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Hydrocracking of Alkylbenzenes and Polycyclic Aromatic Hydrocarbons on Acidic Catalysts. Evidence for Cyclization of the Side Chains

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The simple cyclization of alkyl side chains is accompanied by formation of hydrogen and is therefore a reaction that is repressed at high hydrogen pressure. It is shown that appreciable cyclization accompanied by cracking occurs when certain aromatic hydrocarbons are passed over a nickel sulfide on silica-alumina catalyst, even at hydrogen pressures as high as 75 atm. The products from cyclization are predominantly tetralins and indanes, of lower molecular weight than that of the reactant. For example, with *n*-decylbenzene, 39% of the reactant that cracks forms bicyclic hydrocarbons. The small extent of cyclization of side chains (without cracking) that is thermodynamically possible at 75 atm pressure of hydrogen is calculated. It is shown that this limitation can be exceeded if cyclization is accompanied by cracking or by some other reaction that consumes hydrogen. The hydrocracking pattern of hexaethylbenzene differs markedly from that of hexamethylbenzene and is characterized by de-ethylation as the initial reaction. Cyclization accompanied by cracking occurs as one of the subsequent reactions. The product distribution from the hydrocracking of phenanthrene is discussed in detail. The proposed mechanism based on cyclization accounts for the unexpected product distribution, namely, the formation of tetralin without the formation of attendant light alkanes. Product distributions from the hydrocracking of *n*-butylbenzene, tetralin, anthracene, and pyrene are discussed.

INTRODUCTION

A considerable number of papers has been published on the catalytic cracking of aromatic hydrocarbons, particularly on the dealkylation of alkylbenzenes having less than 12 carbons. Only a few authors have reported on the catalytic cracking of aromatic hydrocarbons of carbon number greater than 12. Appleby *et al.* (*1*) showed that the principal product obtained from processing unsubstituted, condensed aromatic hydrocarbons over silica-alumina catalyst consists of a carbonaceous deposit on the catalyst, the remaining products being methane and hydrogen.

Some data have been reported on the hydrocracking of pure aromatic hydrocarbons over catalysts containing a metal or metal compounds on acidic supports. The hydrocracking of tetralin and *n*-butylbenzene at 371°C over a nickel sulfide on silica-alumina catalyst at 68 atm was reported by Flinn, Larson, and Beuther (*2*). For tetralin, they reported production of light alkanes with a high ratio of branched to unbranched alkanes. Ring opening and hydrogenation were the predominant reactions. Benzene, alkylbenzenes, and substantial quantities of naphthalene were produced also. No hydrocarbons of higher molecular weight than the reactant were identified, and no cyclization was reported. When *n*-butylbenzene was hydrocracked, the principal reaction was dealkylation to butanes and benzene.

TABLE 1

PROCESS CONDITIONS AND PRODUCT DISTRIBUTIONS FOR HYDROCRACKING EXPERIMENTS AT 82 ATM PRESSURE

Reactant:	*n*-Decylbenzene	Hexaethylbenzene		Hexamethylbenzene	*n*-Butylbenzene	Phenanthrene		Anthracene	Tetralin	Pyrene
Catalyst temperature (°C)	288	293	293	288	288	293	298	352	288	349
LHSV	8.0	16.0	2.0	16.0	2.0	16.0	2.0	2.0	1.0	2.0
Moles H_2/mole reactant	12.4	15.3	17.3	11.1	7.8	8.9	10.6	8.4	6.6	9.6
Conversion, total (%)	29.3	99.7	100	76.0	13.8	74.7	>95	93.7	73.4	100
Product in moles/100 moles of reactant										
Methane	—	0.1	1.0	2.3	0.02	Trace	0.2	0.2	—	0.1
Ethane	0.1	175.5	240.2	1.5	0.04	—	0.6	0.3	0.1	0.6
Propane	2.4	1.0	10.0	4.1	0.3	0.2	1.0	3.2	1.2	1.2
Isobutane	2.5	0.9	16.6	20.5	0.4	Trace	1.5	4.8	3.0	1.7
n-Butane	1.2	1.5	19.8	1.6	1.1	Trace	1.3	3.2	0.8	0.5
Isopentane	2.5	1.2	9.8	2.5	0.1	0.1	1.1	2.0	0.8	1.0
n-Pentane	0.2	0.2	1.1	0.2	—	—	0.2	0.1	—	0.1
Isohexanes	3.1	0.9	6.6	1.5	0.05	—	0.2	0.7	0.2	1.5
n-Hexane	0.3	0.1	0.5	—	—	—	0.1	0.1	—	0.9
Isoheptanes	2.7	0.9	3.6	—	—	—	0.1	0.4	0.3	0.1
C_8 Alkanes	0.9	—	—	—	—	—	—	—	—	0.4
C_9 Alkanes	1.6	—	—	—	—	—	—	—	—	—
C_{10} Alkanes	9.2	—	—	—	—	—	—	—	—	—
Total alkanes	26.7	182.3	309.2	34.2	2.0	0.3	6.3	15.0	6.4	8.1
Cyclopentane	—	—	—	—	—	0.2	1.1	0.1	—	0.5
C_6 Cycloalkanes	0.4	0.1	4.8	—	0.2	0.9	3.2	2.4	1.1	11.8
C_7 Cycloalkanes	1.4	0.5	11.5	0.4	0.1	4.6^e	12.5^h	5.4^j	2.4	6.5
C_8 Cycloalkanes	1.2	0.7	12.8	6.8	—	1.6^f	8.8^i	2.5	2.6	2.8
C_9 Cycloalkanes	1.1	0.2	5.4	9.9	—	0.9	1.5	1.3	0.2	2.0
C_{10} Cycloalkanes	0.5	1.1	6.7	3.2	1.7	0.4	—	—	—	—
C_{11} Cycloalkanes	0.3	—	—	—	—	—	—	—	—	—
Total cycloalkanes	4.9	2.6	41.2	20.3	2.0	8.6	27.1	11.7	6.3	23.6
Benzene	9.5	0.1	0.3	—	6.3	1.6	6.5	1.1	7.3	5.6
Toluene	0.6	0.2	1.6	—	0.2	0.3	1.4	1.0	0.8	0.6
C_8 Alkylbenzenes	1.1	0.3	11.8	—	0.1	0.5	1.5	0.8	1.1	0.5
C_9 Alkylbenzenes	0.5	0.1	5.0	1.6	0.1	0.3	0.6	0.3	—	0.5
C_{10} Alkylbenzenes	0.5	1.7^b	17.1	11.3	86.5^c	Trace	0.1	0.3	2.5	0.1
C_{11} Alkylbenzenes	0.5	0.7	6.7	42.7	0.02	—	—	—	—	—
C_{12} Alkylbenzenes	0.4	19.7^b	10.6	24.2	0.3	—	—	—	—	—
C_{13} Alkylbenzenes	—	0.5	0.5	—	—	—	—	—	—	—
C_{14} Alkylbenzenes	—	62.6	0.8	—	3.3	—	—	—	—	—

