

Chapter 4

Introduction to Hydroprocessing Reactions

While production of new catalytic phases such as phosphides, carbides, and nitrides may yield interesting catalysts, it is also of interest to understand the mechanisms of heteroatom removal associated with their use. Thus, we undertook a study of the hydrodenitrogenation reactions of a series of simple amines: *n*-pentylamine, *neo*-pentylamine, *tert*-pentylamine, piperidine, and pyridine. The results for the alkyl series of pentylamines will be presented in Chapter 5, while the results for the C₅ ring structures will be presented in Chapter 6.

The literature reports that the catalytic hydrogenation reactions of amines, thiols, and alcohols are all generally similar, producing condensation products, olefins, and saturated hydrocarbons in their conversion reactions. Examples of published reactions of heteroatomic aliphatic species, cyclic aliphatic species, and simple cyclic aromatics are summarized in Sections 4.1 to 4.3, respectively, and those involving heteroatom exchange in Section 4.4.

4.1. Reactions of alkyl aliphatic species

Schemes 4.1.1 through 4.1.7 summarize the basic reactions of the aliphatic heteroatom ring molecules, and Table 4.1 lists the references. Condensation reactions of alkyl species are reported in sections 4.1.1 to 4.1.3. These are facile types of reactions which occur at low temperature in hydrogen, helium, and vacuum. This type of reaction

(for amines) is reported to proceed through quaternization of the nitrogen of a reactant (alkyl donor) molecule, followed by nucleophilic attack by a non-quaternized (alkyl acceptor) species (6). The observation is that alkyl chains, protons, and the heteroatoms themselves are susceptible to exchange (as shown presently in Section 4.4), and that these reactions can be considered ‘easy’ under typical conditions. Although a heteroatom compound (ammonia, hydrogen sulfide, water) can be generated during condensation, the number of C-X (X = N, S, O) bonds is conserved, so this type of reaction does not lead directly to free hydrocarbons (olefins or saturates).

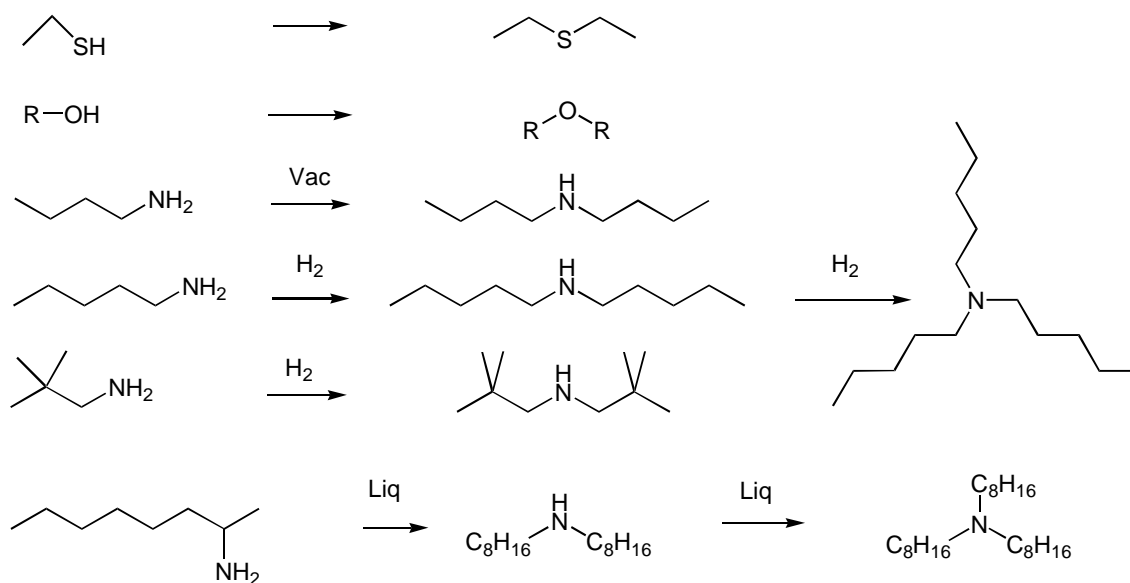
Scheme 4.1.4 reports olefins which have been observed in the products of reactions of alkyl heteroatomic species. The formation of olefins is thought to occur by β -elimination type reactions as reported later in Schemes 5.1 and 5.2.

Dehydrogenation reactions of alcohols, amines, and thiols are summarized in Scheme 4.1.5. These products, like the olefins, are favored by low pressure and lack of hydrogen. Note that decarbonylation can lead to reduction of the hydrocarbon chain length. Thus, operating at high pressure (which selects against dehydrogenation and decarbonylation) is desirable in hydrodeoxygenation situations, such as found in the processing of biologically derived oils.

