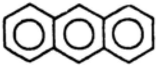
Polynuclear Aromatic Compounds

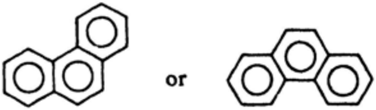
Fused-ring aromatic compounds

Two aromatic rings that share a pair of carbon atoms are said to be *fused.* In this chapter we shall study the chemistry of the simplest and most important of the fused-ring hydrocarbons, **naphthalene**, $C_{10}H_8$, and look briefly at two others of formula $C_{14}H_{10}$, **anthracene** and **phenanthrene**.

Naphthalene



Anthracene



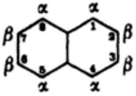
Phenanthrene

All three of these hydrocarbons are obtained from coal tar, naphthalene being the most abundant (5%) of all constituents of coal tar.

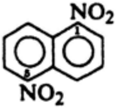
NAPHTHALENE

Nomenclature of naphthalene derivatives

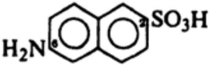
Positions in the naphthalene ring system are designated as in I. Two isomeric monosubstituted naphthalenes are differentiated by the prefixes 1- and 2-, or α- and β-. The arrangement of groups in more highly substituted naphthalenes is indicated by numbers. For example:



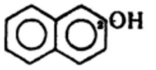
I



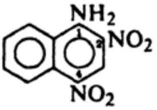
1,5-Dinitronaphthalene



6-Amino-2-naphthalenesulfonic acid



2-Naphthol
β-Naphthol



2,4-Dinitro-1-naphthylamine

Problem How many different mononitronaphthalenes are possible? Dinitronaphthalenes? Nitronaphthylamines?

Structure of naphthalene

Naphthalene is classified as aromatic because its properties resemble those of benzene (see Sec. 10.10). Its molecular formula, $C_{10}H_8$, might lead one to expect a high degree of unsaturation; yet naphthalene is resistant (although less so than benzene) to the addition reactions characteristic of unsaturated compounds. Instead, the typical reactions of naphthalene are electrophilic substitution reactions, in which hydrogen is displaced as hydrogen ion and the naphthalene ring system is preserved. Like benzene, naphthalene is unusually stable: its heat of combustion is 61 kcal lower than that calculated on the assumption that it is aliphatic (see Problem 10.2, p. 323).

From the experimental standpoint, then, naphthalene is classified as aromatic on the basis of its properties. From a theoretical standpoint, naphthalene has the structure required of an aromatic compound: it contains flat six-membered rings, and consideration of atomic orbitals shows that the structure can provide π clouds containing six electrons—the *aromatic sextet* (Fig. 30.1). Ten carbons lie at the corners of two fused hexagons. Each carbon is attached to three other atoms by σ bonds; since these σ bonds result from the overlap of trigonal sp^2 orbitals, all carbon and hydrogen atoms lie in a single plane. Above and below this plane there is a cloud of π electrons formed by the overlap of p orbitals and shaped like a figure 8. We can consider this cloud as two partially overlapping sextets that have a pair of π electrons in common.

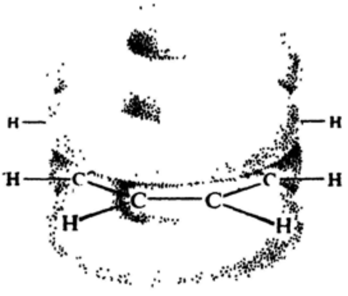
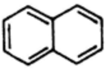
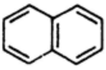


Figure 30.1. Naphthalene molecule. π clouds above and below plane of rings.

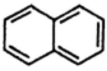
In terms of valence bonds, naphthalene is considered to be a resonance hybrid of the three structures I, II, and III. Its resonance energy, as shown by the heat of combustion, is 61 kcal/mole.



I



II



III

X-ray analysis shows that, in contrast to benzene, all carbon–carbon bonds in naphthalene are not the same; in particular, the C_1—C_2 bond is considerably shorter (1.365 A) than the C_2—C_3 bond (1.404 A). Examination of structures I, II, and III shows us that this difference in bond lengths is to be expected. The C_1—C_2 bond is double in two structures and single in only one; the C_2—C_3 bond is single in two structures and double in only one. We would therefore expect the C_1—C_2 bond to have more double-bond character than single, and the C_2—C_3 bond to have more single-bond character than double.