				—	—	—	—	—	—	—
C_{16} Alkylbenzenes	70.7[a]	15.0	—	—	—	—	—	—	—	—
C_{17} Alkylbenzenes	—	0.4	—	—	—	—	—	—	—	—
C_{18} Alkylbenzenes	—	0.3	—	—	—	—	—	—	—	—
Total alkylbenzenes	86.5	101.8	54.4	79.8	96.8	2.7	10.1	3.5	11.7	7.6
C_9 Fused bicyclic cycloalkanes	0.4	—	—	—	—	0.2	0.5	0.4	3.6	3.6
C_{10} Fused bicyclic cycloalkanes	0.2	—	—	—	—	0.3	9.0	0.4	38.1	3.6
C_{11} Fused bicyclic cycloalkanes	0.2	—	—	—	—	0.4	2.6	0.1	0.4	0.5
C_{12} Fused bicyclic cycloalkanes	0.4	—	—	—	—	0.4	0.6	2.0	0.4	1.1
Total fused bicyclic cycloalkanes	1.2	—	—	—	—	1.3	13.7	2.9	42.5	8.8
Indane	2.1	—	—	—	—	0.2	1.0	0.5	—	1.1
Tetralin and methylindanes	5.5	—	8.0	—	1.6[d]	9.3	17.8	5.1	28.0[l]	11.1
C_{11} Alkyl tetralins and indanes	1.2	—	—	—	—	0.4	2.4	1.4	0.2	4.0
C_{12} Alkyl tetralins and indanes	0.4	—	5.0	—	—	0.4	—	—	0.8	1.6
C_{13} Alkyl tetralins and indanes	—	—	—	—	—	—	—	—	—	—
C_{14} Alkyl tetralins and indanes	—	—	—	—	Trace	—	—	—	0.2	—
Total indanes and tetralins	9.2	—	13.0	—	1.6	10.3	21.2	7.0	29.2	17.8
Ethene	—	10.6	—	—	—	—	—	—	—	—
Propene	—	0.1	—	—	—	—	—	—	—	—
Butenes	—	0.1	—	—	—	—	—	—	—	—
C_{13} Fused tricyclic cycloalkanes	—	—	—	—	—	—	—	1.5	1.1	8.3
C_{14} Fused tricyclic cycloalkanes	—	—	—	—	—	14.0	54.9	26.0	6.4	7.2
Other C_{14} tricyclics	—	—	—	—	—	70.5[g]		52.8	0.7[m]	2.6
Total fused tricyclics	—	—	—	—	—	84.5	54.9	80.3	8.2	18.1
C_{16} Fused tetracyclic cycloalkanes										28.9
Other C_{16} tetracyclics										23.0
Total C_{16} tetracyclics										51.9

[a] Does not include 2.7 moles of higher molecular weight aromatic hydrocarbons.

[b] Contains some fused bicyclic aromatic hydrocarbons.

[c] 86.2 moles *n*-butylbenzene.

[d] 100% methyl indanes.

[e] 85% is methylcyclohexane.

[f] 75% is ethylcyclohexane.

[g] Contains 25.3 phenanthrene; does not include 1.7 moles C_{15}–C_{16}.

[h] 80% is methylcyclohexane.

[i] 43% is ethylcyclohexane.

[j] 54% is methylcyclohexane.

[k] Contains 6.3 anthracene.

