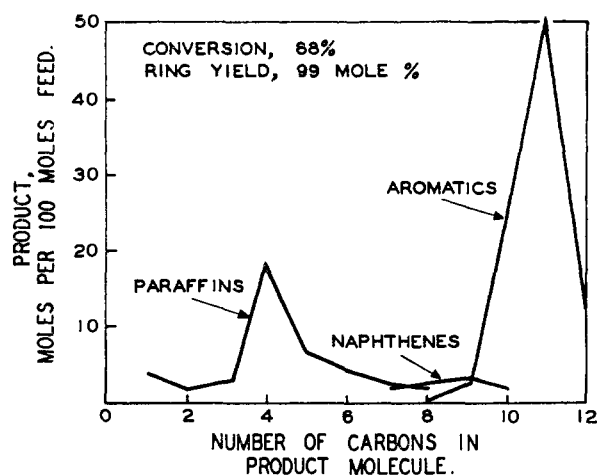(2) H. F. Rase and R. S. Kirk, *Chem. Eng. Prog.*, **50**, 35 (1954).

Fig. 1.—Hydrocracking of hexamethylbenzene, product distribution *vs.* carbon number. Conditions: 349°; 13.6 atm.; moles H_2/mole feed, 1.86; volumes of liquid feed per volume of catalyst per hour, 8.0.

tent of the paring reaction per 100 moles of hexamethylbenzene is measured by the number of moles of carbon in the paraffinic product (excluding methane) minus the number of moles of carbon in the ring compounds that underwent ring cleavage.

Another product characteristic is the high ratio of singly branched paraffins to straight-chain paraffins (iso-to-normal ratio). This ratio is far in excess of the thermodynamic equilibrium value[3] and increases with decreasing reaction temperature.

EFFECT OF TEMPERATURE ON RATIO OF ISO-TO-NORMAL PARAFFINS FROM HEXAMETHYLBENZENE HYDROCRACKING

Run number	D	Equilibrium ratio (one branch)	B	Equilibrium ratio (one branch)
Reacn. temp. (final), °C.	317	317	377	377
Iso-to-normal ratio				
Butanes	20	0.9	6	0.8
Pentanes	50	2.6	9	2.3
Hexanes	30	2.5	14	2.3

Another reaction that occurs is the transfer of methyl groups from one aromatic ring to another. This reaction is well known in acid-catalyzed reactions of methylbenzenes and is usually referred to as disproportionation. For example, two xylene molecules can disproportionate to form toluene and a trimethylbenzene. This reaction cannot occur in the usual way for two hexamethylbenzene molecules. (The possibility of the formation of an intermediate 1,1,2,3,4,5,6-heptamethylbenzenonium ion, which is analogous to a disproportionation product, will be discussed later.) However, once lower molecular weight methylbenzenes are formed, the conventional type of methyl transfer occurs rapidly. A comparison of the distribution of methylbenzenes in the products with the calculated equilibrium composition[4] show that the methyl-

(3) E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 403 (1945).

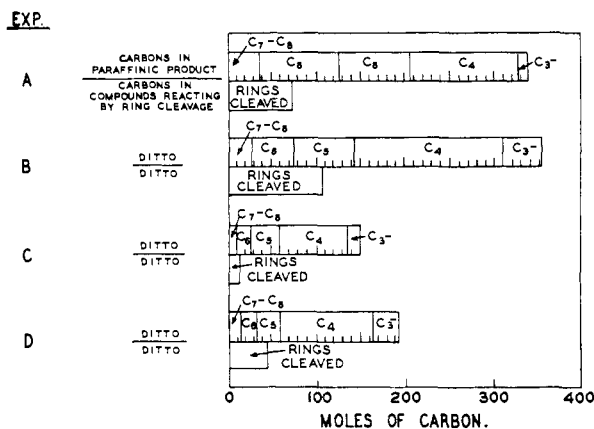(4) C. J. Egan, *J. Chem. Eng. Data*, **5**, 298 (1960).

Fig. 2.—Hydrocracking of hexamethylbenzene; comparison of moles of carbon in light paraffins produced with moles of carbon in compounds reacting by ring cleavage; basis: 100 moles of feed.

benzenes in the products approach the equilibrium distribution. The rapidity of the methyl transfer reaction was also confirmed directly by passing a mixture of *o*-xylene and hexamethylbenzene under the same conditions over the silica–alumina support alone (experiment F, Table I).