For convenience, we shall represent naphthalene as the single structure IV,

IV

in which the circles stand for partially overlapping aromatic sextets.

Although representation IV suggests a greater symmetry for naphthalene than exists, it has the advantage of emphasizing the aromatic nature of the system.

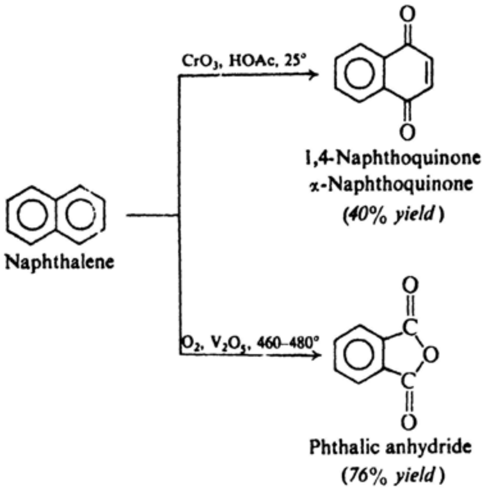
Reactions of naphthalene

Like benzene, naphthalene typically undergoes electrophilic substitution; this is one of the properties that entitle it to the designation of "aromatic." An electrophilic reagent finds the π cloud a source of available electrons, and attaches itself to the ring to form an intermediate carbonium ion; to restore the stable aromatic system, the carbonium ion then gives up a proton.

Naphthalene undergoes oxidation or reduction more readily than benzene, but only to the stage where a substituted benzene is formed; further oxidation or reduction requires more vigorous conditions. Naphthalene is stabilized by resonance to the extent of 61 kcal/mole; benzene is stabilized to the extent of 36 kcal/mole. When the aromatic character of one ring of naphthalene is destroyed, only 25 kcal of resonance energy is sacrificed; in the next stage, 36 kcal has to be sacrificed.

REACTIONS OF NAPHTHALENE

1. **Oxidation.** Discussed in Sec. 30.5.

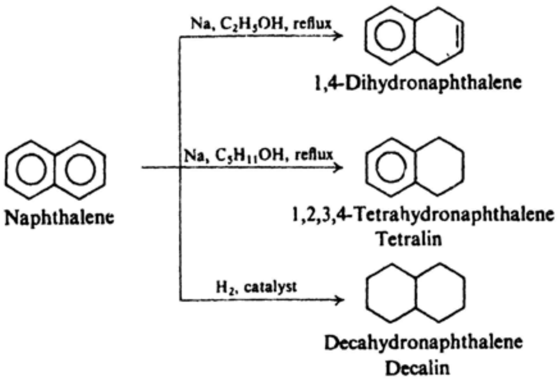


Naphthalene

1,4-Naphthoquinone
α-Naphthoquinone
(*40% yield*)

Phthalic anhydride
(*76% yield*)

2. **Reduction.**



Naphthalene

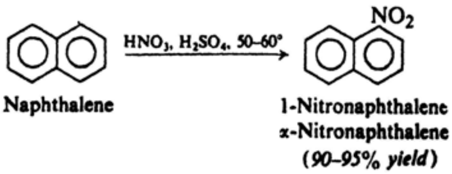
1,4-Dihydronaphthalene

1,2,3,4-Tetrahydronaphthalene
Tetralin

Decahydronaphthalene
Decalin

3. **Electrophilic substitution.** Discussed in Secs. 30.8–30.13.

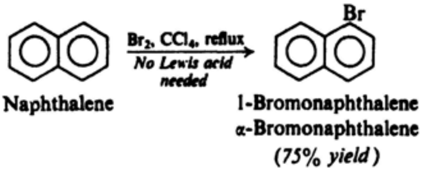
(a) **Nitration.**



Naphthalene

1-Nitronaphthalene
α-Nitronaphthalene
(*90–95% yield*)

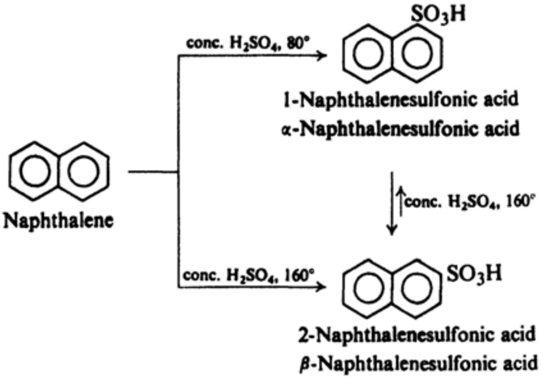
(b) **Halogenation.** Discussed in Sec. 30.8.