[l] Contains 1.4 methylindanes.

[m] One aromatic ring.

It was shown recently (*3*) that an unusual product distribution is obtained when hexamethylbenzene is hydrocracked over a nickel sulfide on silica-alumina catalyst. The principal products are lower molecular weight methylbenzenes and branched alkanes, particularly isobutane. A reaction occurs that, in effect, peels or pares methyl groups from the aromatic ring and eliminates them as branched alkanes with essentially no loss of ring structure. This reaction was named the paring reaction. A mechanism was suggested that produced side chain growth by an isomerization process involving changes in ring size. The larger alkyl side chains are then selectively eliminated by cracking to produce branched alkanes.

This paper describes the hydrocracking over a nickel sulfide on silica-alumina catalyst of (a) three alkylbenzenes that have different types of side chains, namely, *n*-decylbenzene, hexaethylbenzene, and *n*-butylbenzene and (b) several unsubstituted, polynuclear aromatic hydrocarbons. It is shown that cyclization (1) occurs to an appreciable extent even at elevated hydrogen pressure in the cracking of these aromatic hydrocarbons and (2) produces unusual product distributions.

EXPERIMENTAL

The equipment and method of preparation of the nickel sulfide (6.6% nickel) on silica-alumina (10% alumina) catalyst were described previously (*4*). The reservoir containing the reactant was supported in an oven which could be used to melt the reactant if it is a solid at room temperature.

Chemicals. Hexaethylbenzene, *n*-butylbenzene, phenanthrene, and anthracene were Eastman Kodak White Label chemicals and showed no impurity by gas chromatographic (GC) analyses. The pyrene (Eastman White Label), after purification by recrystallization from a mixture of ethanol and benzene, still contained 2% hexahydropyrene.

n-Decylbenzene and tetralin, minimum 99.8% pure, were American Petroleum Institute standard samples (*5*).

Analysis. Liquid products were analyzed by a combination mass spectrometric–gas chromatographic method described by Lindeman and Annis (*6*). Most of the analyses employed a silicone rubber column on a firebrick support. Wherever possible the accuracy of this method of analysis was confirmed by known mixtures of hydrocarbons.

The composition of gaseous products was determined by mass spectrometric analysis.

ALKYLBENZENES

In the following discussion the liquid hourly space velocity (LHSV) signifies the hourly volume of liquid reactant per volume of catalyst. The LHSV varies inversely as the residence time. Table 1 lists the conditions and product distributions of typical experiments.

n-Decylbenzene

Results

Figure 1 shows the product distribution by carbon number. Of the 26.6% *n*-decylbenzene that is converted to lower molecular weight products, 35% is dealkylated to form a C_{10} alkane and benzene and 39% is cyclized to form fused-ring hydrocarbons, principally tetralin.

Discussion

Three potential routes from *n*-decylbenzene to tetralin are shown below:

1. H_2 + *n*-decylbenzene → *n*-butylbenzene + C_6 alkane
and *n*-butylbenzene → tetralin + H_2
2. *n*-Decylbenzene → hexyltetralin + H_2
and H_2 + hexyltetralin → tetralin + C_6 alkane
3. *n*-Decylbenzene → tetralin + C_6 alkane

Table 2 shows that the cyclization of *n*-butylbenzene with formation of molecular hydrogen (Route 1) is thermodynamically favorable only to a small extent at high hydrogen pressure.

In the product from *n*-decylbenzene at 288°, the observed ratio of tetralin to *n*-butylbenzene is greater than 10, which is at least 3300-fold larger than the estimated ratio at equilibrium of 0.003; therefore, the tetralin is not formed by Route 1.

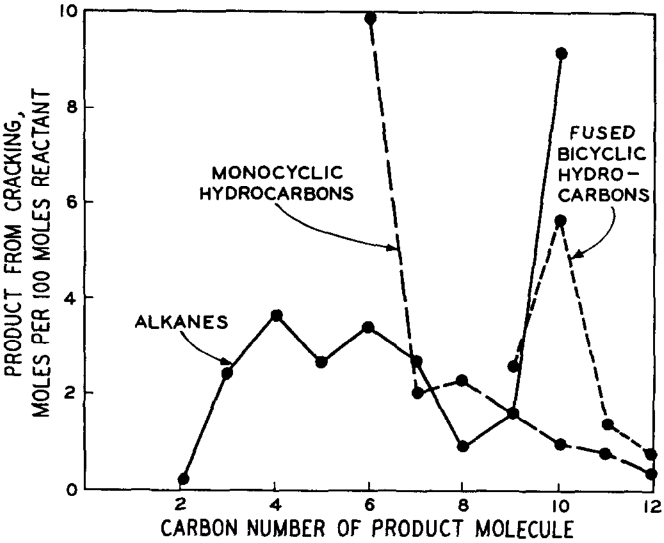


FIG. 1. Hydrocracking of *n*-decylbenzene at 8.0 LHSV, 288°, and 82 atm.