Isomerization of the methylbenzenes occurs rapidly, and the product contains each isomer in approximately the equilibrium concentration.[4]

Hydrogenation–dehydrogenation equilibria are not established between the naphthenes and aromatics in the products. An exact calculation of the equilibria is complicated by the large number of naphthene isomers for which no free energy data are available. A comparison of different experiments, however, shows that the ratio of naphthenes/aromatics does not vary as the cube of the hydrogen partial pressure. This indicates that the rate of hydrogenation and dehydrogenation is slow, and equilibrium is not attained.

With Silica–Alumina Support.—The paring reaction occurs also on the silica–alumina support in the absence of nickel sulfide and hydrogen (experiment E, Table I). Under these conditions, the silica–alumina is deactivated rapidly, and the observed reaction rates are much lower. However, the product distribution, shown in Fig. 3, is essentially the same except that no naphthenes are formed. These data show that the paring reaction of aromatics can occur on a strongly acidic catalyst. An important function of the nickel sulfide and hydrogen is to maintain catalyst activity by preventing buildup of carbonaceous deposits on the catalyst.

Mechanism.—To explain the principal products of the paring reaction, we propose a mechanism involving changes in ring size by isomerization on the acid sites of the catalyst until a side chain of four or more carbon atoms is formed. This side chain then cracks off at the ring to form a lower molecular weight aromatic and either isobutane, isopentane or isohexane. One route of such an isomerization is side chain growth by repeated contraction to a five-membered ring followed by expansion to a six-membered ring. A possible se-

TABLE I

PROCESS CONDITIONS AND PRODUCT DISTRIBUTION

| Hydrocarbons used | Hexamethylbenzene (HMB) | | | | | Mixture: hexamethylbenzene (71.8 mole %) and o-xylene (28.2 mole %) |
	Nickel sulfide on silica–alumina				Silica–alumina	Silica–alumina
Catalyst						
Experiment number	A	B	C	D	E[b]	F
Av. catalyst temp., °C.	350	362	349	317	344	345
Pressure, atm.	41	82	13.6	82	13.6	82
LHSV[a]	2.0	8.0	8.0	8.0	2.0	8.0
Moles H_2/mole HMB	5.6	10.5	1.86	12.1	(N_2/HMB = 0.77)	10.2
Conversion, %	100	97.8	88.0	81.2	84.7	82.0
Product in moles/100 moles of hexamethylbenzene (based on 100% recov. of prod.)						
Methane	3.6	10.3	3.8	7.6	0.2	0.2
Ethane	1.4	4.0	1.5	3.4	0.7	.08
Propane	1.5	7.7	2.8	5.4	5.3	.7
Isobutane	26.0	37.3	13.4	24.6	10.1	2.0
n-Butane	5.3	5.9	5.2	1.3	1.6	0.3
Isopentane	14.8	11.8	6.2	5.1	3.4	.6
n-Pentane	0.6	1.4	0.4	0.1	0.1	.02
Isohexanes	12.1	7.0	2.6	2.9	1.3	.5
n-Hexane	2.5	0.5	0.15	0.1	0.06	.04
C_7-Paraffins	3.7	2.3	.9	.9	.1	.02
C_8-Paraffins	1.4	1.6	.4	.9	.2	.1
C_9-Paraffins	...	...	...	...	.1	...
Methylcyclopentane	5.5	3.7	0.5	0.9	...	.2
Cyclohexane	0.7	0.5	0.1	0.1	...	...
C_7-Naphthenes	9.8	8.8	1.3	2.3	...	...
C_8-Naphthenes	11.5	15.7	2.4	8.0	...	...
C_9-Naphthenes	6.2	8.4	3.2	7.0	...	...
C_{10}-Naphthenes	1.6	2.2	1.4	2.5	...	...
C_{11}-Naphthenes	0.6	0.8	0.2	0.5	...	...
C_{12}-Naphthenes	...	0.1	Trace	Trace	...	...
Toluene	...	...	...	...	...	0.2
Xylenes	0.8	0.2	0.5	0.9	1.4	1.3
Mesitylene	2.3	0.9	0.4	.4	1.9	1.1
Pseudocumene	5.4	3.4	1.4	.5	4.4	2.9
Hemimellitene	0.8	0.7	0.3	...	0.8	0.4
Durene, isodurene	29.4	21.2	21.2	9.0	24.0	24.5
Prehnitene	3.8	2.7	2.7	0.9	3.7	3.1
Other C_{10}-aromatics	...	...	...	...	0.4	0.1
Pentamethylbenzene	15.5	19.3	50.5	43.0	46.5	45.7
Other C_{11}-aromatics	0.3	0.5	0.6	0.5	1.8	0.6
Hexamethylbenzene	...	2.2	12.0	18.8	15.3	18.0
Other C_{12}-aromatics	...	...	0.4	0.3	2.1	0.8
C_{13}-aromatics	...	...	...	...	0.5	.06
Olefins	...	...	...	...	Trace	.2
Summary, total moles						
Paraffins	72.9	89.8	37.4	52.3	23.2	4.8
Naphthenes	35.9	40.2	9.1	21.3	...	...
Aromatics	58.3	51.1	90.0	74.3	102.8[c]	99.0
Total rings	94.2	91.3	99.1	95.6	102.8	99.0
Ring yield, %	94	91	99	95	103[c]	99