Naphthalene

1-Bromonaphthalene
α-Bromonaphthalene
(75% yield)

(c) **Sulfonation.** Discussed in Sec. 30.11.

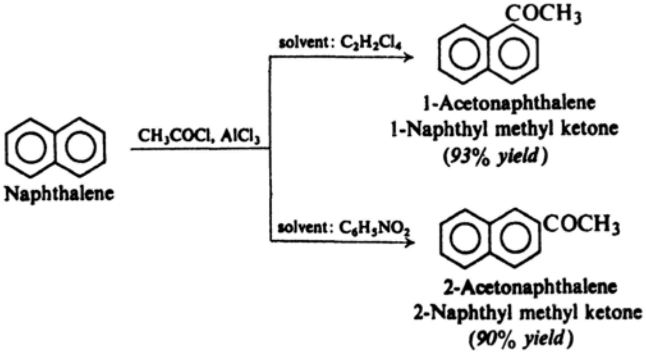


Naphthalene

1-Naphthalenesulfonic acid
α-Naphthalenesulfonic acid

2-Naphthalenesulfonic acid
β-Naphthalenesulfonic acid

(d) **Friedel-Crafts acylation.** Discussed in Sec. 30.10.



Naphthalene

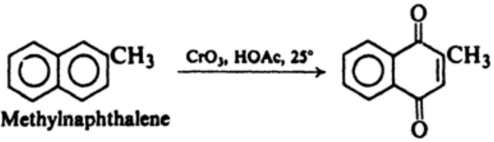
1-Acetonaphthalene
1-Naphthyl methyl ketone
(93% yield)

2-Acetonaphthalene
2-Naphthyl methyl ketone
(90% yield)

Oxidation of naphthalene

Oxidation of naphthalene by oxygen in the presence of vanadium pentoxide destroys one ring and yields phthalic anhydride. Because of the availability of naphthalene from coal tar, and the large demand for phthalic anhydride (for example, see Secs. 30.18 and 32.7), this is an important industrial process.

Oxidation of certain naphthalene derivatives destroys the aromatic character of one ring in a somewhat different way, and yields diketo compounds known as *quinones* (Sec. 27.9). For example:



2-Methylnaphthalene

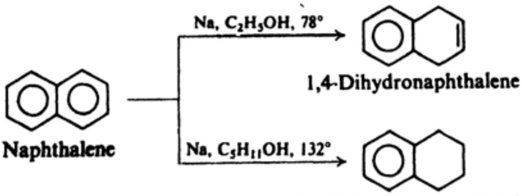
2-Methyl-1,4-naphthoquinone
(*70% yield*)

Because of this tendency to form quinones, it is not always feasible to prepare naphthalenecarboxylic acids as we do benzoic acids, by oxidation of methyl side chains.

Problem Show how 1- and 2-naphthalenecarboxylic acids (α- and β-*naphthoic acids*) can be obtained from naphthalene by way of the corresponding acetonaphthalenes.

Reduction of naphthalene

In contrast to benzene, naphthalene can be reduced by chemical reducing agents. It is converted by sodium and ethanol into 1,4-dihydronaphthalene, and by sodium and isopentyl alcohol into 1,2,3,4-tetrahydronaphthalene (*tetralin*). The temperature at which each of these sodium reductions is carried out is the boiling point of the alcohol used; at the higher temperature permitted by isopentyl alcohol (b.p. 132°), reduction proceeds further than with the lower boiling ethyl alcohol (b.p. 78°).

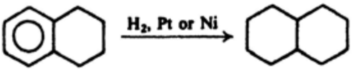


Naphthalene

1,4-Dihydronaphthalene

1,2,3,4-Tetrahydronaphthalene
Tetralin

The tetrahydronaphthalene is simply a dialkyl derivative of benzene. As with other benzene derivatives, the aromatic ring that remains is reduced only by vigorous catalytic hydrogenation.



