THE DEHYDROCYCLIZATION REACTION[1]

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I. Introduction

The purpose of this review is to consider the "vapor-phase" dehydrocyclization reaction from the viewpoint of the synthetic chemist. Consideration is limited to those reactions which are brought about in the "vapor phase" either catalytically or by simple pyrolysis. Although similar reactions may be effected in closed reaction chambers with catalysts or by heating with aluminum chloride, sulfur, selenium, platinum, or palladium, these reactions are not considered, since this liquid-phase work has been reviewed by Linstead (97) and Plattner (137).

The two terms most used to describe this reaction are "cyclodehydrogenation" (115–123) and "dehydrocyclization" (54). Neither term is perfectly suited to describe the various reactions which should be included in this classification.

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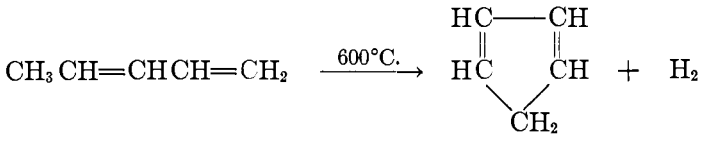
The latter term will be employed in this article to imply ring formation by removal of hydrogen from at least two points in a molecule, or between two or more molecules. This almost always results, under reaction conditions, in an "aromatic" ring. The conversion of heptane to toluene serves as an example. The word "dehydrocyclization" is used here primarily because it has been more frequently and widely employed than the equally useful "cyclodehydrogenation."

Such cyclization reactions have been known for over eighty years; however, it is only in the last fifteen years that they have been studied intensively and systematically. Toward the end of the 1930's, the demand for phthalic anhydride for alkyd resins was increasing so rapidly that it was evident that not enough napthalene could be obtained from coal tar. This led to studies for the separation of aromatics from certain petroleum oils and then to their formation from paraffins and cycloparaffins. The recent colossal demands for cumene to increase the octane rating of fuels for high-compression engines, for benzene and toluene for explosives, for benzene for styrene production for GR-S rubber, and for *o*- and *p*-xylenes as intermediates for the production of phthalic anhydride and terephthalic acid, respectively, have directed the attention of research chemists toward the development of efficient catalysts and the perfection of methods for the conversion of petroleum aliphatics to aromatics. Much industrial research has been devoted to the dehydrocyclization of petroleum-grade C_6, C_7, and C_8 aliphatic paraffins and olefins to benzene, toluene, and xylenes. A recently developed process (55, 56) for improving the octane number of gasoline involves a certain amount of dehydrocyclization. In the "platforming" process petroleum hydrocarbons are passed over a platinum-containing catalyst at 400–500°C. under elevated pressures in a hydrogen atmosphere. Along with some splitting of paraffins, desulfurization, and the dehydrogenation of naphthas, some dehydrocyclization occurs. Most of the industrial work done on this reaction has been devoted to the finding of inexpensive catalysts and optimum operating conditions. The patent literature which has resulted from this work is often repetitious and difficult to evaluate. Wherever possible this review avoids such material in favor of the more critically described work from chemical journals.

II. Scope of the Reaction

A. Benzene System

Except for one instance, the conversion of pentadiene to cyclopentadiene (84), the only monocyclic carbon ring system that has been formed by dehydrocyclization is that of benzene.



1,3-Pentadiene Cyclopentadiene

The formation of cyclopentadiene from 1,3-pentadiene, shown above, is interesting in that the reaction does not seem to be aided by catalysts. Kennedy and Hetzel (84) found that by carrying out the reaction under reduced pressure good conversions to cyclopentadiene were obtained. They showed that the reaction was independent of catalysts and pressure, and suggested dehydrogenation by a free-radical mechanism.

The early work on the pyrolysis of aliphatic compounds to aromatics and the early speculations on the mechanism of such reactions have been thoroughly reviewed by Hurd (73); hence consideration here of this early work will be brief. Berthelot (11, 14, 15) was the first to study in some detail the conversion of acetylene to benzene by pyrolytic condensation. The first dehydrocyclization reaction (pyrolytic) was carried out by Norton and Andrews (109), who showed that small amounts of benzene were present in the products obtained by passing hexane through a hot tube. Although more careful studies of the pyrolysis of aliphatic hydrocarbons were carried out later (73), this approach has proved to be of little value for synthetic work. It was not until the early 1930's that the first patents were issued to cover the use of metal oxides for the conversion of aliphatic hydrocarbons to benzene and its simple derivatives. Taylor (155) has briefly outlined the early patent claims. The first work to be published on the reaction of such metal oxides was that of Moldavskiĭ in 1936 (105). The potential importance of the dehydrocyclization reaction is illustrated by the calculation (10) showing that if 20 per cent of the gasoline produced in 1940 were dehydrocyclized and the products nitrated, 85,000,000,000 pounds of explosives could be manufactured annually. (Of course, this vast amount of aromatics could just as easily be used for the production of drugs, dyes, plastics, etc.)

Table 1 summarizes the paraffins and olefins that have been dehydrocyclized to aromatic compounds. Under the column headed "aromatic products" the notation "aromatics" indicates that the individual products were not isolated, but that the aromatics were simply determined as a group. It is at once apparent that chromium oxide is the most widely used catalyst, either straight or in combination with other oxides, preferably aluminum. Most of the reactions listed have been carried out in the temperature range 450–550°C.

The only other group of aliphatic compounds which has been successfully dehydrocyclized to aromatic compounds is that of the alcohols. Komarewsky, Riesz, and Thodos (89), working with a chromia–alumina catalyst at 450–475°C., showed that 1-hexanol was converted to benzene, 1-heptanol to toluene, and 1-octanol to a mixture of ethylbenzene, toluene, and xylenes. Repeating this work with pure chromia instead of the alumina-supported material, the reaction was found to take a different course (87), ketones being the final products. A four-step mechanism was suggested: (*1*) dehydrogenation of alcohol to aldehyde, (*2*) aldol condensation, (*3*) loss of carbon monoxide from aldol to give a secondary alcohol, and (*4*) dehydrogenation of the secondary alcohol to a ketone. A small amount of aromatization occurred concurrently, 1-hexanol giving phenol, 1-heptanol giving *o*-cresol, and 1-octanol yielding 2,6-dimethylphenol. No doubt the

TABLE 1

Dehydrocyclization of paraffins and olefins to aromatic compounds

COMPOUND	TYPE OF CATALYST	AROMATIC PRODUCTS	REFERENCES
n-Pentane	Cr_2O_3	Aromatics	(69, 77)
2-Methylpentane	Cr_2O_3	Aromatics	(69)
2,3-Dimethylpentane	Cr_2O_3–Al_2O_3	Toluene	(66)
3-Ethyl-2-methylpentane	Cr_2O_3–Al_2O_3	Ethylbenzene, toluene, *o*- and *m*-xylenes	(66)
3-Ethyl-3-methylpentane	Cr_2O_3–Al_2O_3	Ethylbenzene, toluene, *o*- and *m*-xylenes	(66)
2,2,3-Trimethylpentane	Cr_2O_3–Al_2O_3	*m*-Xylene	(66)
2,3,3-Trimethylpentane	Cr_2O_3–Al_2O_3	*m*-Xylene	(66)
2,2,4-Trimethylpentane	Cr_2O_3–Al_2O_3	*p*-Xylene	(66, 112)
2,2,4-Trimethylpentane	MoO_3–Al_2O_3	Toluene, benzene, xylenes, naphthalene	(51, 52, 134, 160)
2,2,4-Trimethylpentane	Cr_2O_3	Aromatics	(111, 113, 114)
2,2,4-Trimethylpentane	Cr_2O_3–Al_2O_3	Aromatics	(69, 111)
2,3,4-Trimethylpentane	Cr_2O_3–Al_2O_3	*o*- and *p*-Xylenes	(66)
2-Methyl-2-pentene	Cr_2O_3	Aromatics	(40, 154)
3-Methyl-2-pentene	Cr_2O_3	Aromatics	(40, 154)
2-Ethyl-1-butene	Cr_2O_3	Aromatics	(40, 154)
n-Hexane	Cr_2O_3	Benzene	(54, 69, 105)
n-Hexane	Pt–carbon	Benzene	(82)
n-Hexane	Mo_2O_3–Al_2O_3	Benzene	(51)
2-Methylhexane	Cr_2O_3	Toluene	(69)
2-Methylhexane	Pt–carbon	Toluene	(82)
3-Ethylhexane	Cr_2O_3–Al_2O_3	Ethylbenzene	(66)
2,2-Dimethylhexane	Cr_2O_3–Al_2O_3	*m*-Xylene	(66, 91)
2,2-Dimethylhexane	Pt–carbon	Toluene, *m*-xylene	(80)
2,3-Dimethylhexane	Cr_2O_3–Al_2O_3	*o*- and *p*-Xylenes	(66, 91)
3,3-Dimethylhexane	Cr_2O_3–Al_2O_3	Ethylbenzene, toluene, *o*-, *m*-, and *p*-xylenes	(66)
3,3-Dimethylhexane	Pt–carbon	1,1-Dimethylcyclohexane, toluene, *m*-xylene	(79, 80)
2,5-Dimethylhexane	Active carbon, Fe–carbon	*p*-Xylene	(104)
2,5-Dimethylhexane	Cr_2O_3	*p*-Xylene	(69, 105)

2,5-Dimethylhexane	Pt–carbon	*p*-Xylene	(78, 81)
1-Hexene	Cr_2O_3	Benzene	(69)
2-Hexene	Cr_2O_3	Benzene	(69)
2-Methyl-2-hexene	Cr_2O_3	Aromatics	(113, 114)
5-Methyl-2-hexene	Cr_2O_3	Aromatics	(40, 154)
2,2-Dimethyl-3-hexene	Cr_2O_3–Al_2O_3	*m*-Xylene	(91)
1-Hexyne	Cr_2O_3–Al_2O_3	Benzene	(92)
Heptane	Cr_2O_3	Toluene	(40, 54, 65, 69, 105, 111, 113, 114, 132, 145, 154, 159, 160)
Heptane	Cr_2O_3–Al_2O_3	Toluene	(20, 66, 100, 111, 147, 153, 160)
Heptane	CeO_2–Al_2O_3; V_2O_5–Al_2O_3; ThO_2–Al_2O_3	Toluene	(20, 153)
Heptane	Pd–Cr_2O_3; Ni–Cr_2O_3; Cu–Cr_2O_3; ZnO–Cr_2O_3; MoO_2–Cr_2O_3; MnO–Cr_2O_3; SiO_2–Cr_2O_3; ZrO_2–Cr_2O_3; SnO_2–Cr_2O_3; CeO_2	Toluene	(37, 153)
Heptane	MoO_3; V_2O_5–Mo_2O_3–Al_2O_3; V_2O_5–Cr_2O_3–Al_2O_3; Cr_2O_3–Mo_2O_3–Al_2O_3; V_2O_5–Cr_2O_3–Mo_2O_3–Al_2O_3	Toluene	(54)
Heptane	MoO_3–Al_2O_3	Toluene	(51, 65, 143, 144, 160)
Heptane	FeF_3–MnF_2	Toluene	(75)
Heptane	Cr_2O_3–K_2O–Al_2O_3	Toluene	(1)
Heptane	V_2O_3–Al_2O_3	Toluene	(136, 153, 160)
Heptane–heptene	Ammonium aluminomolybdate; ammonium thoriomolybdate; ammonium chromomolybdate; ammonium cobaltomolybdate; ammonium nickelomolybdate; ammonium vanadomolybdate; ammonium phosphovanadomolybdate; aluminum phosphate; phosphomolybdic acid	Toluene	(65)
2-Methylheptane	Cr_2O_3–Al_2O_3	*m*-Xylene	(66, 91)
3-Methylheptane	Pt–carbon	Ethylbenzene, xylenes	(82)
3-Methylheptane	Cr_2O_3	Aromatics	(69)
3-Methylheptane	Cr_2O_3–Al_2O_3	Ethylbenzene, *o*- and *p*-xylenes	(66)