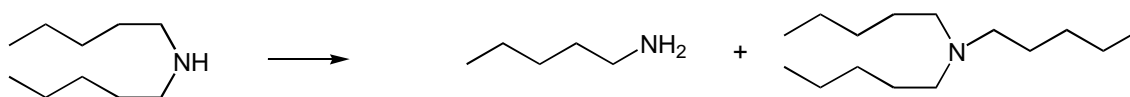
Scheme 4.1.6 reports saturated hydrocarbons which have appeared in the products of reactions of alkyl heteroatomic molecules. Whether these molecules are created as a result of direct hydrogenolysis of C-N bonds, or by β -elimination followed by hydrogenation is of fundamental interest in this work. We will argue that the β -elimination pathway is observed to be easier than the direct hydrogenolysis route and is therefore preferred.

Scheme 4.1: Reactions of alkylamines.

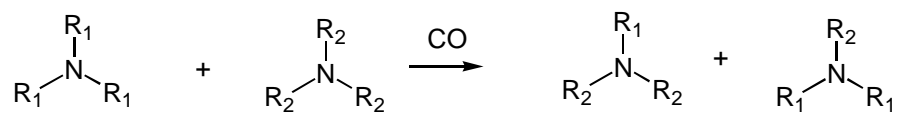
4.1.1. Formation of di- and tri- alkyl species