Tetralin

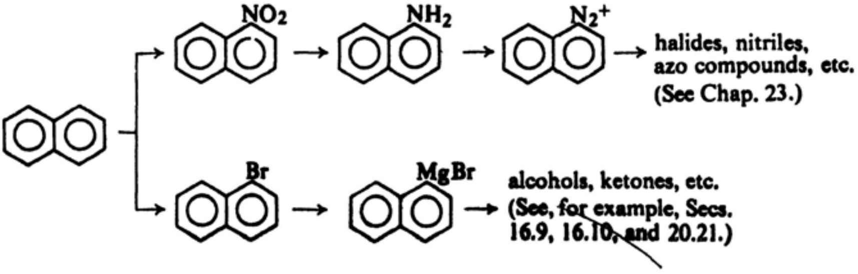
Decalin

Nitration and halogenation of naphthalene

Nitration and halogenation of naphthalene occur almost exclusively in the 1-position. Chlorination or bromination takes place so readily that a Lewis acid is not required for catalysis.

As we would expect, introduction of these groups opens the way to the preparation of a series of *alpha*-substituted naphthalenes: from 1-nitronaphthalene via the amine and diazonium salts, and from 1-bromonaphthalene via the Grignard reagent.

Synthesis of α-substituted naphthalenes



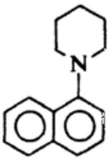
Problem 30.6 Starting with 1-nitronaphthalene, and using any inorganic or aliphatic reagents, prepare:

(a) 1-naphthylamine
(b) α-iodonaphthalene
(c) α-naphthonitrile
(d) α-naphthoic acid (1-naphthalenecarboxylic acid)
(e) α-naphthoyl chloride
(f) 1-naphthyl ethyl ketone
(g) 1-(aminomethyl)naphthalene, $C_{10}H_7CH_2NH_2$
(h) 1-(*n*-propyl)naphthalene
(i) α-naphthaldehyde
(j) (1-naphthyl)methanol
(k) 1-chloromethylnaphthalene
(l) (1-naphthyl)acetic acid
(m) N-(1-naphthyl)acetamide

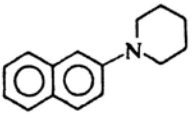
Problem 30.7 Starting with 1-bromonaphthalene, and using any inorganic or aliphatic reagents, prepare:

(a) 1-naphthylmagnesium bromide
(b) α-naphthoic acid (1-naphthalenecarboxylic acid)
(c) 2-(1-naphthyl)-2-propanol (dimethyl-1-naphthylcarbinol)
(d) 1-isopropylnaphthalene
(e) 1-naphthylcarbinol ($1\text{-}C_{10}H_7CH_2OH$)
(f) methyl-1-naphthylcarbinol (1-(1-naphthyl)ethanol)
(g) 2-(1-naphthyl)ethanol

Problem 30.8 (a) When 1-chloronaphthalene is treated with sodium amide, $Na^+NH_2^-$, in the secondary amine *piperidine* (Sec. 31.12), there is obtained not only I but also II,



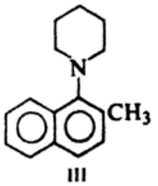
I



II

in the ratio of 1:2. Similar treatment of 1-bromo- or 1-iodonaphthalene yields the same products *and in the same* 1:2 *ratio*. Show all steps in a mechanism that accounts for these observations. Can you suggest possible factors that might tend to favor II over I?

(b) Under the conditions of part (a), 1-fluoro-2-methylnaphthalene reacts to



III

yield III. By what mechanism must this reaction proceed?

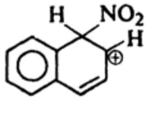
(c) Under the conditions of part (a), 1-fluoronaphthalene yields I and II, but in the ratio of 3:2. How do you account for this different ratio of products? What two factors make the fluoronaphthalene behave differently from the other halonaphthalenes?

30.9 Orientation of electrophilic substitution in naphthalene

Nitration and halogenation of naphthalene take place almost exclusively in the α-position. Is this orientation of substitution what we might have expected?

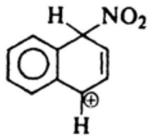
In our study of electrophilic substitution in the benzene ring (Chap. 11), we found that we could account for the observed orientation on the following basis: (a) the controlling step is the attachment of an electrophilic reagent to the aromatic ring to form an intermediate carbonium ion; and (b) this attachment takes place in such a way as to yield the most stable intermediate carbonium ion. Let us see if this approach can be applied to the nitration of naphthalene.

Attack by nitronium ion at the α-position of naphthalene yields an intermediate carbonium ion that is a hybrid of structures I and II in which the positive charge is accommodated by the ring under attack, and several structures like III in which the charge is accommodated by the other ring.