[a] Volumes of liquid at 220° per volume of catalyst per hour. [b] Run was made in a nitrogen atmosphere. [c] Believed to be within experimental error of 100% ring yield.

quence of reactions is shown below. For convenience, all carbonium ion intermediates are shown in classical forms; only resonance forms and 1,2-shifts are employed.

The cyclopentadienyl cationic intermediates postulated in this mechanism are similar to that proposed by Condon[5] as an intermediate in the formation of ethylbenzene from xylenes. There is strong supporting evidence for the existence of such an intermediate in the work of de Vries[6] who has

(5) F. E. Condon in Emmett's "Catalysis," Vol. VI, Reinhold Publishing Corp., New York, N. Y., 1958, p. 111.
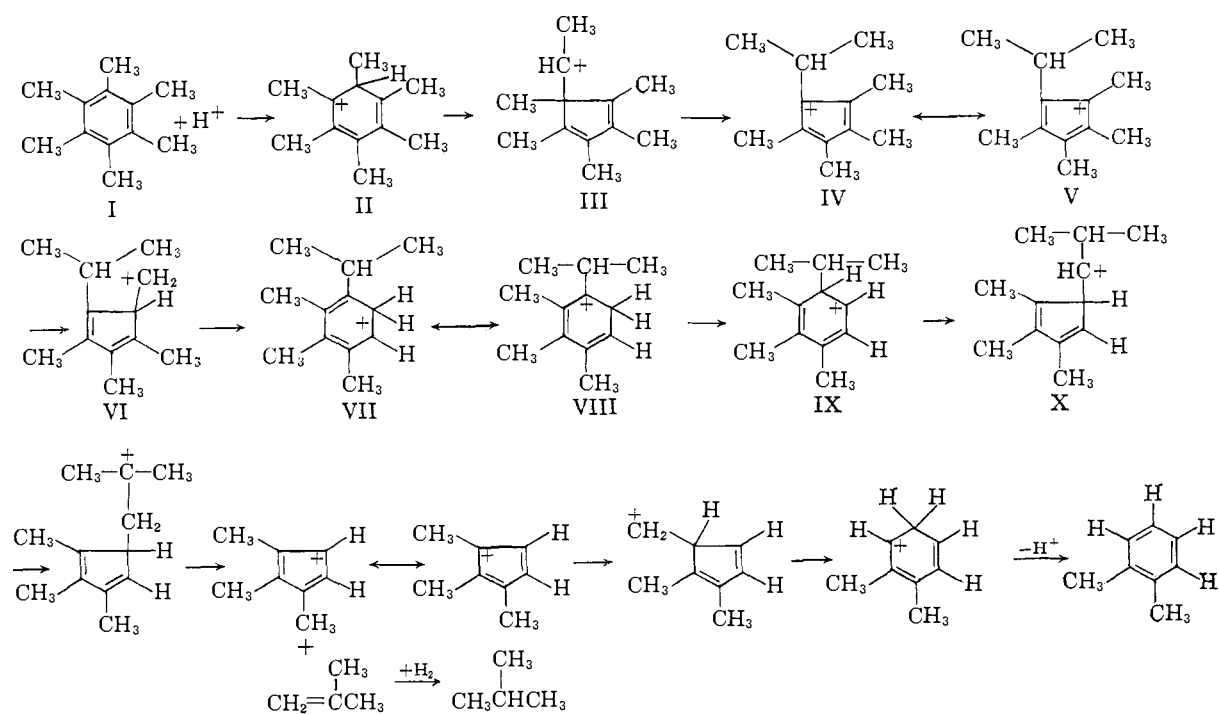
found that stable cyclopentadienyl cations can be prepared from pentamethylcyclopentadiene and from hexamethylcyclopentadiene by hydride ion abstraction, and that hexamethylcyclopentadienyl cation expands in the presence of acid and heat to form pentamethylbenzene. Winstein and Battiste[7] have shown that the expansion of hexamethylcyclopentadienyl cation to pentamethylbenzene occurs also during solvolysis under acidic conditions. Their researches indicate that intermediates such as III and VI, are more precisely represented by a nonclassical description.[8] As more information on the specific nature of these ions becomes available, it may be desirable to represent ions like IV and V, as well as those like III and VI, with non-classical structures.