4.1.2. Disproportionation of diamines

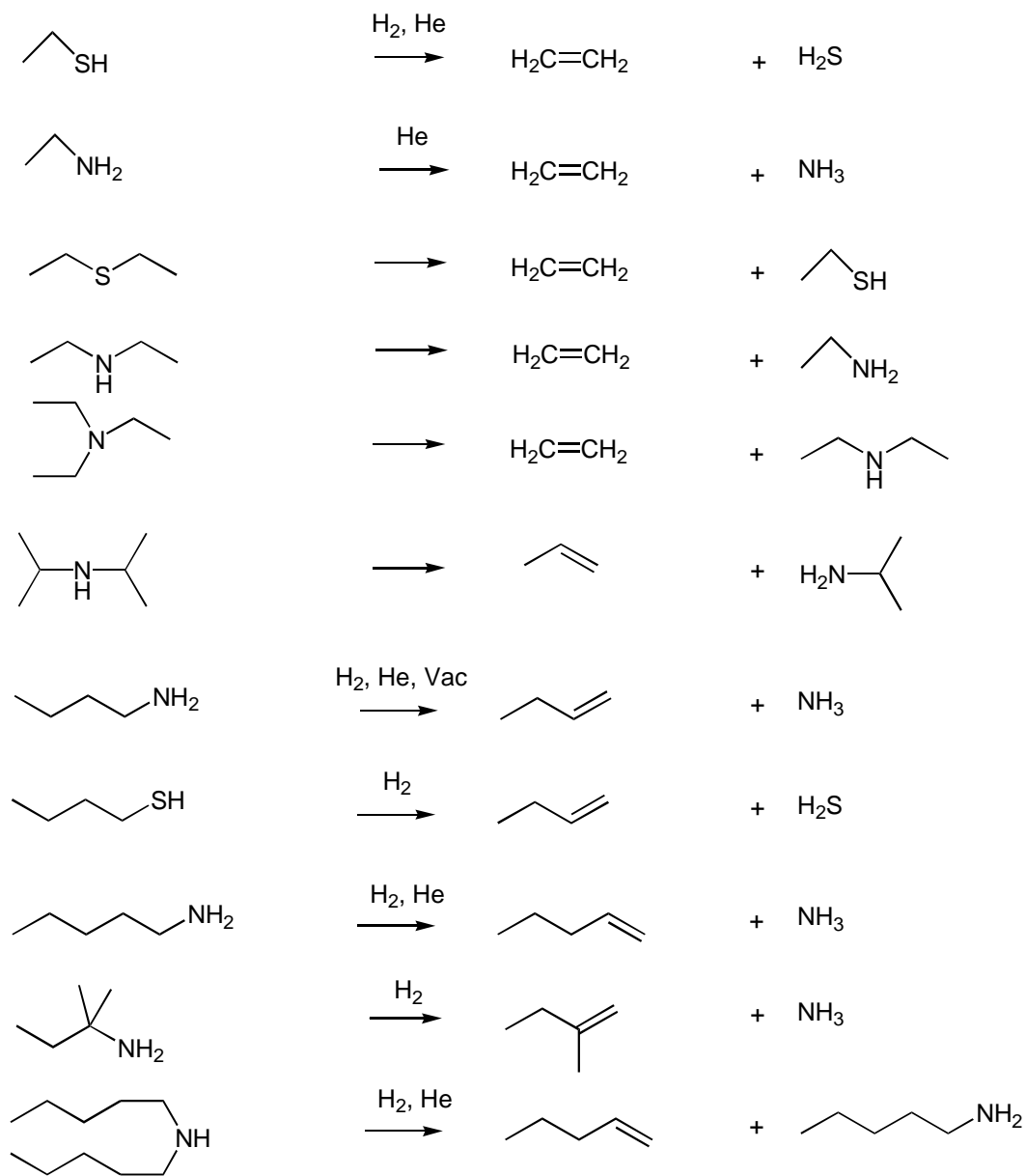


4.1.3. Alkyl transfer



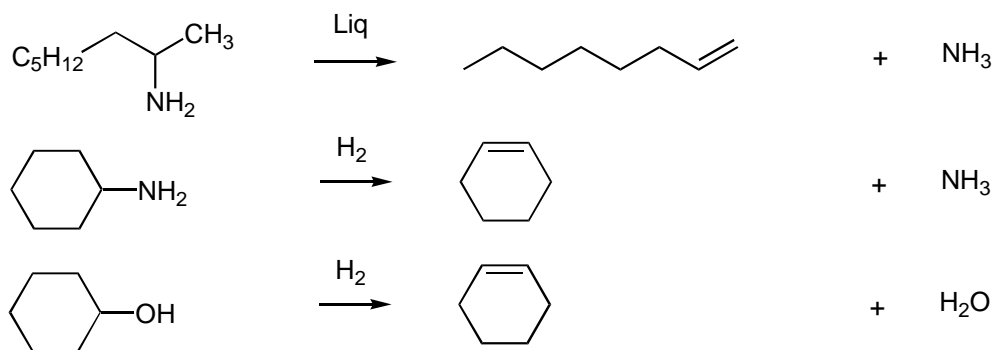
Scheme 4.1: cont... Reactions of alkylamines.

4.1.4. Production of olefins.

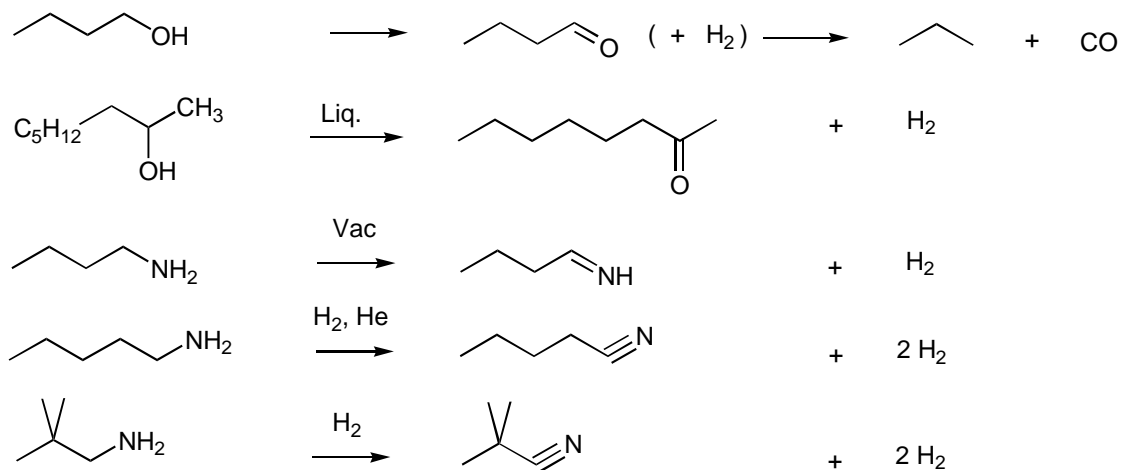


Scheme 4.1: cont... Reactions of alkylamines.

4.1.4. cont... Production of unsaturated hydrocarbons.