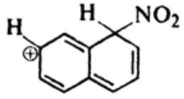
I

More stable:
aromatic sextet preserved



II

More stable:
aromatic sextet preserved

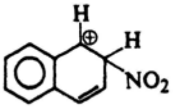


III

Less stable:
aromatic sextet disrupted

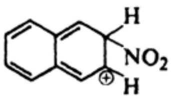
Alpha attack

Attack at the β-position yields an intermediate carbonium ion that is a hybrid of IV and V in which the positive charge is accommodated by the ring under attack, and several structures like VI in which the positive charge is accommodated by the other ring.



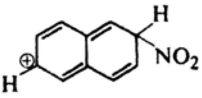
IV

More stable:
aromatic sextet preserved



V

Less stable:
aromatic sextet disrupted



VI

Less stable:
aromatic sextet disrupted

Beta attack

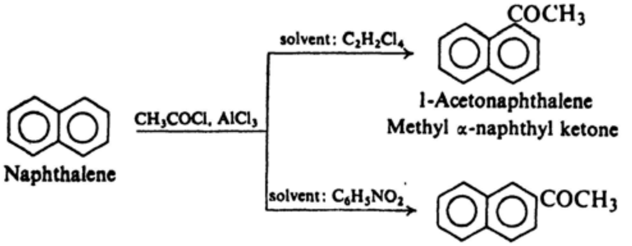
In structures I, II, and IV, the aromatic sextet is preserved in the ring that is not under attack; these structures thus retain the full resonance stabilization of one benzene ring (36 kcal/mole). In structures like III, V, and VI, on the other hand, the aromatic sextet is disrupted in both rings, with a large sacrifice of resonance stabilization. Clearly, structures like I, II, and IV are much the more stable.

But there are two of these stable contributing structures (I and II) for attack at the α-position and only one (IV) for attack at the β-position. On this basis we would expect the carbonium ion resulting from attack at the α-position (and also the transition state leading to that ion) to be much more stable than the carbonium ion (and the corresponding transition state) resulting from attack at the β-position, and that nitration would therefore occur much more rapidly at the α-position.

Throughout our study of polynuclear hydrocarbons, we shall find that the matter of orientation is generally understandable on the basis of this principle: of the large number of structures contributing to the intermediate carbonium ion, the important ones are those that require the smallest sacrifice of resonance stabilization. Indeed, we shall find that this principle accounts for orientation not only in electrophilic substitution but also in oxidation, reduction, and addition.

30.10 Friedel-Crafts acylation of naphthalene

Naphthalene can be acetylated by acetyl chloride in the presence of aluminum chloride. The orientation of substitution is determined by the particular solvent used: predominantly *alpha* in carbon disulfide or solvents like tetrachloroethane, predominantly *beta* in nitrobenzene. (The effect of nitrobenzene has been attributed to its forming a complex with the acid chloride and aluminum chloride which, because of its bulkiness, attacks the roomier *beta* position.)

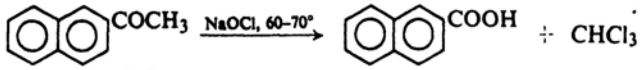


Naphthalene

1-Acetonaphthalene
Methyl α-naphthyl ketone

2-Acetonaphthalene
Methyl β-naphthyl ketone

Thus acetylation (as well as sulfonation, Sec. 30.11) affords access to the *beta* series of naphthalene derivatives. Treatment of 2-acetonaphthalene with hypohalite, for example, provides the best route to β-naphthoic acid.



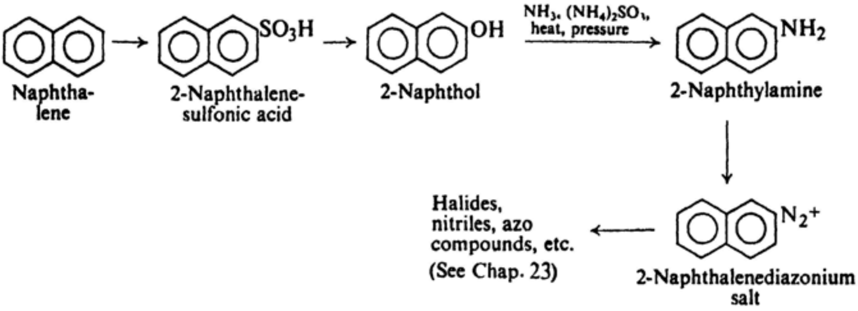
2-Acetonaphthalene
Methyl β-naphthyl ketone

β-Naphthoic acid
(88% yield)

Acylation of naphthalene by succinic anhydride yields a mixture of *alpha* and *beta* products. These are separable, however, and both are of importance in the synthesis of higher ring systems (see Sec. 30.19).