It was suggested by Miller[9] that side chain growth might occur also by a mechanism involving repeated expansion to a seven-membered ring (cycloheptadienyl cation) followed by contraction to a six-membered ring. Expansion of an aromatic cation to a seven-membered ring has been shown to occur by Nelson, et al.,[10] in the solvolysis of 1,4-dihydrobenzyl p-toluenesulfonates. Although a cycloheptadienyl intermediate will equally well account for the observed product distribution, the cyclopentadienyl cation is believed likely to be the more stable and hence the more probable intermediate. Further experimental data will be required before a final decision can be reached.

The mechanism shown above results in the production of a xylene as a primary product. However, little xylene is recovered because of rapid methyl transfer from heavier aromatics, such as

(6) L. de Vries, J. Am. Chem. Soc., 82, 5242 (1960).
(7) S. Winstein and M. Battiste, ibid., 82, 5244 (1960).
(8) M. Simonetta and S. Winstein, ibid., 76, 18 (1954).
(9) L. E. Miller, private communication.
(10) N. A. Nelson, J. H. Fassnacht and J. U. Piper, ibid., 81, 5009 (1959).

hexamethylbenzene, to form large amounts of C_{10}- and C_{11}-aromatics. The data from experiment F (Table I), wherein a mixture of xylene and hexamethylbenzene was used, demonstrate that the methyl transfer is sufficiently rapid to account for the observed low xylene concentration in the product.
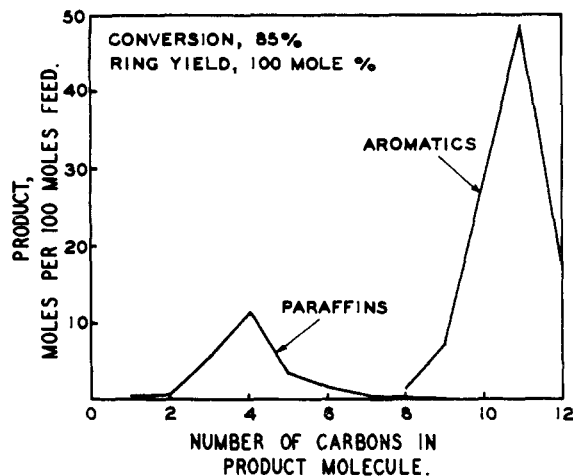
Fig. 3.—Reaction of hexamethylbenzene on silica-alumina in a nitrogen atmosphere, product distribution vs. carbon number. Conditions: 344°; 13.6 atm.; mole N_2/mole feed, 0.77; volumes of liquid feed per volume of catalyst per hour, 2.0.

The methyl transfer reaction may occur also with some of the other intermediates in the paring reaction. In addition, methyl transfer may precede the paring reaction; for example, part of the C_{11}-aromatics may be formed by an unusual disproportionation of hexamethylbenzene, which involves the formation of the 1,1,2,3,4,5,6-heptamethylbenzenonium ion. One resonance form of
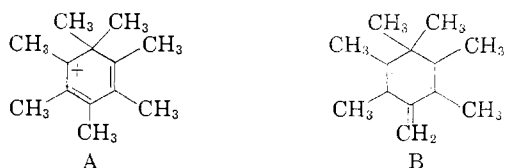
CH₃ CH₃ / CH₃ … CH₃ / CH₃ … CH₃ / CH₃
A

CH₃ CH₃ / CH₃ … CH₃ / CH₃ … CH₃ / CH₂
B

this ion is A. Doering, et al.,[11] have shown this ion to be the terminal product of a Friedel–Crafts methylation of methylbenzenes. The conjugate base, $C_{13}H_{20}$, B, is stronger than hexamethylbenzene and probably would not be desorbed from the catalyst. This heptamethylbenzenonium ion can react via changes in ring size and undergo the paring reaction as previously suggested.