Data are not available for calculation of the simple cyclization of *n*-decylbenzene to hexyltetralin (Route 2), but it seems reasonable that this cyclization would also be unfavorable to about the same degree. If, however, cracking accompanies cyclization and occurs in such a way that no hydrogen is produced, it is thermodynamically possible (as shown in Table 2) to form large amounts of tetralin-type and indane-type hydrocarbons from monocyclic aromatic hydrocarbons (Route 3). These results suggest that tetralin and the indane-type hydrocarbons are formed by Route 3 wherein cyclization is accompanied by cracking in a manner similar to that shown on page 188.

TABLE 2
CYCLIZATION OF ALKYLBENZENES[a]

Equation	Molal ratio of tetralin to reactant at equilibrium at 75 atm of hydrogen and 82 atm total pressure		
	227°C	327°C	427°C
n-Butylbenzene (g) = Tetralin (g) + Hydrogen (g)	0.001	0.005	0.019
n-Decylbenzene (g) = Tetralin (g) + 2-Methylpentane (g)	8400	5800	4200

[a] Calculated from data on *n*-butylbenzene (*7*), *n*-decylbenzene (*7*), 2-methylpentane (*7*), and tetralin (*8*).

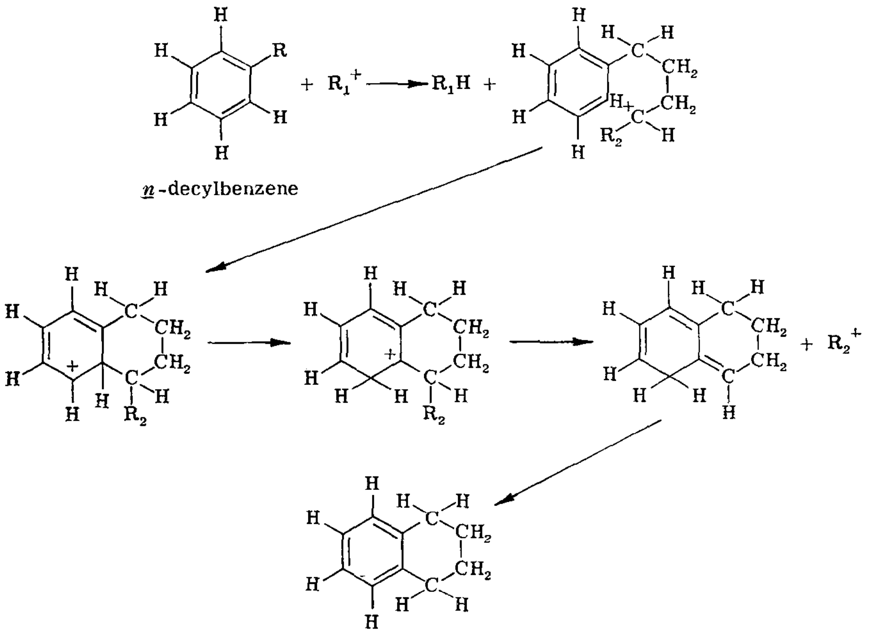
n-Butylbenzene

Results

At 288°C butyl group transfer and dealkylation are the predominant reactions. Cyclization occurs only to a small extent, and the cyclized products are methylindanes.

Discussion

From the previous discussion, the extent of cyclization of butylbenzene should be limited by equilibrium to a low value because the cyclization cannot be accompanied by facile cracking. (Cyclization with cracking to form indane and methane is a possibility, but cracking to produce methane does not occur readily over acidic catalysts.) The amount of methylindanes formed is about that expected from estimates of the equilibrium. Free energy data are not available for calculation of the equilibrium exactly, but it is expected to be of the same magnitude as that for the analogous reaction of *n*-butylbenzene to form tetralin and hydrogen. The observed ratio of methylindanes to *n*-butylbenzene is 0.018, which is of the order of magnitude of the calculated ratio of tetra-



lin to *n*-butylbenzene at equilibrium of 0.003.

Other unpublished results from this laboratory show that at higher conversions of *n*-butylbenzene only a slight increase in the formation of methylindanes from *n*-butylbenzene occurs, thus indicating that equilibrium had been approached.

Tetralin is not produced, probably because production of tetralin from *n*-butylbenzene requires formation of a primary carbonium ion.

Hexaethylbenzene

Results

Figures 2 and 3 show graphically that the product distribution by carbon number from hexaethylbenzene changes markedly with contact time. Thus, at long contact times secondary, sequential reactions are important.

At short contact time (16 LHSV), the product contains essentially only ethane, ethene, and polyethylbenzenes (principally

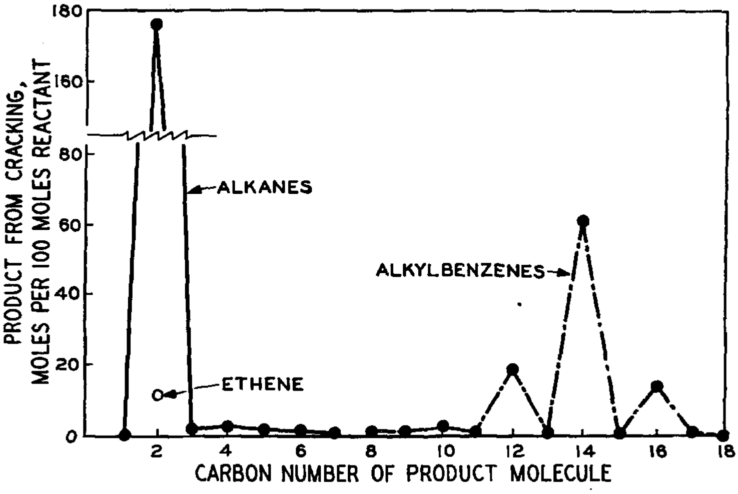


FIG. 2. Hydrocracking of hexaethylbenzene at 16.0 LHSV, 293°, and 82 atm.