TABLE 1—*Concluded*

COMPOUND	TYPE OF CATALYST	AROMATIC PRODUCTS	REFERENCES
4-Methylheptane	Pt–carbon	*m*-Xylene	(82)
2,2-Dimethylheptane	Cr_2O_3–Al_2O_3	*m*-Xylene	(91)
1-Heptene	Cr_2O_3	Toluene	(40, 69, 113, 114, 154)
1-Heptene	Cr_2O_3–SnO_2	Toluene	(153)
1-Heptene	V_2O_3–Al_2O_3	Toluene	(135)
2-Heptene	Cr_2O_3	Aromatics	(69)
3-Heptene	Cr_2O_3	Aromatics	(40, 154)
3-Heptene	V_2O_3–Al_2O_3	Toluene	(135)
2-Methyl-6-heptene	Cr_2O_3–Al_2O_3	Toluene	(91)
3-Methyl-3-heptene	Cr_2O_3	Aromatics	(113)
1-Heptyne	Cr_2O_3–Al_2O_3	Toluene, benzene	(92)
Octane	Cr_2O_3	Ethylbenzene, *o*-xylene	(69, 105)
Octane	Cr_2O_3–Al_2O_3	Ethylbenzene, toluene, *o*-, *m*-, and *p*-xylenes	(54, 66)
Octane	Cr_2O_3–CoO–Al_2O_3; Cr_2O_3–CoO	Aromatics	(148, 148a)
Octane	Ni–Al_2O_3	Toluene	(88)
Octane	Active carbon, Fe–carbon	*o*-Xylene	(104)
Octane	Pt–carbon	Aromatics	(81)
Octane	TiO_2; MoO_2; ZnO; MoS_2	*o*-Xylene	(106)
4-Methyloctane	Pt–carbon	Propylbenzene, *m*-ethylmethylbenzene, aromatics	(82)
2,6-Dimethyloctane	Pt–carbon; MoS_2	*p*-Cymene	(83)
2,7-Dimethyloctane	Cr_2O_3	*m*-Isopropylmethylbenzene	(105)
2,7-Dimethyloctane	Ni–Al_2O_3	Aromatics	(83)
2,7-Dimethyloctane	Pt–carbon	*m*-Isopropylmethylbenzene	(81)
Octene	Cr_2O_3	*o*-Xylene	(105)
1-Octene	Cr_2O_3	Aromatics	(40, 154)
1- and 2-Octenes	Cr_2O_3–Al_2O_3	Xylenes	(111)
2-Octene	Cr_2O_3	Aromatics	(40, 69)
Nonane	Cr_2O_3	*n*-Propylbenzene, *o*-ethylmethylbenzene	(69)

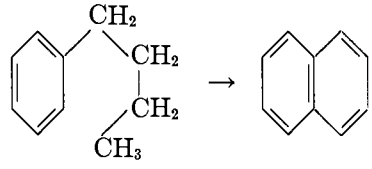
Nonane	Cr_2O_3–Al_2O_3	*n*-Propylbenzene, *o*-ethylmethylbenzene, indene	(66)
n-Butylcyclopentane	Pt–carbon	*o*-Ethyltoluene	(81)
sec-Butylcyclopentane	Pt–carbon	Aromatics	(81)
Decane	Ni–Al_2O_3	Toluene	(88)
Decane	Cr_2O_3–Al_2O_3	Benzene, toluene, ethylbenzene, *o*-xylene, propylbenzene, butylbenzene, ethyl-*o*-xylene, diethylbenzene, *o*-methylpropylbenzene, naphthalene	(66, 68, 142)
Decane	Cr_2O_3	Aromatics	(77)
Isoamylcyclopentane	Pt–carbon	Aromatics	(81)
Hendecane	Al_2O_3	Aromatics	(72)
n-Tetradecane	Cr_2O_3–Al_2O_3	Anthracene and phenanthrene are two of many compounds obtained	(66)

reason why other functional groups have not been investigated is due to the instability of the common groups at temperatures of 400–500°C.

B. POLYNUCLEAR AROMATIC SYSTEMS

1. Naphthalene

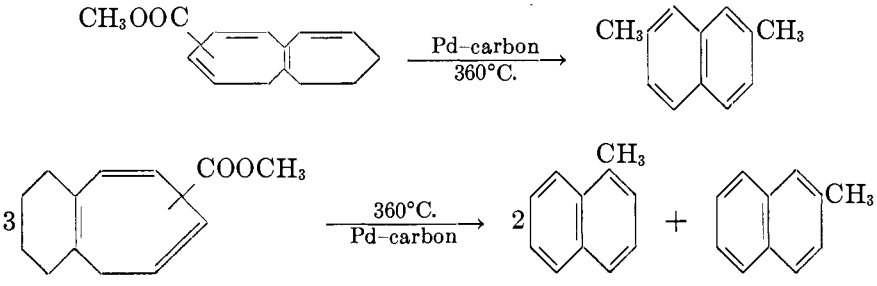
It has long been known (74) that naphthalene results from the pyrolysis of hydrocarbons or mixtures of hydrocarbons. Ferko (38) in 1887 found that ethylbenzene yielded naphthalene along with styrene, biphenyl, anthracene, phenanthrene, toluene, and benzene. More recent work with chromia catalysts at about 500°C. has shown that butylbenzene may be dehydrocyclized to naphthalene in yields as high as 50 per cent per pass (66, 101, 105, 108).



Butylbenzene Naphthalene

Pyrolysis of 1-phenyl-1,3-butadiene (96) also yields naphthalene, which is likewise formed when *o*-diethylbenzene is treated with a zinc oxide–calcium oxide on alumina catalyst at 600°C. (70). Cyclopentene undergoes bimolecular dehydrocyclization at 450°C. in the presence of a vanadium trioxide on alumina catalyst to give naphthalene (133). Passing 1,2-benzocyclo-1-heptene (19) over lead oxide on pumice gave naphthalene.

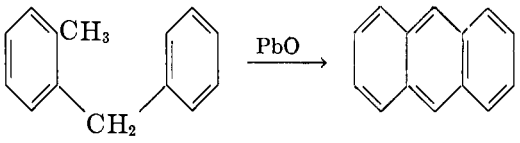
The only substituted naphthalenes which have been prepared by dehydrocyclization are the methylnaphthalenes, obtained by the rearrangement-dehydrocyclization of seven-membered rings as follows (71):



2. Anthracene and phenanthrene

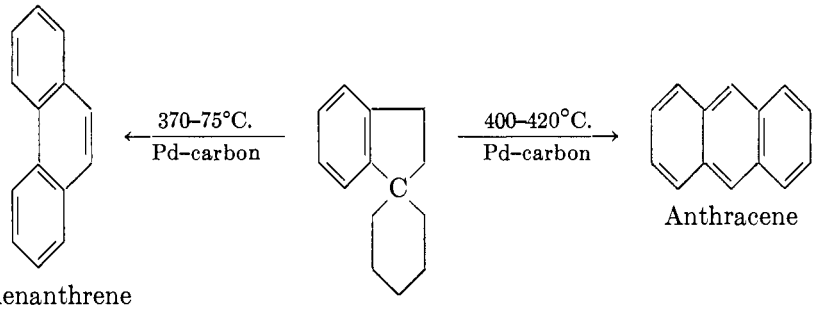
Anthracene has been obtained by the pyrolysis of toluene (12, 43), ethylbenzene (38), or a mixture of benzene and styrene (13). The catalytic dehydrogena-

tion of tetradecane also gives some anthracene as well as phenanthrene (66). Good conversions to anthracene were obtained (7) by the dehydrocyclization of *o*-benzyltoluene with lead oxide as follows:



o-Benzyltoluene Anthracene

Anthracene has also been formed by rearrangement-dehydrocyclization from spirocyclohexane-1,1-indane (95), as indicated below:

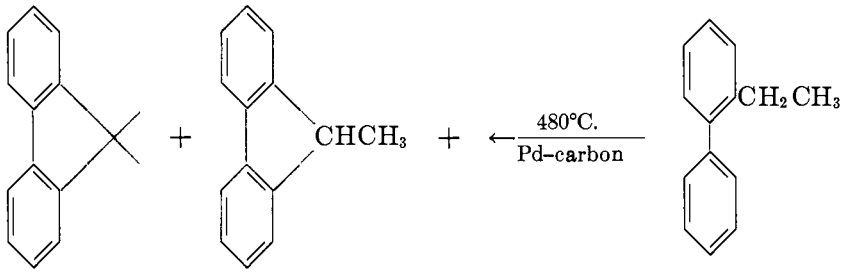


Phenanthrene Anthracene

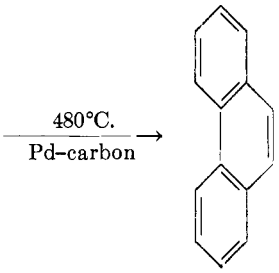
Thus, depending on the conditions employed, the above reaction can take two courses. In this connection it is interesting to note that 1,4-dibutylbenzene (101) is dehydrogenated at 500°C. with chromium oxide to give a 17 per cent yield of phenanthrene with the formation of no anthracene. This is in line with the greater resonance stabilization of phenanthrene compared to anthracene (130 *vs.* 116 kcal.).

Phenanthrene has been prepared by a variety of methods, both pyrolytic and catalytic. Graebe (43) obtained some phenanthrene by the pyrolysis of toluene, stilbene, or bibenzyl (42). Zelinskiĭ and Titz (164, 165), using a platinum–carbon catalyst, dehydrogenated 1,2-diphenylethane, 1,2-diphenylethylene, and 1,2-dicyclohexylethane to phenanthrene. Mattox and Grosse (101) found when using a chromium-on-alumina catalyst at 550°C. that the reaction took a different course and that 1,2-diphenylethane yielded no phenanthrene but instead gave toluene and diphenylethylene. Dewar and Read (28), in attempting to extend this reaction, dehydrogenated 1,2-di(*p*-methoxyphenyl)ethane and the corresponding olefin and obtained in each case only phenanthrene rather than the expected 2,7-dimethoxyphenanthrene. Pyrolysis of *o,o'*-bitolyl (103) gives phenanthrene. Orchin (116) has shown that where both the phenanthrene and the fluorene ring have the possibility of being formed from 2-ethylbiphenyl,

formation of the fluorene ring takes precedence, fluorene and 9-methylfluorene being the main products with only a small amount of phenanthrene forming:



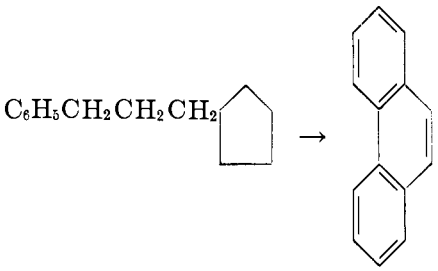
Fluorene 9-Methylfluorene 2-Ethylbiphenyl



Phenanthrene

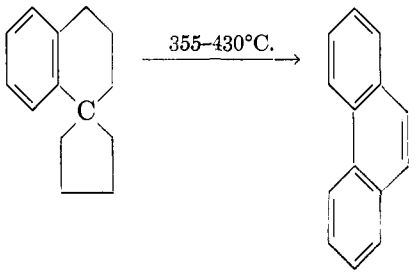
Graebe (47) had previously shown that conducting either 9-ethyl- or 9-methylfluorene through a hot tube gave some phenanthrene. Barbier (6) discovered that ethylene and biphenyl undergo bimolecular dehydrocyclization (pyrolytic) to give phenanthrene.