The yield of methane and ethane in the paring reaction is low because of the difficulty of cleaving a methyl or ethyl group from the ring. Propyl groups crack somewhat more readily to form propane. However, a side chain containing four or more carbons cleaves rapidly. Although steady state concentrations of cationic intermediates with a butyl side chain may be very low, once these species are formed cracking occurs readily.

In the presence of nickel sulfide on silica–alumina and hydrogen, some hydrogenation of aromatics to naphthenes occurs. It is therefore possible that with this catalyst part of the C_9-naphthenes and isoparaffins in the product may be formed by means of a naphthenic intermediate, hexamethylcyclohexyl cation. This ion would isomerize to give products with different side chains. The studies of Pines and Shaw[12] show that a similar isomerization of ethylcyclohexane proceeds through a carbonium ion mechanism involving repeated ring expansions and contractions with eventual attainment of equilibrium isomer distribution. Thus, if a hexamethylcyclohexyl cation intermediate is formed, one might expect rapid establishment of equilibrium among its isomers, followed by cracking of the C_4-side chains. The reactions of

(11) W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards and G. Laber, Tetrahedron, 4, 178 (1958).

(12) H. Pines and A. W. Shaw, J. Am. Chem. Soc., 79, 1474 (1957).

hexamethylcyclohexane have been studied also, and the results, which confirm this hypothesis, will be presented in a later publication.

Because the quantity of naphthene formed is relatively small, particularly in experiment C, a mechanism involving only naphthenes as intermediates is inadequate. We propose, therefore, that a major fraction of the product is formed directly from the aromatic through a route involving changes in ring size. Additional support for this conclusion is that hexamethylbenzene undergoes the paring reaction with the silica–alumina support alone and forms no naphthenes.

The mechanism postulated for the paring reaction indicates that it can occur only with aromatics containing at least 10 carbon atoms because 10 carbon atoms is the minimum necessary to form isobutane and still leave an aromatic nucleus. This is consistent with the experimental data obtained with the C_6- to C_9-aromatics where the paring reaction is found to be minor. Some paring can occur with lower molecular weight aromatic feeds, such as mesitylene, because the methyl transfer reaction forms some molecules sufficiently large to undergo paring.

Small amounts of alkylbenzenes other than methylbenzenes with carbon numbers of 11 and 12 can be detected in the product, proving that side chain growth does occur. However, the products from the paring reaction of hexamethylbenzene are characterized by the absence of large amounts of aromatics having ethyl and propyl side chains. This fact suggests that the adsorbed species that are undergoing side chain growth by successive ring contractions and expansions usually do not desorb from the catalyst before they have grown a sufficiently large side chain which can be eliminated by cracking.

The hydrocracking of other aromatic and naphthenic hydrocarbons under these conditions will be described in future publications.

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Carbonyl Reactions. XI. Deuterium Exchange in the Acid-catalyzed Isomerization of cis-Benzalacetophenone[1]

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In 60% aqueous dioxane, cis-benzalacetophenone is rapidly isomerized to trans-benzalacetophenone by 3-molar sulfuric acid. Using sulfuric acid-d_2 in dioxane–deuterium oxide, no deuterium is introduced during the isomerization. The isomerization is faster in sulfuric acid-d_2 than in ordinary sulfuric acid. These results confirm the previously proposed mechanism, which involves as the rate-determining step the addition of water to the oxonium salt of cis-benzalacetophenone. The mechanism of hydration of α,β-unsaturated aldehydes and ketones is discussed in light of these results.

Introduction

In the previous paper of this series,[1] the isomerization of cis-benzalacetophenone to trans-benzal-

(1) Previous report, D. S. Noyce, W. A. Pryor and P. A. King, J. Am. Chem. Soc., 81, 5423 (1959).

(2) National Institutes of Health Post-Doctoral Fellow, 1959–1960.

acetophenone by acid was investigated under a variety of conditions. The rate of isomerization did not parallel the acidity function H_0. It was also shown that β-phenyl-β-hydroxypropiophenone must be excluded as an intermediate in the isomerization, since the rate of dehydration is