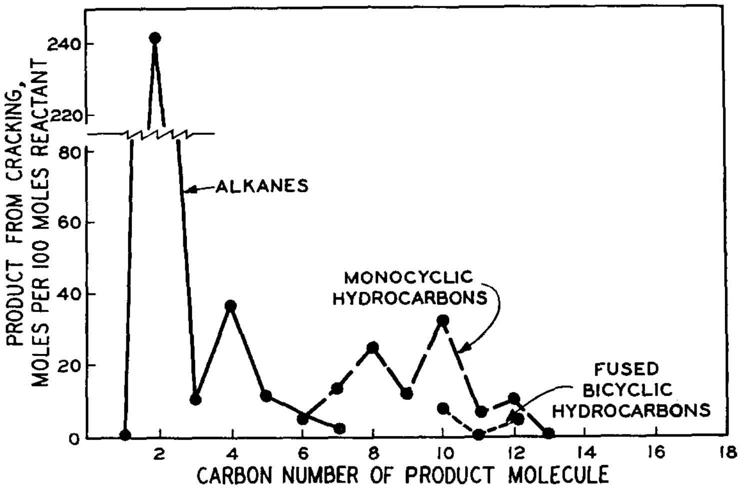


FIG. 3. Hydrocracking of hexaethylbenzene at 2.0 LHSV, 293°, and 82 atm.

tetraethylbenzene). The primary reaction is deethylation almost exclusively.

At longer contact time (2 LHSV), other products are formed in significant quantities.

1. Alkanes heavier than ethane are produced, with butane predominating. The ratio of isobutane to *n*-butane is low (0.8).

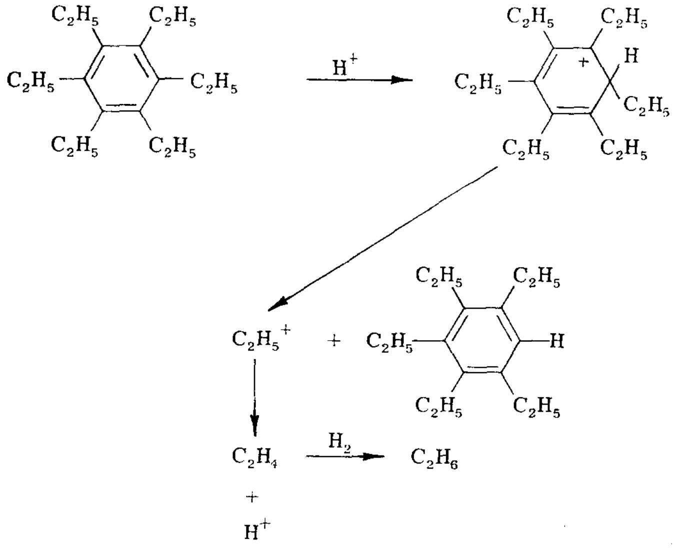
2. The product from cracking contains substantial quantities of C_{10} to C_{12} tetralin-type and indane-type hydrocarbons. Although these are not completely separated from the C_{10} to C_{12} alkylbenzenes in the GC analyses, semiquantitative mass spectrometric analyses show that these fused ring aromatic hydrocarbons comprise about one-third of the C_{10} to C_{12} portion.

3. Alkylbenzenes of even carbon number still predominate, but the product contains significant quantities of odd carbon number aromatic hydrocarbons.

4. Within the limits of accuracy, essentially no loss of ring structures occurs during cracking.

Discussion

The initial reaction in the hydrocracking of hexaethylbenzene to form ethane and pentaethylbenzene can be accounted for by a conventional carbonium ion dealkylation mechanism.



This tendency to lose ethyl groups readily appears to be characteristic of hexa- and pentaethylbenzenes and is in contrast to ethylbenzene which does not lose an ethyl group readily under these conditions. Molecular models show that the ethyl groups in hexaethylbenzene are close. Steric strain may contribute to weakening of the bonds to the ring, thereby facilitating dealkylation. After loss of one or two groups, further de-ethylation occurs less readily, as shown by a comparison of the results at the two contact times. An increase in the contact time of 8-fold increases the number of moles of ethane and ethene by only 1.35-fold.

The ethyl cation is desorbed as ethene and later hydrogenated to ethane on a catalytic hydrogenation site. At the short contact time, the concentration of ethene in the product exceeds by a factor of 10^7 the concentration that is in equilibrium with ethane and hydrogen at these conditions. This indicates that the hydrogenation rate is slower than the initial de-ethylation rate. The ethyl cation may also be hydrogenated by hydride ion transfer from other hydrocarbon molecules or by molecular hydrogen by direct heterolytic splitting on the nickel sulfide as mentioned by Frey *et al.* (*9*).