A number of reactions have been conducted in which dehydrocyclization occurs by way of rearrangement. Denisenko (25) processed 3-cyclopentyl-1-phenylpropane at 315°C. over a platinum–carbon catalyst, obtaining phenanthrene:

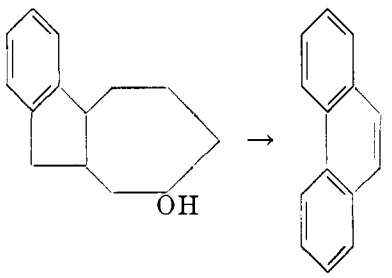


Phenanthrene

Spirocyclopentane-1,1-tetralin (93) undergoes dehydrogenation with rearrangement as follows:

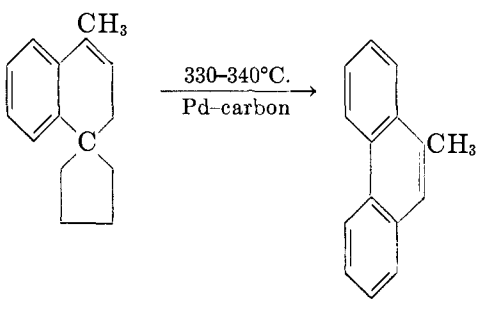


Cyclohexylcycloheptylmethane undergoes rearrangement-dehydrocyclization (34) at 300°C. on platinum–carbon to give phenanthrene. Nunn and Rapson (110) observed the following rearrangement-dehydrocyclization:



Phenanthrene

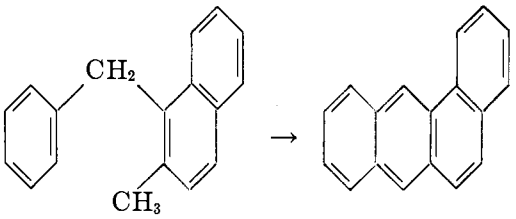
A few instances are recorded where substituted anthracenes and phenanthrenes have been formed by dehydrocyclization. The pyrolysis of *p*-xylene or 4,4-dimethylbibenzyl (103) has been reported to yield 2,6-dimethylanthracene. Pyrolysis of ditolylmethane or ditolylethane yields 2-methylanthracene (39). Processing benzylmethylphenylcarbinol over platinum–carbon gave 9-methylphenanthrene (163). 1-Phenyl-3-(*o*-methylcyclopentyl)propane rearranges with dehydrogenation at 315°C. on platinum–carbon to give 1-methylphenanthrene (26). 1-(3-Cyclohexylpropyl)-2-methylcyclopentane under the same conditions gives the same product (27). Levitz and Bogert (94) have shown that 9-methylphenanthrene may be obtained by the following rearrangement-dehydrocyclization:



9-Methylphenanthrene

Pyrolysis of a mixture of styrene and xylene yields a methylanthracene (91a). Methylanthracenes were also obtained by pyrolyzing the sulfuric acid condensation products between styrene and various methylbenzenes (91a).

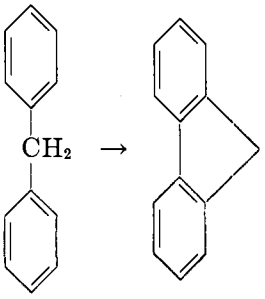
Pyrolysis of 1-benzyl-2-methylnaphthalene (30) yields 1,2-benzanthracene:



1,2-Benzanthracene

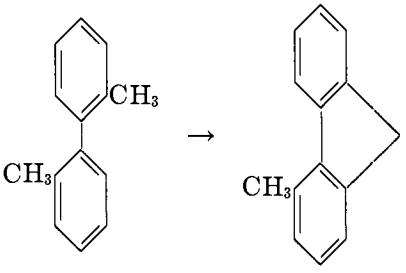
3. Fluorene

Graebe (42, 44) first prepared fluorene pyrolytically by passing diphenylmethane through a glowing tube:



Diphenylmethane Fluorene

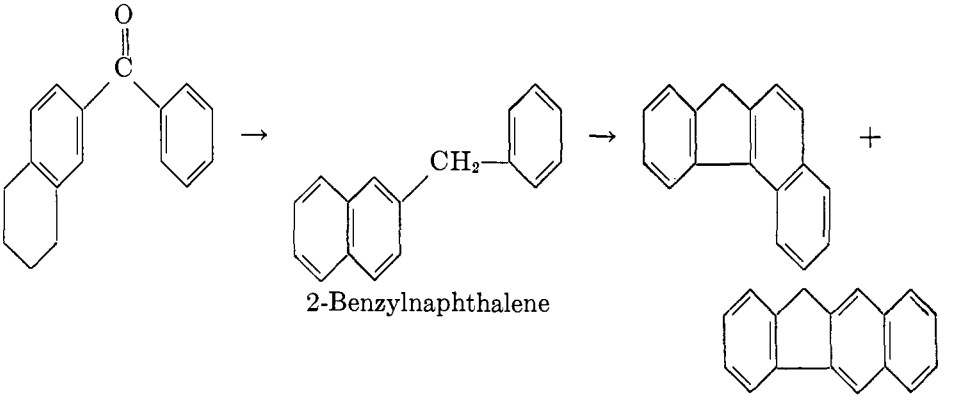
Little hydrogen is evolved in this reaction, it being consumed in the splitting of the diphenylmethane into benzene and toluene. This same reaction has been carried out catalytically with diphenylmethane and with dicyclohexylmethane (165), using a platinum–carbon catalyst at 300°C. Orchin (115) has dehydrogenated 2-methylbiphenyl to fluorene with a palladium–carbon catalyst at 450°C., while under the same conditions *o,o'*-bitolyl (122) gave 4-methylfluorene.



o,o'-Bitolyl 4-Methylfluorene

The reaction takes a quite different course when dehydrogenation is carried out with sulfur (9) in the liquid phase. Under these conditions dehydrogenation occurs between the methyl groups, giving phenanthrene. Orchin and Woolfolk

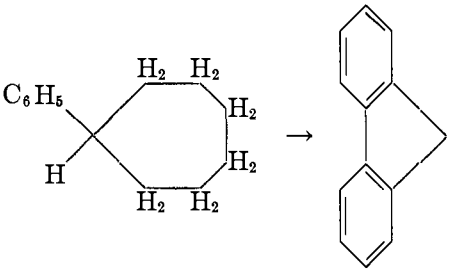
(122) were unable to find any phenanthrene in the vapor-phase dehydrocyclization. Dehydrogenation of 2-ethylbiphenyl, as mentioned earlier, yields both fluorene and 9-methylfluorene. By processing benzoyltetrahydronaphthalene over a chromia–alumina catalyst, both 2,3-benzfluorene and 3,4-benzfluorene were obtained along with naphthalene and 2-benzylnaphthalene (123):



2-Benzylnaphthalene

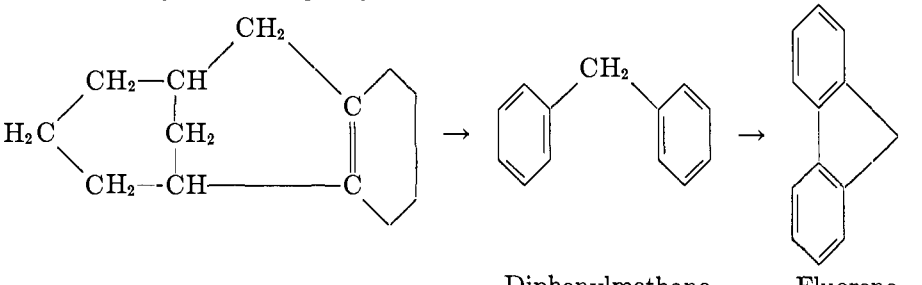
The major product from the reaction was 2-benzylnaphthalene, suggesting that first dehydrogenation of the nucleus occurred and that the hydrogen formed served to reduce the keto group, after which cyclization occurred. A similar reaction occurs with butyrophenone (101), which undergoes catalytic dehydrogenation to give 30 per cent conversion to naphthalene.

The rearrangement-dehydrocyclization of phenylcycloheptane (131) gives fluorene as follows:



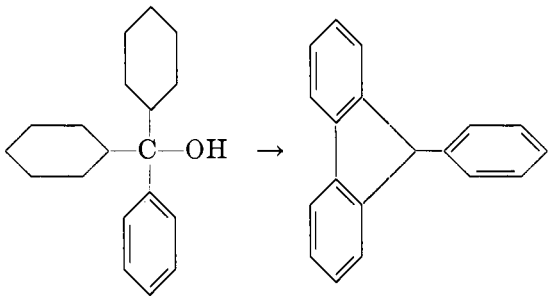
Phenylcycloheptane Fluorene

Dehydrogenation (33) of 2,3-benzbicyclo[3,3,1]-2-nonene has been shown to give fluorene by way of diphenylmethane:



Diphenylmethane Fluorene

Combined dehydrogenation and dehydration of dicyclohexylphenylcarbinol yield 9-phenylfluorene (163),

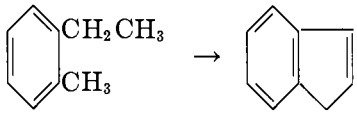


Dicyclohexylphenylcarbinol 9-Phenylfluorene

while the completely aromatic triphenylcarbinol gives no fluorene, only triphenylmethane. Possibly more drastic conditions would convert the triphenylmethane into 9-phenylfluorene. Methyldiphenylcarbinol gave 9-methylfluorene and ethyldiphenylcarbinol gave the corresponding ethylfluorene.

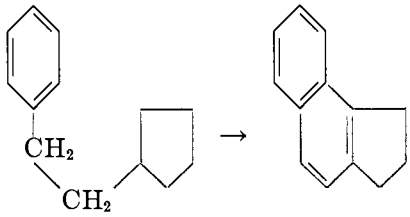
4. Indene

Indene has been made by the dehydrocyclization of *o*-ethyltoluene (35):



o-Ethyltoluene Indene

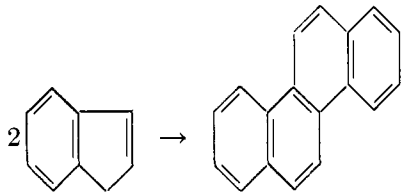
The reaction is carried out by means of a chromia catalyst at temperatures of 540–620°C. or with an iron oxide catalyst at 650–700°C. With ethylxylenes the products were methylindenes. *n*-Propylbenzene also undergoes dehydrocyclization, as expected, to give indene (66). Denisenko (25) found that 2-cyclopentyl-1-phenylethane dehydrogenates to give a compound that is probably 4,5-benzindane:



On pyrolysis 2-methyl-1-phenylethylcyclopentane (27) appears to yield 9-methyl-4,5-benzindene.

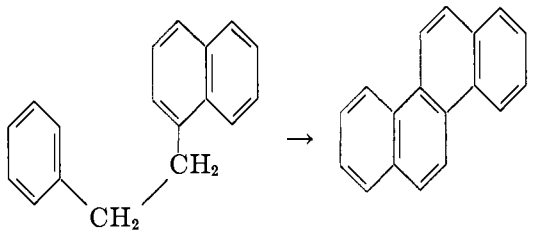
5. Chrysene

Chrysene may be prepared by the bimolecular dehydrocyclization of indene, either pyrolytically (149) or catalytically (99).



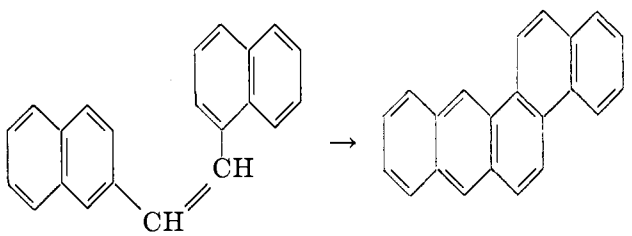
Indene Chrysene

Chrysene has also been prepared by the pyrolytic dehydrocyclization of 1-phenyl-2-naphthylethane by Graebe and Bungener (48).



2-Naphthyl-1-phenylethane Chrysene

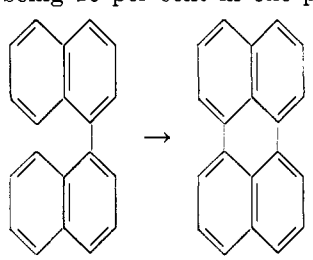
The benzchrysene, picene, has been similarly prepared by Hirn (67) as follows:



Picene

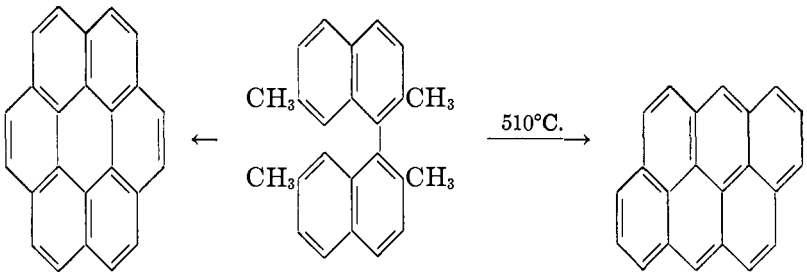
6. Miscellaneous

Orchin and his colleagues have been investigating the synthesis of polynuclear aromatic hydrocarbons by dehydrocyclization in order to understand better the occurrence of such compounds in coal tar. They have pointed out (120) that many of the compounds isolated and identified in the products from the carbonization of coal can be accounted for by assuming their formation from simpler compounds present in coal. Orchin and Friedel (117) prepared perylene by the dehydrogenation of α,α'-binaphthyl over a palladium–carbon catalyst at 490°C., the conversion being 10 per cent in one pass.