The α-substituted naphthalenes, like substituted benzenes, are most commonly prepared by a sequence of reactions that ultimately goes back to a nitro compound (Sec. 30.8). Preparation of β-substituted naphthalenes, on the other hand, cannot start with the nitro compound, since nitration does not take place in the β-position. The route to β-naphthylamine, and through it to the versatile diazonium salts, lies through β-naphthol. β-Naphthol is made from the β-sulfonic acid; it is converted into β-naphthylamine when heated under pressure with ammonia and ammonium sulfite (the **Bucherer reaction,** not useful in the benzene series except in rare cases).

Synthesis of β-substituted naphthalenes



Naphthols undergo the usual reactions of phenols. Coupling with diazonium salts is particularly important in dye manufacture (see Sec. 23.17); the orientation of this substitution is discussed in the following section.

Problem 30.12 Starting from naphthalene, and using any readily available reagents, prepare the following compounds:

(a) 2-bromonaphthalene	(d) β-naphthoic acid
(b) 2-fluoronaphthalene	(e) β-naphthaldehyde
(c) β-naphthonitrile	(f) 3-(2-naphthyl)propenoic acid

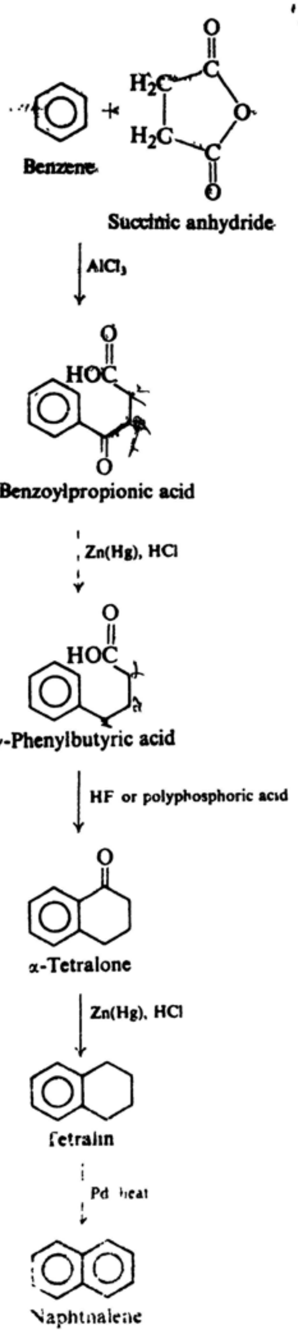
Problem 30.13 Diazonium salts can be converted into nitro compounds by treatment with sodium nitrite, usually in the presence of a catalyst. Suggest a method for preparing 2-nitronaphthalene.

Orientation of electrophilic substitution in naphthalene derivatives

We have seen that naphthalene undergoes nitration and halogenation chiefly at the α-position, and sulfonation and Friedel-Crafts acylation at either the α- or β-position, depending upon conditions. Now, to what position will a *second* substituent attach itself, and how is the orientation influenced by the group already present?

Orientation of substitution in the naphthalene series is more complicated than in the benzene series. An entering group may attach itself either to the ring that already carries the first substituent, or to the other ring; there are seven different

THE HAWORTH SYNTHESIS



Friedel-Crafts acylation

Clemmensen reduction

Ring closure:
Friedel-Crafts acylation

Clemmensen reduction

Aromatization:
dehydrogenation

Figure Haworth synthesis of naphthalene derivatives.

substituted benzene. One seldom generates the benzene ring in the course of a synthesis.