It was shown previously (*3*) that hexamethylbenzene undergoes the paring reaction wherein branched alkanes (principally isobutane) are eliminated with essentially no loss in ring structures (Table 1). In the paring reaction, side chain growth occurs by isomerization to produce the larger alkyl fragments which are selectively removed by cracking. Because of the similarity between hexamethylbenzene and hexaethylbenzene, it might be expected that the paring reaction would predominate with hexaethylbenzene also. The contrast between the product distributions from hexamethylbenzene and hexaethylbenzene at 16 LHSV is striking. Essentially no alkanes heavier than ethane are formed from hexaethylbenzene because de-ethylation occurs more rapidly than paring. The paring reaction of hexaethylbenzene is a secondary reaction that occurs with the partially de-ethylated product, as evidenced by the sizeable quantities of alkanes heavier than ethane in the longer contact experiment. These could not have been formed by ring saturation and cleavage because ring structure is conserved in cracking. Additional evidence that intramolecular isomerization of the type postulated in the paring reaction does occur is the presence of aromatic hydrocarbons of odd carbon number in the product at long contact time. The lack of methane shows that these are not the result of demethylation of the beta carbons from the ethyl groups.

Paring of hexaethylbenzene produces more *n*-butane than isobutane in sharp contrast to the product from hexamethylbenzene. With the mechanism proposed previously for the paring reaction, it is difficult to form a *n*-butyl or *sec*-butyl side chain as only methyl side chains are present initially. With ethyl groups involved in the side chain growth, *n*-butyl and *sec*-butyl side chains are more likely, and the ratio of branched to unbranched alkanes is low. For growth of C_5, C_6, and C_7 side chains, more isomerization occurs, and the ratios of branched to unbranched alkanes are high.

The cyclization of side chains to form tetralin-type and indane-type hydrocarbons of lower molecular weight may be accounted for by the same types of intermediates that explain the product from the paring reaction. The initial species may be partially de-ethylated carbonium ions that can increase the length of a side chain by a ring contraction process similar to that found to occur with hexamethylbenzene (*3*).

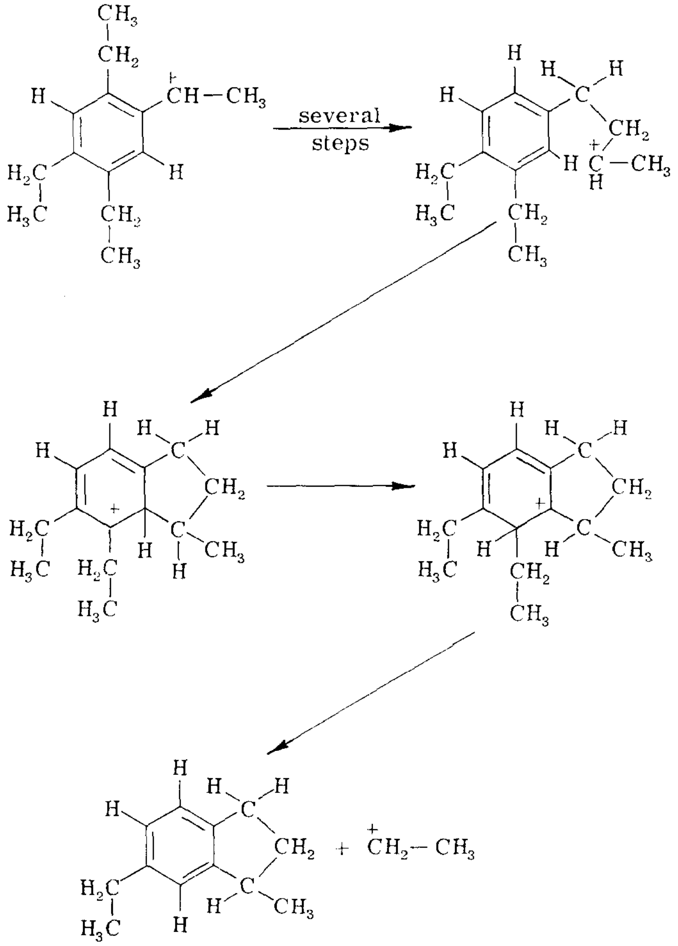
As with *n*-decylbenzene, the combination of cyclization with cracking produces no net hydrogen.

FUSED-RING AROMATIC HYDROCARBONS

Phenanthrene

Results

Figures 4 and 5 show the product distributions for experiments at two contact



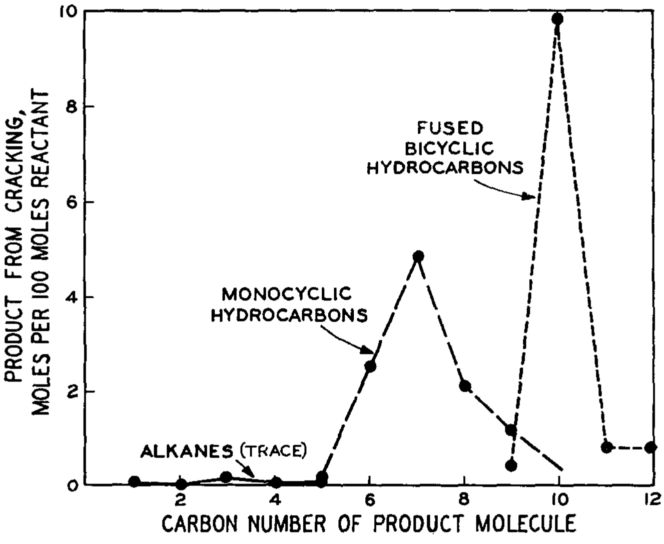


FIG. 4. Hydrocracking of phenanthrene at 16.0 LHSV, 293°, and 82 atm.