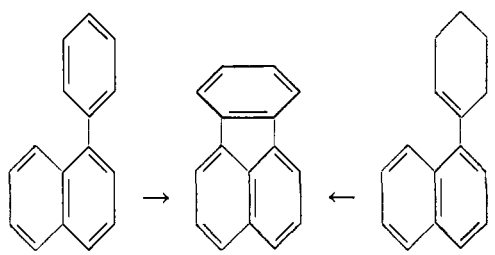
α,α'-Binaphthyl Perylene

An attempt to extend this reaction to the synthesis of coronene (117) by the dehydrogenation of the tetramethyl analog did not take the expected course, and the product formed appeared to be anthanthrene.



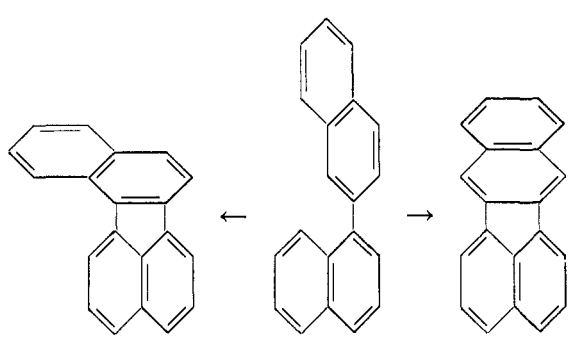
Coronene Anthanthrene

Dehydrogenation of 1-phenylnaphthalene with chromia gave fluoranthene, as did 1-cyclohexenylnaphthalene (118).



1-Phenyl-naphthalene Fluoranthene 1-Cyclohexenyl-naphthalene

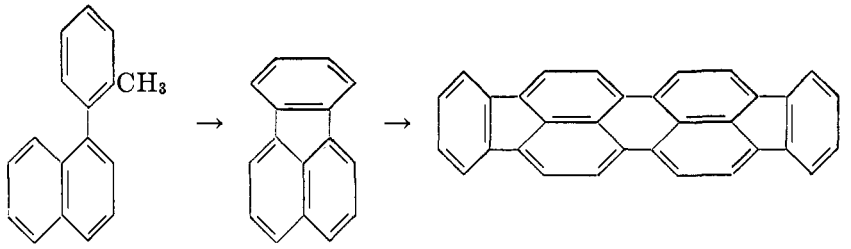
With α,β'-binaphthyl under similar conditions two compounds were obtained which appear to be benzfluoranthenes:



α,β'-Binaphthyl

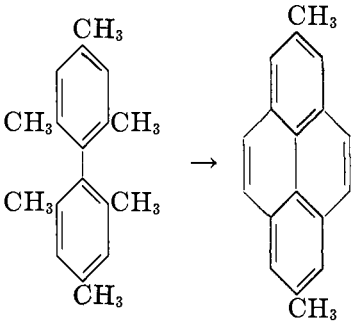
In an attempt to dehydrogenate 1-*o*-tolylnaphthalene to obtain a methylfluoranthene the reaction took an unexpected turn and yielded a compound which appeared to be periflanthene (120). It was suggested that, possibly, fluoranthene

was first formed and then underwent bimolecular dehydrocyclization to give periflanthene:



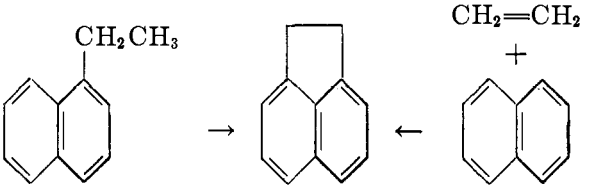
1-*o*-Tolylnaphthalene Fluoranthene Periflanthene

Recently it has been shown (121) that small amounts of dimethylpyrene can be obtained by the dehydrocyclization of bimesityl:



Bimesityl Dimethyl-pyrene

Acenaphthene was one of the earliest aromatic molecules to be made by pyrolytic dehydrogenation. It may be formed by passing either 1-ethylnaphthalene (16) or a mixture of naphthalene and ethylene (38) through a hot tube.

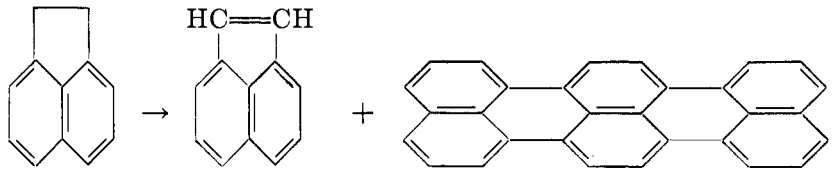


1-Ethylnaph-thalene Acenaph-thene Naphtha-lene

Pyrolysis of benzene and ethylene (13) also gives some acenaphthene.

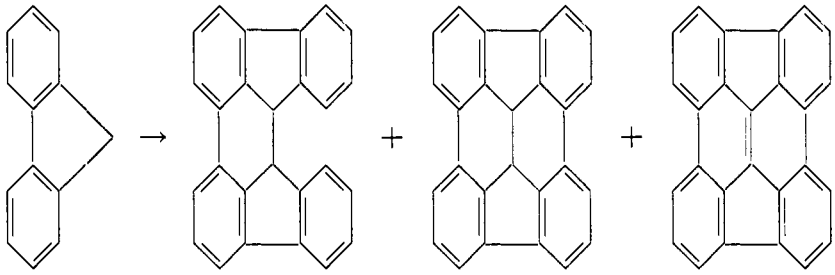
Acenaphthene itself undergoes dehydrogenation and decomposition accompanied by cyclization at high temperatures to give acenaphthylene and chalcacene

(29). Apparently acetylene is first removed and then the chalcacene is formed by trimolecular condensation.



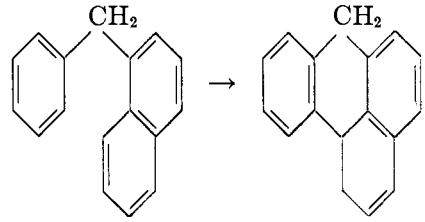
Acenaphthylene Chalcacene

Fluorene (31) undergoes bimolecular dehydrocyclization under reduced pressure and at high temperature to yield a mixture of three products, as follows:



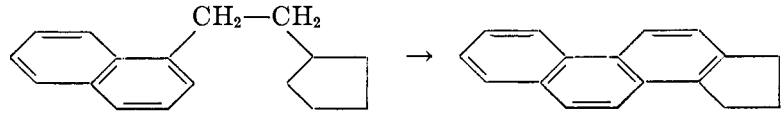
Fluorene Difluorenylene Dihydrorubicene Rubicene

Scholl and Seer (146) pyrolyzed 1-benzylnaphthalene and thus converted it into dihydrobenzanthrene.

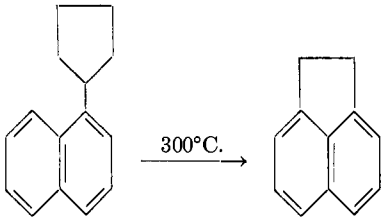


1-Benzylnaphthalene Dihydrobenzanthrene

Dehydrogenation of 1-α-naphthyl-2-cyclopentylethane (5) with platinum–carbon at 320°C. goes according to the following equation,

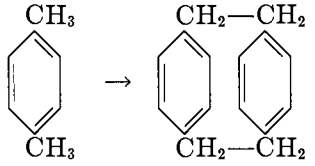


while 1-cyclopentylnaphthalene (5) apparently loses two carbon atoms during dehydrocyclization at 300°C. as indicated below:



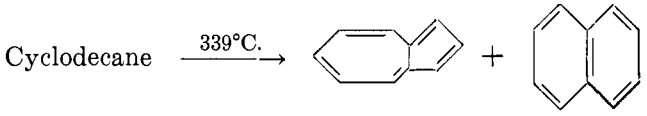
1-Cyclopentylnaphthalene

Recently Brown and Farthing (21) discovered a novel reaction in which *p*-xylene by low-pressure pyrolysis gives a substance which they have called di-*p*-xylylene.



p-Xylene Di-*p*-xylylene

An interesting transannular dehydrocyclization has been discovered by Prelog and Schenker (137a). By passing cyclodecane or cyclodecene over a palladium on carbon catalyst a 20 per cent conversion to azulene was obtained. Naphthalene was formed as a by-product.



Azulene Naphthalene

Cyclodecanol and cyclodecanone at higher temperatures with alumina and palladium also gave azulene and naphthalene.

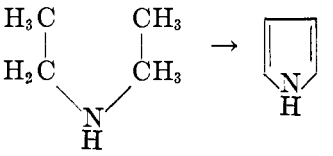
C. HETEROCYCLES

1. Nitrogen heterocycles

(a) Pyrrole and pyridine

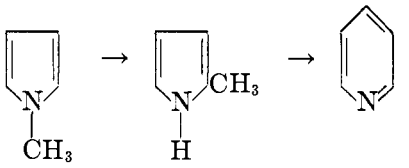
It has been known since the very early work in organic chemistry that a number of heterocyclic molecules can be made by the pyrolytic dehydrogenation of suitable starting compounds; however, very little work has been conducted using dehydrogenation catalysts. No doubt a reinvestigation of some of these pyrolytic dehydrogenations with modern catalysts would reveal more rapid and selective reaction conditions.

Pyrrole has been reported to be formed from the pyrolytic dehydrogenation of diethylamine (8).



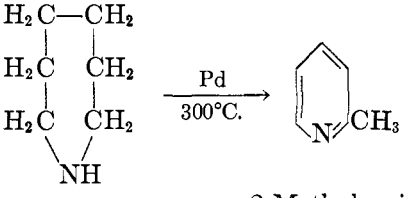
Diethylamine Pyrrole

Pyridine has been made by a number of rearrangement-dehydrocyclizations. The pyrolysis of *N*-methylpyrrole (126, 127) gives pyridine by way of 2-methylpyrrole.



N-Methylpyrrole 2-Methylpyrrole Pyridine

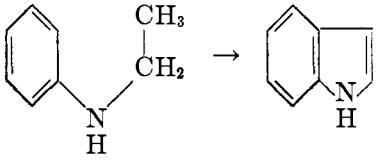
N-Benzylpyrrole (127) gives 3-phenylpyridine rather than *N*-phenylpyridine. Hoping to take advantage of this type of rearrangement, Pictet and Rilliet (130) pyrolyzed *N*,*N*-dipyrrolylmethane in an attempt to get nicotine; however, only decomposition products were obtained. 2-Methylpyridine has been obtained by dehydrogenation with palladium on asbestos as follows (32):



2-Methylpyridine

(b) Indole and carbazole

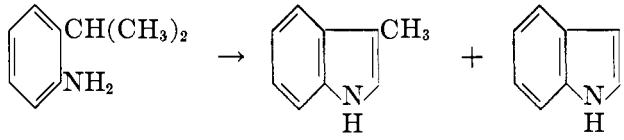
Baeyer and Caro (2) first showed that small amounts of indole could be formed by passing *N*-ethylaniline through a hot tube:



N-Ethylaniline Indole

Later it was found (23) that *N*,*N*-dimethyl-*o*-toluidine was converted by pyrolysis into *N*-methylindole, while *N*-methyl-*o*-toluidine at 330°C. with a nickel

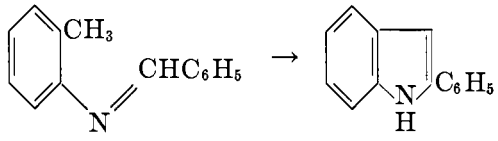
catalyst formed indole (22). More recently (53, 61) the catalytic conversion of *o*-ethylaniline to indole has been investigated. With a chromium oxide–copper on carbon catalyst (61) 32 per cent conversion of *o*-ethylaniline to indole was obtained at 670°C. Gresham and Brunner (53) obtained a 31 per cent conversion at 650°C., using a titania gel catalyst. The attempt (61) to extend this reaction to other *o*-alkylanilines was not very successful, the high temperatures necessary for reaction causing the starting material and the products to crack. Thus, *o*-isopropylaniline gave some skatole along with indole:



o-Isopropylaniline Skatole Indole

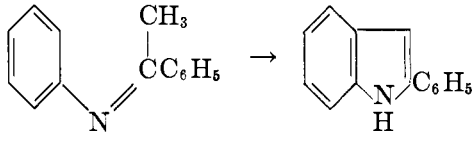
2,4-Diaminoethylbenzene was extensively decomposed, and no aminoindoles could be isolated from this reaction.

Substituted indoles have been made from aromatic anils. Pictet (125) showed that the pyrolysis of benzal-*o*-toluidine yielded 2-phenylindole.