While compounds containing other aromatic ring systems, too, are often prepared from the parent hydrocarbon, there are important exceptions: syntheses in which the ring system, or part of it, is actually generated. Such syntheses usually involve two stages: **ring closure** (or **cyclization**) and **aromatization.**

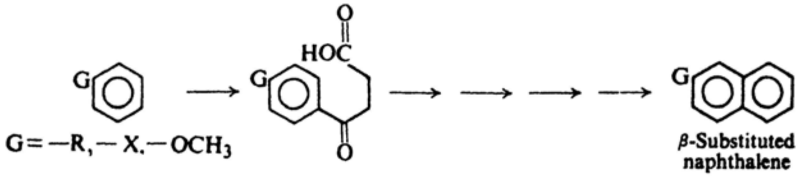
As an example, let us look at just one method used to make certain naphthalene derivatives: the **Haworth synthesis** (developed by R. D. Haworth at the University of Durham, England). Figure 30.2 (p. 987) shows the basic scheme, which would yield naphthalene itself (not, of course, actually prepared in this way).

All the steps are familiar ones. The reaction in which the second ring is formed is simply Friedel-Crafts acylation that happens to involve two parts of the same molecule. Like many methods of ring closure, this one does not involve a new reaction, but merely an adaptation of an old one.

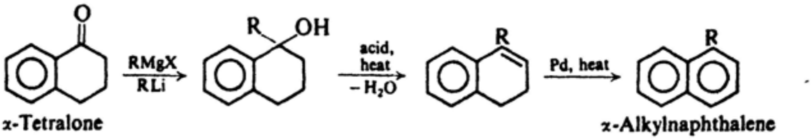
Problem Why is ring closure possible after the first Clemmensen reduction but not before?

To obtain substituted naphthalenes, the basic scheme can be modified in any or all of the following ways:

(a) A substituted benzene can be used in place of benzene and a β-substituted naphthalene obtained. Toluene or anisole or bromobenzene, for example, undergoes the initial Friedel-Crafts reaction chiefly at the *para* position; when the ring is closed, the substituent originally on the benzene ring must occupy a β-position in naphthalene.

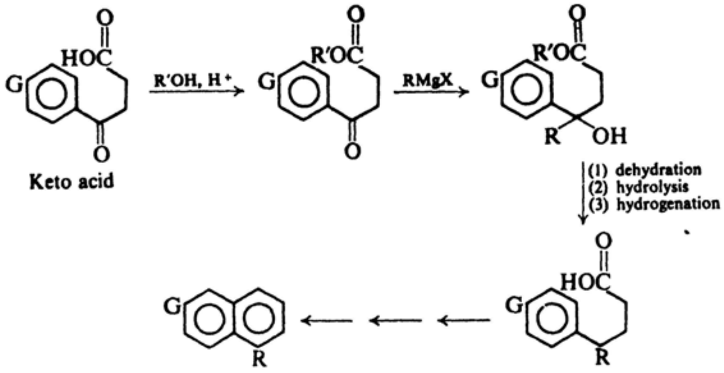


(b) The intermediate cyclic ketone (an α-tetralone) can be treated with a Grignard reagent, and an alkyl (or aryl) group introduced into an α-position.



(c) The original keto acid (in the form of its ester) can be treated with a Grignard reagent, and an alkyl (or aryl) group introduced into an α-position.

The success of this reaction depends upon the fact that a ketone reacts much faster than an ester with a Grignard reagent.



Keto acid

1,6-Disubstituted naphthalene

By proper combinations of these modifications, a wide variety of substituted naphthalenes can be prepared.

Problem Outline all steps in the synthesis of the following compounds, starting from benzene and using any necessary aliphatic and inorganic reagents:

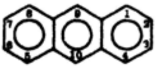
(a) 2-methylnaphthalene
(b) 1-methylnaphthalene
(c) 1,4-dimethylnaphthalene
(d) 1,7-dimethylnaphthalene
(e) 1,6-dimethylnaphthalene
(f) 1,4,6-trimethylnaphthalene
(g) 1-ethyl-4-methylnaphthalene
(h) 7-bromo-1-ethylnaphthalene
(i) 1-phenylnaphthalene

Problem Outline the Haworth sequence of reactions, starting with naphthalene and succinic anhydride. What is the final hydrocarbon or hydrocarbons? (Remember the orientation rules for naphthalene.) Check your answer in Sec. 30.19.

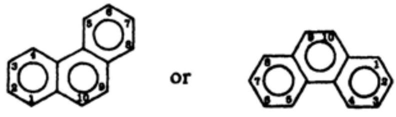
ANTHRACENE AND PHENANTHRENE

Nomenclature of anthracene and phenanthrene derivatives

The positions in anthracene and phenanthrene are designated by numbers as shown:



Anthracene



Phenanthrene

Examples are found in the various reactions that follow.