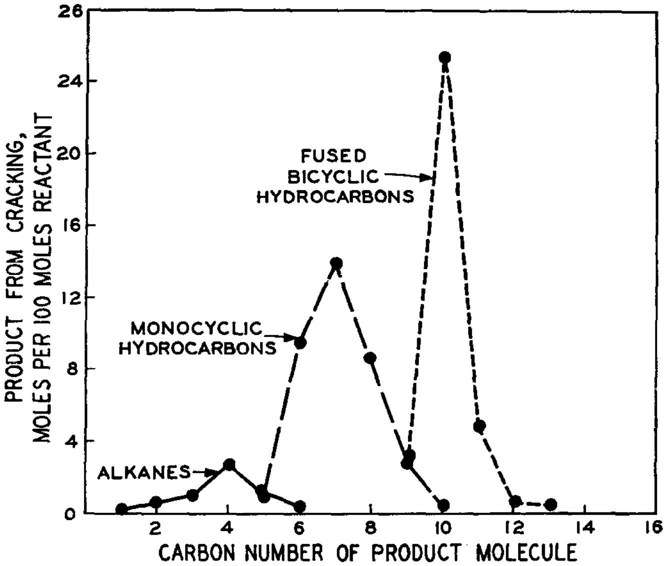


FIG. 5. Hydrocracking of phenanthrene at 20 LHSV, 298°, and 82 atm.

times. The predominant product in the hydrocracking of phenanthrene is tetralin. The next most important product is methylcyclohexane. In the experiment at the shorter contact time (16 LHSV), for each hundred moles of reactant, 14 moles crack to lower molecular weight species, forming 9 moles of tetralin. The surprising result is that no comparable amount of light alkanes is also formed, only a trace of butane being observed. Apparently, the initial reaction that yields tetralin does not form butane.

Saturation and partial hydrogenation are important also. Most of the C_{14} products result from hydrogenation without cracking. A large fraction of these contain only one aromatic ring.

Discussion

The product distribution from phenanthrene indicates that three types of reactions are occurring:

1. Cleavage of one of the terminal rings to form an alkane and a bicyclic such as tetralin. This reaction, which results in alkane formation, is minor.

2. Ring saturation and cleavage of the central ring. This accounts for the appreciable amounts of methylcyclohexane and ethylcyclohexane produced. [Methylcyclohexane is a major product from hydrocracking perhydrophenanthrene (*10*).]

3. An unusual cracking reaction that produces bicyclic hydrocarbons, principally tetralin, without producing an equivalent amount of light alkanes. This is the predominant reaction. A suggested mechanism that leads to this type of product distribution is shown below.

(a) Partial hydrogenation of the polynuclear aromatic.

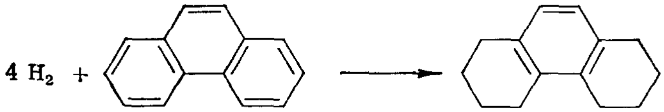
(b) Opening of one of the cycloalkane rings to form a *n*-butyl side chain.

(c) Alkyl transfer of the side chain to another reactant molecule.

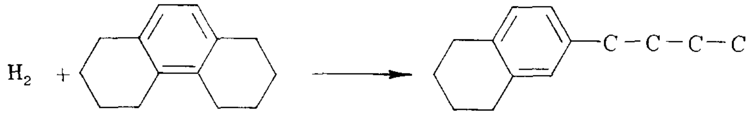
(d) Ring closure accompanied by hydrogenation to form a tetracyclic hydrocarbon.

(e) Cracking of a central cycloalkane ring to give a tetralin and a cycloalkane.

(a)



(b)



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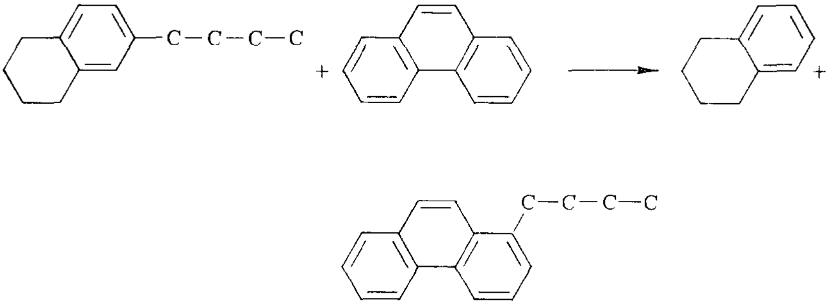