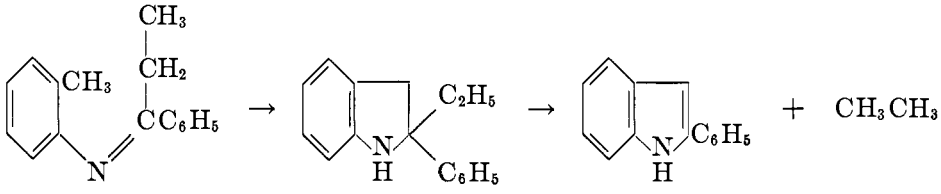
Benzal-*o*-toluidine 2-Phenylindole

This reaction has also been conducted catalytically with chromium catalysts (58). Under these conditions at 550°C., 31 per cent conversion to 2-phenylindole occurred, while anisal-*o*-toluidine gave about 10 per cent 2-(*p*-methoxyphenyl)indole. Acetophenone anil may be dehydrocyclized at 550°C. (58) with the above-mentioned catalyst to give a 22 per cent yield of 2-phenylindole as follows:



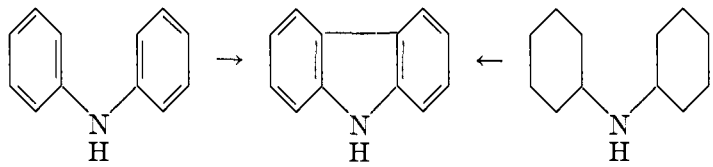
Acetophenone anil 2-Phenylindole

With acetophenone *p*-tolylimide 5-methyl-2-phenylindole was obtained. Propiophenone *o*-toluidine underwent dehydrogenation in an unexpected manner to give 2-phenylindole, the reaction proceeding probably as follows:



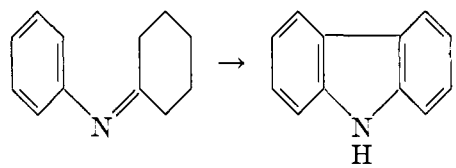
2-Phenylindole

Graebe (41, 45) first prepared carbazole pyrolytically from diphenylamine. Later it was shown (165) that the reaction proceeded smoothly at 300°C. with a platinum catalyst and either diphenylamine or dicyclohexylamine.



Diphenylamine Carbazole Dicyclohexylamine

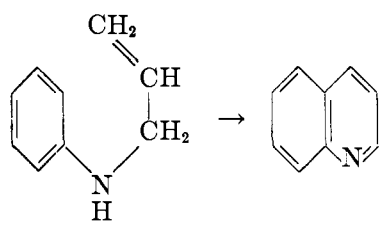
Meyer and Hofmann (103) also pyrolyzed diphenylamine to carbazole but reported that they were unable to carry out the analogous reaction with β-dinaphthylamine. The catalytic dehydrocyclization of *N*-cyclohexylideneaniline also yields carbazole (59), as indicated below:



N-Cyclohexylideneaniline Carbazole

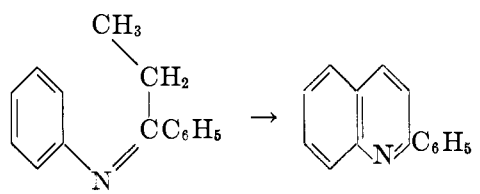
(c) Quinoline and isoquinoline

Quinoline has been prepared (85) by the pyrolytic dehydrocyclization of allylaniline.



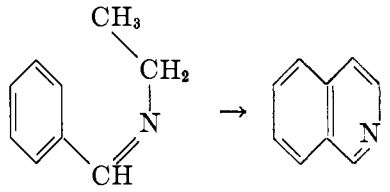
Allylaniline Quinoline

Also, the pyrolytic rearrangement-dehydrogenation of 2-methylindole gives quinoline (127). The catalytic dehydrogenation (58) at 510°C. of propiophenone anil gives 2-phenylquinoline in 20 per cent conversion.



Propiophenone anil 2-Phenylquinoline

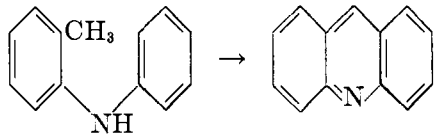
One instance of the formation of isoquinoline by dehydrocyclization is recorded in the pyrolysis (129) of benzylideneëthylamine as follows:



Benzylideneëthylamine Isoquinoline

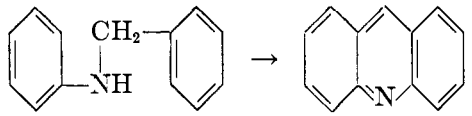
(d) Acridine

The acridine nucleus was first obtained through pyrolytic dehydrogenation by Graebe (46) as follows:



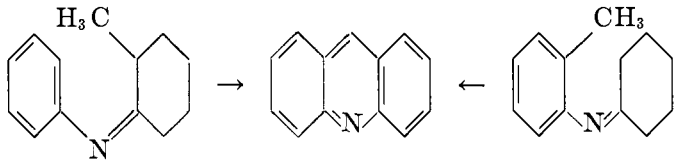
Acridine

Using di-*o*-tolylamine Graebe obtained methylacridine. Later, Meyer and Hofmann (103) obtained a good yield of acridine by the pyrolysis of *N*-benzylaniline:



N-Benzylaniline Acridine

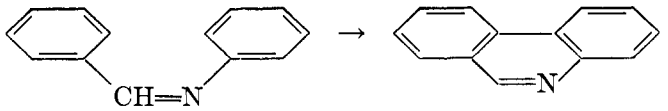
Recently (59) acridine has been synthesized by the catalytic dehydrocyclization of *N*-(2-methylcyclohexylidene)aniline (29 per cent yield) and of *N*-cyclohexylidene-*o*-toluidine (15 per cent) at 550°C:



N-(2-Methylcyclohexylidene)aniline Acridine *N*-Cyclohexylidene-*o*-toluidine

(e) Phenanthridine

Phenanthridine has been prepared by the pyrolysis of benzanilide (103) and by the pyrolytic dehydrogenation of benzalaniline (46, 128).

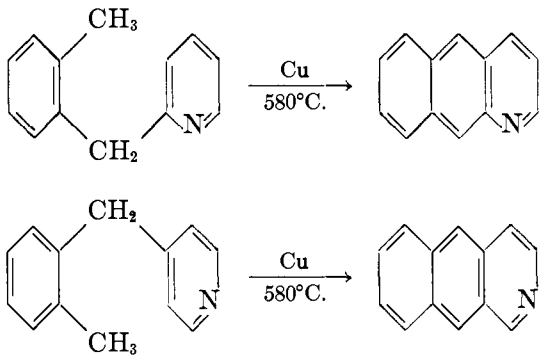


Benzalaniline Phenanthridine

The method illustrated above was the first and for some time the only method for the preparation of phenanthridine. A more careful investigation of this reaction by Pyl (138) showed that large amounts of benzonitrile and benzene were formed, as well as phenanthridine. Phenanthridine may also be prepared by the rearrangement-dehydrocyclization of *N*-methylcarbazole (127). 1- and 3-Methylphenanthridines result from the pyrolysis of benzylidenetoluidines (128a).

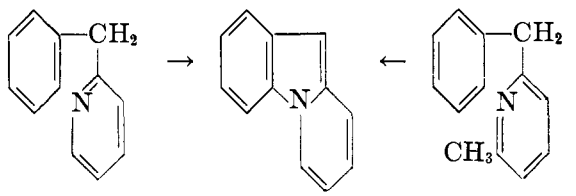
(f) Miscellaneous

von Braun and Nelles (17) have accomplished the synthesis of anthrapyridines by the dehydrogenation of substituted pyridines with a copper catalyst at 580°C. as follows:



They dehydrogenated a mixture of the α- and γ-*o*-methylbenzylpyridines and obtained a mixture of the two anthrapyridines, which they were able to separate by crystallization. Using a mixture of the corresponding α-methylpyridines under the same conditions, they isolated the methylanthrapyridines.

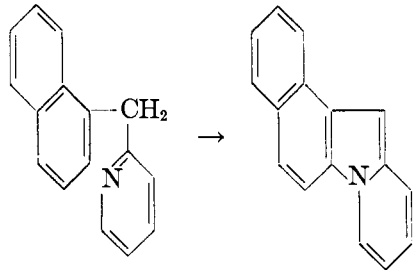
With the benzylpyridines under the same conditions derivatives of indole were obtained (18) in which a nitrogen atom is bonded to three carbon atoms:



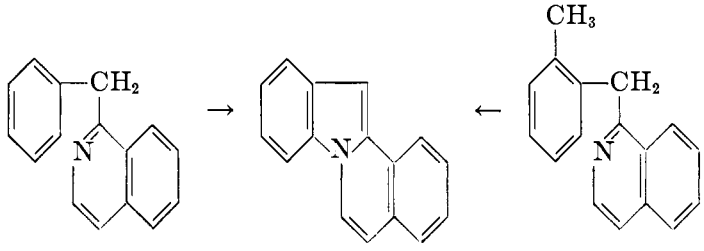
I II III

In the above example a mixture of the α- and γ-benzylpyridines was dehydrogenated, but only the α compound was affected, the γ-benzylpyridine remaining unchanged. With a benzylpicoline (III), dehydrogenation and demethylation

occurred with the formation of II. That the naphthalene ring undergoes dehydrogenation in the same fashion was shown as follows:



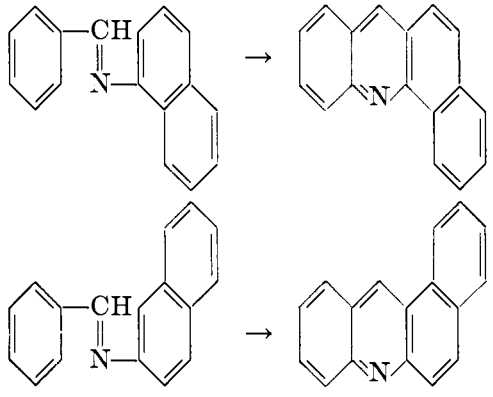
Dehydrogenation of 1-benzylisoquinoline was also investigated and apparently proceeds as follows:



1-Benzylisoquinoline

The 1-*o*-methylbenzylisoquinoline suffers demethylation along with dehydrogenation to give the same product as benzylisoquinoline.

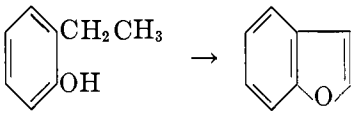
Pictet and Erlich (128a) pyrolyzed the α- and β-benzalnaphthylamines to what they supposed were α- and β-chrysidines; however, it was later shown (161a) that the products were α- and β-naphthacridines, the reactions apparently occurring as follows:



2. Oxygen heterocycles

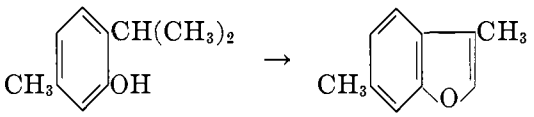
The oxygen heterocycles synthesized by dehydrocyclization are limited to benzofuran and dibenzofuran (phenylene oxide) and their simple derivatives.

Benzofuran can be formed by the catalytic dehydrocyclization of *o*-ethylphenol at about 600°C., using either palladium (62) or chromium oxide–copper on carbon (63) catalysts. Conversions of 10–14 per cent benzofuran were obtained.



o-Ethylphenol Benzofuran

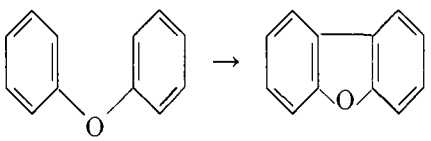
With *o*-allylphenol, a 31 per cent yield per pass of 2-methylbenzofuran was obtained (62), while thymol gave a 17 per cent yield of 3,6-dimethylbenzofuran (63):



Thymol 3,6-Dimethylbenzofuran

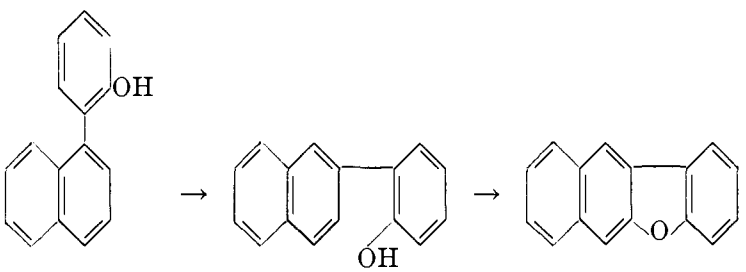
Dehydrogenation of isopropylphenol (63) gave an 18 per cent yield of 3-methylbenzofuran.