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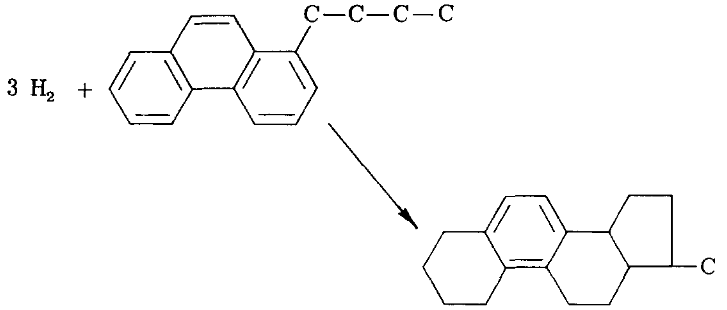
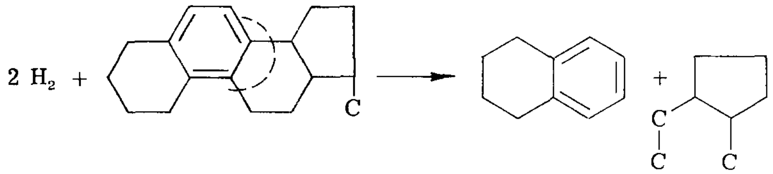


(e)



This mechanism accounts for the lack of formation of alkanes by the combination of a butyl group transfer and a cyclization reaction. It also accounts for the formation of tetralin which is the major product at low conversions.

The relative extents of the three types of cracking reactions are shown below. To compute the distribution shown, all alkanes were assumed to be formed from Reaction 1. After deduction of an equivalent quantity of bicyclics, the remaining bicyclics were assumed to be formed by Reaction 3. Monocyclic compounds required to balance Eq. 3 were deducted, and the balance was assumed to be formed by Reaction 2.

	Moles of phenanthrene reacting by this route in the 16 LHSV experiment
1. Phenanthrene → bicyclic + alkane	0.3
2. Phenanthrene → 2 monocyclics	2.7
3. 2 Phenanthrenes → 2 bicyclics + monocyclic	11.3

This computation shows that the complex process represented by Eq. 3 is by far the most important initial mode of reaction and results in a product that consists almost entirely of cyclic hydrocarbons. In the 2 LHSV experiment, more light alkanes are formed; but the processes leading to cyclic species are still predominant.

Anthracene

The rate of hydrocracking of anthracene is considerably lower than that of its isomer, phenanthrene. Conversion from tricyclic hydrocarbons at 352°C is 20% with anthracene as contrasted to 45% with phenanthrene at a 54°C lower temperature. Anthracene produces more light alkanes than phenanthrene, but this is believed to be due to the higher catalyst temperature rather than the difference in structure. Tetralin is still a predominant cyclic product from cracking, but there is less evidence that cyclization is a major reaction with anthracene at 352°C.

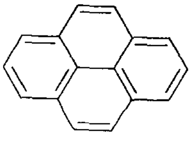
Tetralin

Tetralin was hydrocracked at 288°C, 82 atm, and 1 LHSV. In addition to the reactions reported by Flinn *et al.* (*2*) (at 371°C), the presence of sizable quantities of C_{14} fused ring, tricyclic perhydroaromatics is shown by the gas chromatographic–mass spectrometric analysis. This result demonstrates that alkyl transfer followed by cyclization of the butyl group occurs to a significant extent. Saturation of the aromatic ring may occur during cyclization and thereby is a means of avoiding the production of hydrogen (which is a thermodynamically unfavorable reaction under these conditions).

Pyrene

Pyrene, a tetracyclic C_{16} aromatic hydrocarbon was hydrocracked at 349°C. All of the pyrene was partially hydrogenated. The product distribution is quite similar to that from phenanthrene in that tetralin is the most predominant product, and the amount of light alkanes formed is small. The principal monocyclic cycloalkane product is methyl cyclopentane from pyrene in contrast to C_7 cycloalkanes from phenanthrene.

It is interesting to note that formation of a bicyclic hydrocarbon from pyrene (shown below) by simple cleavage should produce also at least one alkane. However,



there are 27 moles of bicyclic hydrocarbons in the product and only 8 moles of alkanes. Also, in order to form methylcyclopentane, a C_{10} cyclic hydrocarbon is the expected accompanying product. Again, essentially no C_{10} cyclic hydrocarbons are formed. It is concluded, therefore, that the hydrocracking of pyrene is complex. It probably occurs by a mechanism similar to that of phenanthrene.

COMPARISON OF HYDROCRACKING AND CATALYTIC CRACKING OF POLYCYCLIC AROMATIC HYDROCARBONS

Appleby *et al.* (*1*) report that phenanthrene, anthracene, and pyrene when contacted with silica-alumina catalyst at 500°C produce large quantities of coke and small quantities of gases (namely, methane and hydrogen) as the principal products. Their study demonstrates the refractory nature of these hydrocarbons in catalytic cracking. In contrast, hydrocracking with a nickel sulfide on silica-alumina catalyst gives a product consisting of lower molecular weight hydrocarbons with only small amounts of gas or coke. Partial hydrogenation of polycyclic aromatic hydrocarbons occurs readily in hydrocracking, and the resulting partially hydrogenated species are subsequently cracked.

ACKNOWLEDGMENTS

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