Pyrolysis of diphenyl ether (50, 103) yields dibenzofuran. Very little hydrogen is evolved in this reaction, it being consumed in the hydrogenolysis of the diphenyl ether to phenol and benzene.



Diphenyl ether Dibenzofuran

Orchin and Reggel (119) dehydrogenated 1-(*o*-hydroxyphenyl)naphthalene over a chromia–alumina catalyst at 490°C. with the following result:

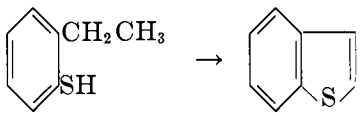


3. Sulfur heterocycles

Thiophenes have been prepared by the reaction of hydrocarbons, saturated and unsaturated, with sulfur or hydrogen sulfide (141). The mechanism of this reaction is very complex; although it could conceivably involve a dehydrocyclization reaction, the subject is not covered in this review. A somewhat more straight-

forward case is that of the cyclization of *n*-propyl disulfide to β,β-dimethylthiophene (73, p. 703).

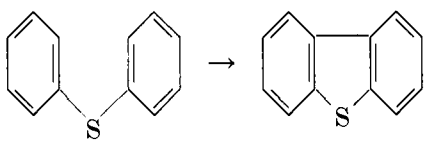
Thianaphthene (benzothiophene) and 2-methylthianaphthene have been obtained by the dehydrocyclization of *o*-ethylthiophenol and *o*-*n*-propylthiophenol (57) with a chromia–alumina catalyst at 450°C. A yield of thianaphthene of 42 per cent was obtained.



o-Ethylthiophenol Thianaphthene

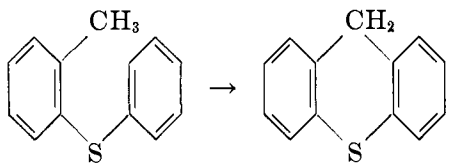
Treatment of styrene with hydrogen sulfide in the presence of an iron sulfide catalyst at 600°C. gave excellent yields of thianaphthene (107). Ethylbenzene and hydrogen sulfide under similar conditions (60) also gave thianaphthene.

Graebe (44) obtained dibenzothiophene by the pyrolysis of diphenyl sulfide:



Diphenyl sulfide Dibenzothiophene

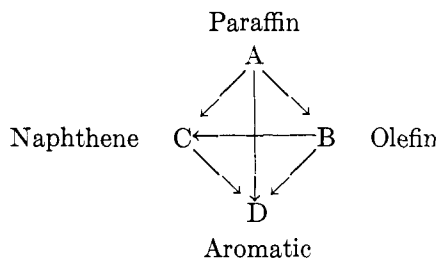
Thioxanthene has been made by the pyrolysis of phenyl *o*-tolyl sulfide (49).



Phenyl *o*-tolyl sulfide Thioxanthene

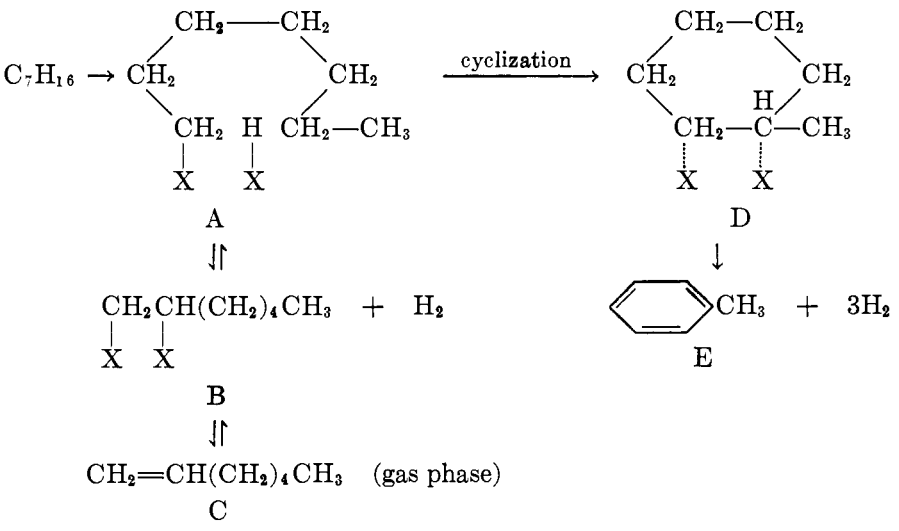
III. Mechanism of the Reaction

The details of the mechanism of the catalytic dehydrocyclization reaction are still not completely understood. Unfortunately not a great amount of work has been done on this aspect of the reaction and that which has been done is limited almost entirely to the conversion of simple paraffins and olefins into benzene and its alkyl derivatives. There are a number of paths such a reaction might take, and the following diagram (69) outlines the possibilities:



So far, neither naphthenes nor cyclic olefins, with one exception, have been isolated nor have they been expected, since Balandin and Brussow (4) showed that the rates of dehydrogenation of these compounds are much greater than for the dehydrogenation of the paraffins or the cyclization of the olefins. The one instance of the isolation of a naphthene was reported by Kazanskiĭ, Liberman, and Batuev in the dehydrogenation of 3,3-dimethylhexane (80). Using a platinum–carbon catalyst and operating at 300°C. they were able to isolate a 3 per cent yield of 1,1-dimethylcyclohexane; on this basis they suggested that naphthenes are intermediates in the dehydrocyclization reaction. Komarewsky and Shand (91) attempted to isolate naphthenes from the dehydrogenation of compounds such as 2,2-dimethylhexane and 2,2-dimethylhexene, which have quaternary carbon atoms and hence would not be capable of forming aromatics without isomerization or splitting off one carbon atom. Working with a chromium oxide catalyst at 465°C. they were unable to isolate any cycloparaffins; very probably their conditions were not mild enough to prevent isomerization.

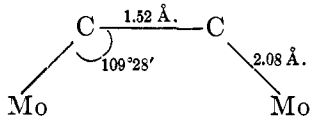
It seems reasonable that the first step in the reaction is the conversion of the aliphatic hydrocarbon into an olefin or an absorbed olefin (54, 66, 69, 132, 134, 150, 151). The next step is probably the conversion of the olefin to a naphthene which may or may not exist in the free state, i.e., the naphthene which is formed on the surface may never escape from the surface but be dehydrogenated to the aromatic, which then leaves the surface. The work of Kazanskiĭ *et al.* above would argue against this. Pitkethly and Steiner (132, 150, 151, 152) have suggested the following mechanism:



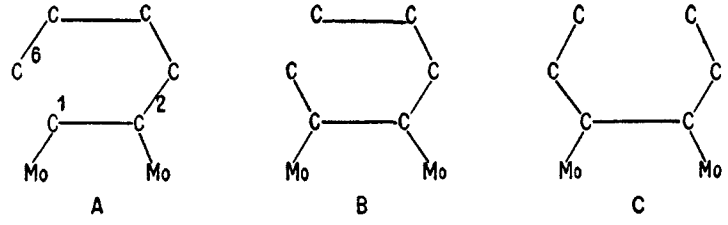
In the above mechanism it is postulated that heptane is first converted to form A, the so-called half-hydrogenated state. Earlier work (36) on the exchange of hydrogen for deuterium with ethylene indicated the existence of such forms.

Whether this is converted directly to the naphthene or first to the olefin, which is then cyclized, it is not possible to say. The naphthene is then very rapidly dehydrogenated to the aromatic. The last step, the dehydrogenation of the naphthenes, has been extensively studied by Balandin, who has postulated (3) that the six hydrogen atoms of cyclohexane, for example, are removed simultaneously to give, in this case, benzene. This is possible because the naphthene can be adsorbed onto the face of an octahedral crystal of the proper dimensions. Balandin has shown that those metals possessing the proper crystal structure with the right interatomic distances are effective catalysts. This so-called multiplet theory does not apply satisfactorily to the oxide catalysts. Balandin's theory has recently been reviewed by Trapnell (157). Pitkethly and Steiner (132) have also suggested an alternative mechanism in which the paraffin is converted directly to the olefin, which then cyclizes to the naphthene, which is in turn dehydrogenated to the aromatic. A similar mechanism involving an olefin intermediate (54) has also been suggested.

Herington and Rideal (65) investigated the dehydrogenation of mixtures of heptane and heptene on various molybdate catalysts (see table 1) and came to the conclusion that the first step in the dehydrocyclization reaction is the conversion of the paraffin to the olefin, which is held to the catalyst by two-point contact as follows:



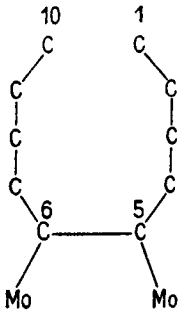
It is pointed out that the different products obtained from the paraffins above hexane can be explained by assuming that the double bond, from the two-point contact position, can migrate rapidly to all positions in the chain. Thus, hexene could be held in the following three ways on a catalyst surface:



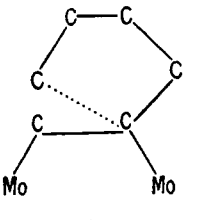
In these configurations it is assumed that only A could lead to ring-closure, since in the other cases the ends of the chain are held away from the catalyst surface. In structure A, if the probability that carbon 1 will react with carbon 6 is p, then the total probability that hexane will react to form an aromatic hydrocarbon is $2p/5$. In the case of the normal paraffins, C_nH_{2n+2}, where n is greater than 9, certain central atoms can react in two ways to give six-membered rings. For example, in the case of n-decane, as indicated below, carbon atom 1 can react with 6 or carbon atom 10 with 5. The probability that the pair 5–6 can

react is therefore $2p$. If it is assumed that reaction cannot occur as shown in E, then the probability for the normal paraffin can be shown to be

$$P = \frac{2(n - 5)p}{n - 1}$$



D



E

For the standard conditions of operation the velocities of conversion for the different hydrocarbons will be proportional to the probabilities of reaction, i.e.,

$$k_1 = \text{constant} \times P$$

where

$$k_1 = \log \frac{1}{1 - \alpha}$$

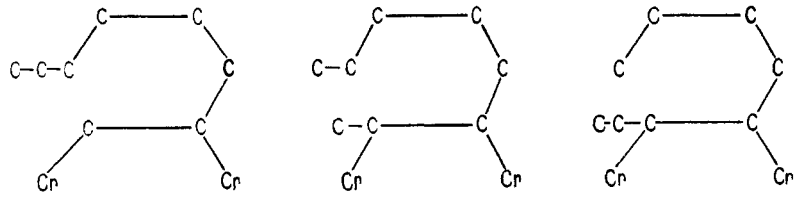
and α = the fraction converted. Taking the constant as 0.282 and using previous experimental data (69), Herington and Rideal obtained agreement between the observed cyclization and the calculated rate of cyclization despite the fact that the isomers formed were not those predicted. Their results are listed in table 2. *n*-Hexane, *n*-heptane, and 2-methylhexane all gave only the expected products, that is, benzene from the first, and toluene from the latter two. *n*-Octane was expected to give mostly ethylbenzene, while actually the main product appeared to be *o*-xylene. 3-Methylheptane was expected to give 33 per cent ethylbenzene, while actually only 5 per cent of this compound was found. 2,5-Dimethylhexane did not yield 100 per cent *p*-xylene as anticipated, and *n*-nonane gave no *n*-propylbenzene.

The lack of agreement between the observed isomers and the predicted ones is due in part to the analytical data used. Other investigators (see table 1) have reported the formation of ethylbenzene from octane and *n*-propylbenzene from nonane.

For the first time, Herington and Rideal were able to obtain evidence for the formation of a five-membered ring compound in the dehydrocyclization of heptane. Only traces of the compound were formed; they suggested that it is a cyclopentadiene or a fulvene.

Herington and Rideal (66), in considering the isomerization during cyclization of the longer-chain paraffins such as octane, have decided that this isomerization must occur during the cyclization step. They reason as follows: Hydrocarbons

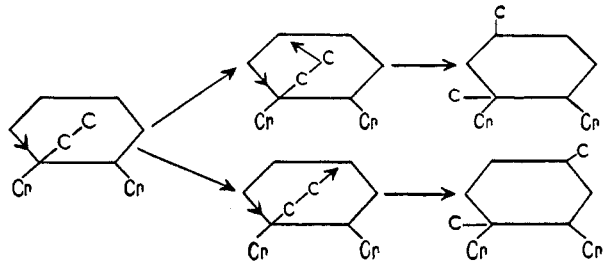
such as ethylbenzene, xylenes, and mesitylene do not undergo isomerization under the conditions of dehydrocyclization, nor do the corresponding naphthenes; therefore, isomerization does not occur after ring-closure. Since the products obtained by cyclizing *n*-octane and octane–octene mixtures on two different catalysts and at two different temperatures were identical, they conclude that isomerization takes place during ring-closure. The following diagrams show the possible ways in which *n*-octane can be adsorbed by two-point contact on a chromium catalyst:



F G H

In table 3 are given the calculated and observed products from the dehydrocyclization of some paraffins (66). The calculations are based on the simple probabilities as stated above.

One can see from diagrams F, G, and H that there are two configurations which would lead to the formation of ethylbenzene and one which would give *o*-xylene. Thus, the expected yield of ethylbenzene according to Herington and Rideal would be 66⅔ per cent and that of *o*-xylene 33⅓ per cent. They reason that the *m*- and *p*-xylenes are formed from ethylbenzene, structure H above being most likely to undergo isomerization by either of the following two paths:



The above mechanism is supported by the calculation of the relative amounts of *m*- and *p*-xylene formed. Plans of the chair and boat forms of cyclohexane are shown below. In these diagrams the triangles represent carbon atoms and the circles represent hydrogen atoms. Attachment of the molecule to the catalyst surface is by two adjacent carbon atoms. In the chair form both faces are similar, a and b having three hydrogen atoms in each plane and six in the periphery. In the boat form there are two hydrogens on one face and four on the other. Therefore, if one hydrogen is replaced by an ethyl group in structure a or b, then each structure has two hydrogens, which might be displaced in the isomerization of the ethyl group. In each instance *m*-xylene would be formed. Structure d could

TABLE 2

Agreement between observed and calculated rates of cyclization

PARAFFIN	P/p	PER CENT CONVERSION TO AROMATICS	
		Observed	Calculated
Pentane	0.00	3	0
n-Hexane	0.40	20	23
2-Methylpentane	0.00	5	0
n-Heptane	0.66	36	35
2-Methylhexane	0.66	31	35
n-Octane	0.84	46	42
3-Methylheptane	0.84	35	42
2,5-Dimethylhexane	1.14	52	52
2,2,4-Trimethylpentane	0.00	3	0
n-Nonane	1.00	58	48

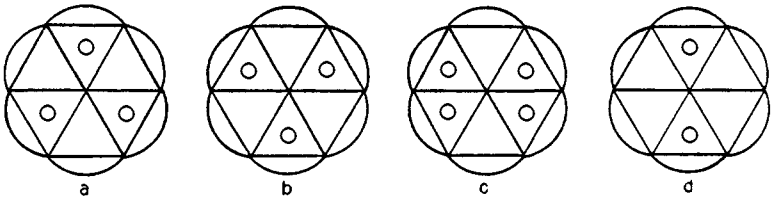
TABLE 3

Products of the dehydrocyclization of some paraffins

HYDROCARBON	PRODUCTS	YIELD	
		Observed	Calculated
		per cent	*per cent*
n-Octane	Monosubstituted benzenes*:	33	66
	o-Xylene	33	33
	m-Xylene	27	0
	p-Xylene	7	0
3-Methylheptane	Monosubstituted benzenes*:	15	33
	m-Xylene	25	33
	p-Xylene	60	33
3-Ethylhexane	Ethylbenzene	100	100

* Ethylbenzene and toluene.

yield only *p*-xylene, and presumably in structure c meta isomerization would be favored over para.

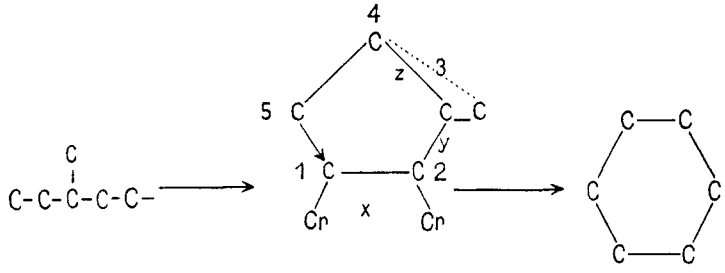


Chair form Boat form

Assuming that at the moment of ring-closure the probabilities are equal for chair and boat forms, then if the probability that the configuration will be a is p, the probability that it will be b is also p, and the total probability that it will be c plus d will be $2p$. There are four ways in which it may be c and two in which it may be d, so the probability for c is $\frac{4}{6}2p$ and for d $\frac{2}{6}2p$. Thus the total

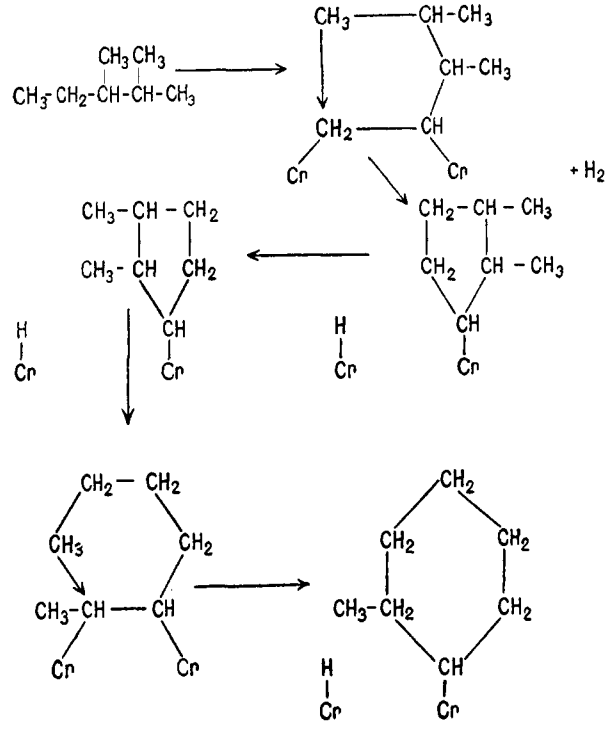
probability for *m*-xylene (a, b, and c) is $^{2}0/_{6}p$ and for *p*-xylene (d) it is $^{4}/_{6}p$, and one would expect a meta–para ratio of $^{5}/_{1}$. One would therefore expect a 28 per cent yield of *m*-xylene and a 6 per cent yield of *p*-xylene, values which are in good agreement with those observed, as indicated in table 3.

Herington and Rideal (66) also consider the cyclization of pentanes which do not contain a long enough chain to give directly a six-membered aromatic ring, but which actually do give aromatic products (see table 1). The fact that compounds with only four carbons in a straight chain, such as 2,3-dimethylbutane and 2,2,3,3-tetramethylbutane, do not give any aromatics while pentanes do, indicates to them that a five-membered ring is involved in the isomerization step. They point out that ethylcyclopentane and *trans*-1,2-dimethylcyclopentane both undergo dehydrogenation to toluene and that the same catalyst under the same conditions yields 30 per cent toluene from the 2,3-dimethylpentane, 20 per cent from ethylcyclopentane, and 27 per cent from *trans*-1,2-dimethylcyclopentane. This shows that the rate of aromatization from cyclopentane derivatives is not greater but slower than from substituted pentanes, suggesting that the slow step is the rupture of the five-membered ring. They investigated the dehydrocyclization of seven different derivatives of pentane (i.e., the longest straight chain had five carbons) and found that the rates were practically the same. This suggested that the rate-controlling step is the same in each case, i.e., rupture of the five-membered ring. They advanced the following mechanism for the cyclization of 3-methylpentane:



The products may be accounted for by using the following set of empirical rules: If one considers the pentane chain chemisorbed at carbon atoms 1 and 2 with the ring closing from 5, it appears that the *z* bond is broken unless carbon 3 carries an ethyl group, or carbon atoms 2 and 3 each have methyl groups, in which case it is the *y* bond which is broken. For subsequent closure to a six-membered ring it appears that if carbon 3 or 4 is a quaternary atom, the link is remade to one of the carbons attached to this quaternary atom. If there is no quaternary atom, then the links with either of the two groups adjacent to the bond broken are equally likely. Finally, it seems that if ring-closure produces ethylbenzene, half of this appears as toluene. These rules seem to account for the products from the dehydrogenation of seven pentanes and two quaternary substituted hexanes, as is indicated in table 4.

The following mechanism is suggested for the formation of toluene from 2,3-dimethylpentane:



Recently Raik (139, 140) has considered the mechanism of the dehydrocyclization reaction from a probability standpoint similar to that of Herington and Rideal. Raik does not think that two-point contact is important and starts with the following assumptions: (*1*) The carbon atoms between which bonds are broken or formed are adsorbed consecutively, not simultaneously. (*2*) The aromatization process occurs in two stages: first, the formation of a hexamethylenic ring and second, dehydrogenation of the ring to an aromatic hydrocarbon. (*3*) The structure of the new molecule, if more than one is possible, is determined by which of the carbon atoms in the starting molecule collide first with the catalytic surface. (*4*) It is assumed that the probability of absorption of a carbon atom is in direct proportion to the number of hydrogen atoms it contains. (*5*) If the main chain of the paraffin consists of six to nine carbon atoms, closure of the six-membered ring occurs only between those atoms which have four carbon atoms between them. Thus for example, with *n*-heptane,

$$\underset{1}{CH_3}\underset{2}{CH_2}\underset{3}{CH_2}\underset{4}{CH_2}\underset{5}{CH_2}\underset{6}{CH_2}\underset{7}{CH_3}$$

only carbon atoms 1, 2, 6, and 7, to which are bonded ten hydrogen atoms, would be capable of closing together. Since the total number of hydrogen atoms in the molecule is sixteen, the probability of cyclization, p, is $^{10}/_{16}$. Raik, like Herington and Rideal, assumes that the relation $K \cdot p = \log 1/(1 - \alpha)$ applies.

Table 5 contains data by Kazanskiĭ, Plate, and Liberman (82) compared with the calculations of Raik using the same data. Of the five compounds listed, four are in very good agreement. The value of K used in calculating the yields in table 5 was 0.0174, as determined with 3-methylheptane.

Raik has found that an additional assumption is necessary to explain the behavior of chromium oxide catalysts in dehydrocyclization. As mentioned above, he postulates that the probability of absorption of primary, secondary, and tertiary carbon atoms is 3, 2, and 1. The relative chemical activity for carbon from primary to tertiary, as established from the energy of activation in the formation of free radicals, is 1, 2, and 10, according to Tilichev (156). Raik

TABLE 4

Products of the dehydrogenation of pentanes and hexanes

HYDROCARBON	PRODUCTS	YIELD	
		Observed	Calculated
		per cent	*per cent*
2,3-Dimethylpentane	Toluene	100	100
2,2,3-Trimethylpentane	*m*-Xylene	100	100
2,2,4-Trimethylpentane	*p*-Xylene	100	100
2,3,3-Trimethylpentane	*m*-Xylene	100	100
2,3,4-Trimethylpentane	*o*-Xylene	60	50
	p-Xylene	40	50
3-Ethyl-2-methylpentane	Ethylbenzene	12.5	12.5
	Toluene	12.5	12.5
	o-Xylene	25	25
	m-Xylene	50	50
3,3-Dimethylhexane	Ethylbenzene	10	10
	Toluene	10	10
	o-Xylene	40	40
	m-Xylene	20	20
	p-Xylene	20	20
2,2-Dimethylhexane	*m*-Xylene	100	100

cross-multiplies these two sets of reactivities and obtains 3, 4, and 10, values which he believes represent the probability of absorption of primary, secondary, and tertiary carbon atoms on a chromium oxide catalyst. Thus, for example, with *n*-hexane the probabilities of absorption would be as follows:

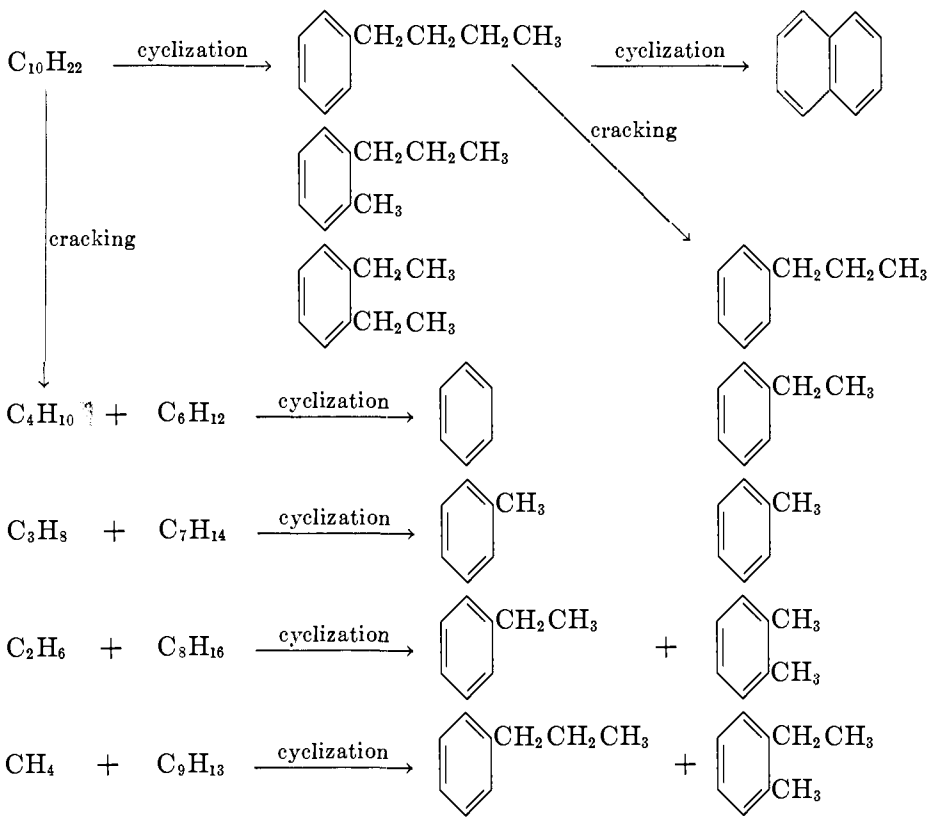
$$\overset{3}{CH_3}—\overset{4}{CH_2}—\overset{4}{CH_2}—\overset{4}{CH_2}—\overset{4}{CH_2}—\overset{3}{CH_3}$$

The probability of cyclization would not be $6/14$, as with platinum, but $6/22$. Using the data employed by Herington and Rideal (69), Raik obtained the results shown in table 6, which may be compared with those in table 2.

While the mechanisms postulated above by Herington and Rideal and by Raik stand in need of more experimental data and are not the last word on the mechanism of the dehydrocyclization reaction, they do constitute very useful working hypotheses on which to base further work.

Plate and Golvina (134) have criticized the mechanism of Herington and Rideal for the cyclization of 2,2,4-trimethylpentane, since they could isolate no five-membered ring compounds.

Rozenberg (142) has analyzed the products from the dehydrocyclization of *n*-decane with a chromia–alumina catalyst and suggests that the products can be accounted for by a combination of cyclization and cracking reactions, as follows:



It is interesting to note that he reports no *m*- or *p*-xylene. If octene is formed by cracking, then on the basis of Herington and Rideal's results one would expect these two products. It is possible that in analyzing the complex reaction mixture these two products were missed by Rozenberg. He observed that the ratio of disubstituted benzenes to monosubstituted benzenes in the products was 1.2–1.4 to 1; this, he says, confirms the idea that cyclization occurs more readily between two secondary carbon atoms than between secondary and primary atoms.

Obolenstev and Usov (112) have suggested that a three-membered ring is the intermediate in the dehydrocyclization of 2,2,4-trimethylpentane. Such a ring, they suggest, would then rearrange to give 2,5-dimethyl-2-hexene or 2,5-dimethylhexane, either of which could then cyclize.

Kazanskiĭ and Plate (82) observed in cyclizing various branched and straight-chain paraffins over a platinum–carbon catalyst at about 310°C. that the greater the branching of the chains and the higher the molecular weight the greater the amount of aromatic compounds formed. This is, of course, in line with the mechanism postulated by Herington and Rideal.

TABLE 5

Dehydrocyclization of paraffins

STARTING MATERIAL	YIELD OF AROMATIC CORRECTED TO		p†	CALCULATED YIELD
	Per cent by weight	Molecular concentration		
				per cent
n-Hexane	0.9*	0.73	6/14	1.7
2-Methylhexane	2.7*	2.50	(9+3)/16	2.9
3-Methylheptane	3.5	3.50	(13+3)/18	3.5
4-Methylheptane	2.0*	2.00	10/18	2.2
4-Methyloctane	3.6	3.90	(12+3)/20	3.9

* The values of yield were after two consecutive passes through the catalyst.

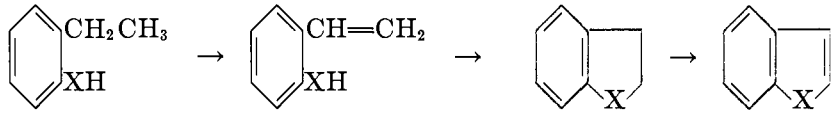
† The second number in the numerator indicates the added probability due to the branched methyl group.

TABLE 6

Dehydrocyclization with chromium oxide catalyst

STARTING MATERIAL	EXPERIMENTAL YIELD	p	CALCULATED YIELD
	per cent		*per cent*
n-Hexane	20	6/22	20
n-Heptane	36	14/26	36
2-Methylhexane	31	(9+3)/31	27.5
n-Octane	46	22/30	45.5
3-Methylheptane	35	(17+3)/35	37.5
2,5-Dimethylhexane	52	(12+12)/40	39
n-Nonane	58	30/34	52

The following mechanism, which has been suggested (61) for the dehydrocyclic formation of the indicated heterocycles, is similar to that shown above for the cyclization of the paraffins and olefins:



X = S, O, NH.

The relative order of ease of cyclization of the three compounds is: SH > OH > NH_2. This is the same order in which these groups tend to dissociate a proton and it may be that the cyclization of these compounds occurs by addition of the ortho functional group across the ethylene side chain.

IV. Catalysts

The problems of preparation and the mechanism of action of dehydrogenation catalysts are still far from being really understood. It would be impossible to evaluate critically all of the work that has been done to develop suitable catalysts and to understand the numerous elements and their compounds that have been used as catalysts and catalyst supports. The purpose of this section is to discuss the use of the best catalysts for dehydrocyclization. Table 1 lists the various catalysts which are useful; for the details of preparation the reader should consult the original work. Komarewsky and Riesz (90) have given a general discussion of the laboratory aspects of the preparation of heterogeneous catalysts.

Chromium oxide, alone or supported on alumina, is the most widely used catalyst. While there are a great many procedures for the preparation of active chromia catalysts (for good examples see 1, 147, and 159), it is only recently that some understanding of the theoretical problems has developed. Selwood (147) has shown that in the conversion of heptane to toluene there is good correlation between the activity and the magnetic susceptibility of the catalyst. He presents evidence for the fact that as the chromium content of a chromia–alumina catalyst is decreased, the chromium atoms become more dispersed and there is less Heisenberg exchange interaction between them. Thus the dispersion of the chromium over the surface permits the existence of more uncoupled electrons, which is indicated by the increased magnetic susceptibility. That it is these electrons which are involved in catalytic activity has also been suggested by others (102). Selwood has observed that as the chromium content of the catalyst is decreased from 5 per cent to 2 per cent, the activity of the catalyst per unit weight rises rapidly; the magnetic susceptibility shows a roughly parallel rise. His data indicate that the chromia is not spread over the alumina in a monolayer, but tends to clump in islands a few layers deep. It is these "active spots" on which the catalytic reactions occur.

Russell and Stokes (143), however, found with an alumina-supported molybdena catalyst, that the molybdena seemed to be held in monolayers and that the activity of the catalyst for the conversion of heptane to toluene increased linearly as more molybdena was added until a complete monolayer was attained. Evidence for correlation of surface area with the dehydrogenation ability of chromia–alumina has been given by Owen (124).

While the oxide catalysts such as molybdena and chromia are most active in the temperature range 450–600°C., the metallic catalysts palladium and platinum are active in the range 300–400°C. Although these latter catalysts are not as active in the dehydrocyclization reaction, they have an advantage in that their activity occurs at lower temperatures and thus under less drastic conditions. These catalysts are usually supported on either charcoal (98, 166) or asbestos (98, 162).

A catalyst which is particularly effective in the dehydrogenation of nitrogen compounds to heterocycles is a chromia–copper on carbon catalyst (58, 63). The same catalyst is active when supported with alumina instead of carbon; however, the alumina causes more side reactions and charring than the carbon support.

V. Apparatus

An introduction to laboratory technic in vapor-phase reactions has been given by Komarewsky and Riesz (90); hence this discussion will be limited to a survey of some of the best described apparatus for dehydrogenations. Figure 1 pictures a very commonly used set-up for vapor-phase reactions. This apparatus, which

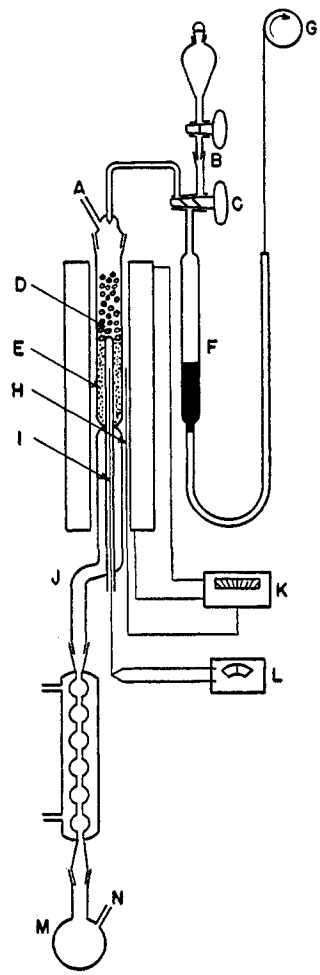


Fig. 1. Apparatus for dehydrogenation in the vapor phase

we have found to be satisfactory for small-scale work (61), is similar to that described by Hoog, Verheus, and Zuiderweg (69). We have found that a Pyrex catalyst tube J is quite satisfactory for dehydrogenation up to temperatures of 600°C. and can be used for short runs even at 650°C., although under these conditions considerable warping and bending of the tube occur. For temperatures above 625°C. quartz should be used. Considerable work has been done using steel tubes which are not easily broken; however, these have the disad-

vantage that one cannot observe the start of charring as readily and that elements in the steel may function catalytically. This latter point may or may not be important, depending on the purpose of the experiment.

For the introduction of the liquid sample onto the catalyst a convenient mechanism which gives a very smooth and uniform rate of flow is shown in B-C-F-G. G is a spindle attached to a geared-down motor shaft. The spindle is attached by means of a copper wire or, better, Nylon cord, to a Tygon tube which is connected to reservoir F containing mercury. Turning the spindle (different sizes may be used for different rates) raises the tube and causes the mercury to displace the lighter liquid into the catalyst tube. B is simply a convenient attachment for filling and refilling the cylinder F. This assembly is useful for work with small samples of the order of 5–100 ml. For larger samples it is more convenient to use a small pump, designs for a number of which have been reported (24, 158). Actually, for preparative purposes fair results may be had by simply using a dropping funnel which is connected directly to the catalyst tube. Herbst and Manske (64) have described an easily assembled unit. Herington and Rideal (65) used gases obtained by electrolysis to displace liquid paraffins into the reaction chamber at a very uniform rate. For relatively volatile substances introduction may be accomplished by distillation with a uniform heat source or by bubbling an inert gas through the heated liquid and thus sweeping the vapor into the reaction zone (76). With solids, cylinder F may be surrounded by a jacket through which steam can be passed. For very high melting solids, F can be wound with resistance wire and heated electrically.

A, in figure 1, is a port through which gases may be introduced either for the reduction of the catalyst or as diluents.

One may use a separate preheating unit (69) to heat the incoming vapors to the temperature of the catalyst or one can place a layer of Pyrex beads, or better quartz chips, over the catalyst, as illustrated in D. The catalyst E is supported by a constriction in the reaction tube; for careful work its temperature must be watched by means of a thermocouple and potentiometer such as L. Even though the temperature of the furnace is controlled by thermocouple H with regulator K, the reaction may be so endothermic or exothermic as to affect greatly the actual temperature of the catalyst. For more precise control of temperature, the catalyst tube may be surrounded by a heat-transfer bath such as Dowtherm or lead (90). High-frequency dielectric heating has also been used (86). In the apparatus of figure 1 the liquid and solid reaction products are stopped by the condenser and collected in flask M. Low-boiling liquids and gases pass off through N and may be collected in suitable traps.

A simple apparatus for the dehydrogenation of small amounts of material (1–2 g.) has been described (95). Apparatus of the general type pictured in figure 1 is also detailed in the literature (54, 111).

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