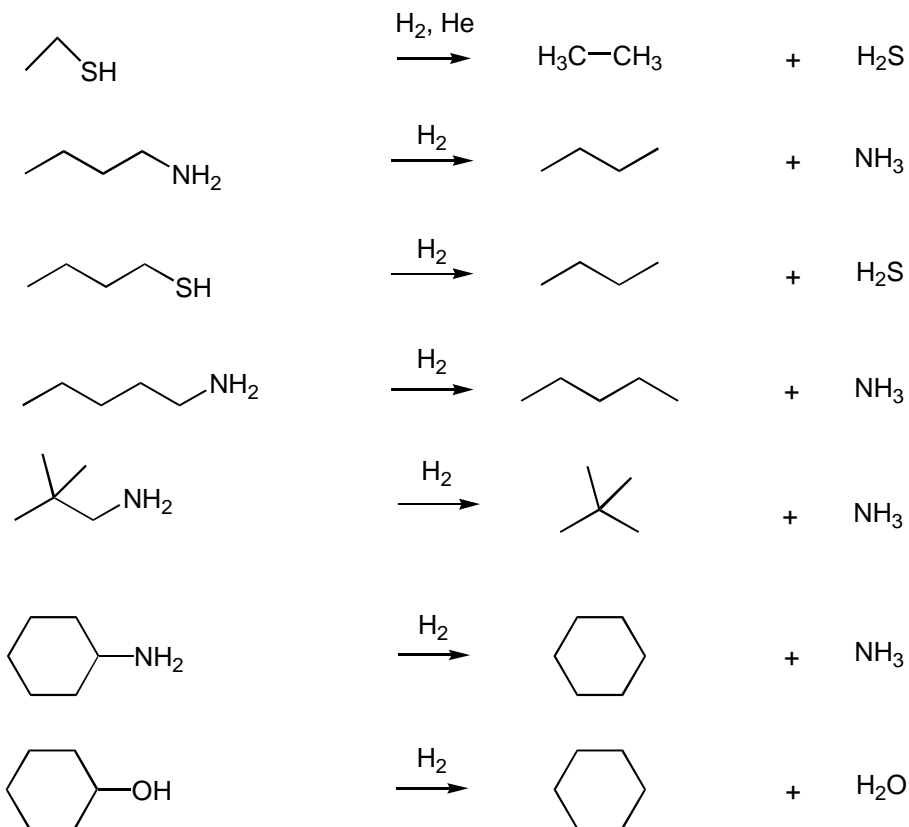


4.1.5. Dehydrogenation and decarbonylation.



Scheme 4.1: cont... Reactions of alkylamines.

4.1.6. Production of saturated hydrocarbons



4.1.7. Isomerization of olefins

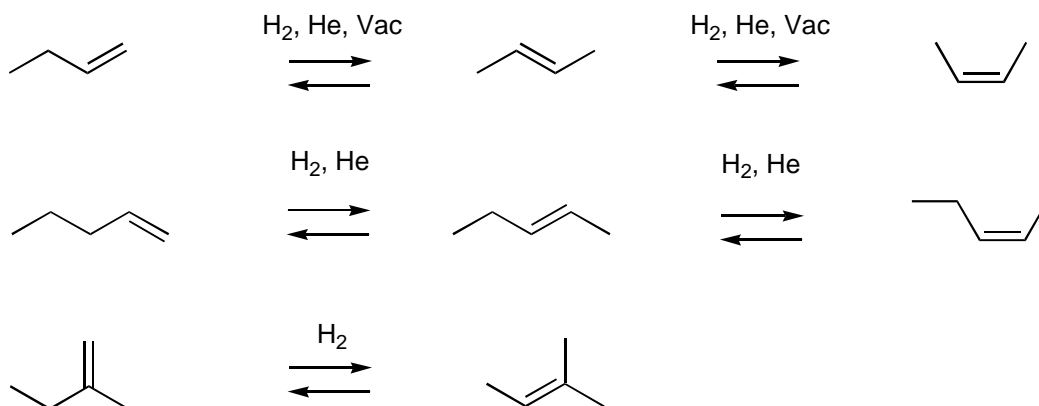


Table 4.1: Reactions involving alkyl amines, thiols, and alcohols.

Reaction	Reactant	Product	Citation
4.1.1.1	ethanethiol	diethylsulfide	(1, 2)
4.1.1.2	alkyl alcohol	dialkylether	(3)
4.1.1.3	<i>n</i> -butylamine	di(<i>n</i> -butyl)amine	(4)
4.1.1.4	<i>n</i> -pentylamine	di(<i>n</i> -pentyl)amine	(5, 6, 7, 8)
“	“	tri(<i>n</i> -pentyl)amine	(5, 6, 7)
4.1.1.5	<i>neo</i> -pentylamine	di(<i>neo</i> -pentyl)amine	(5, 6)
4.1.1.6	2-(<i>n</i> -octyl)amine	di(<i>n</i> -octyl)amine	(9)
“	“	tri(<i>n</i> -octyl)amine	(9)
4.1.1.7	cyclohexylamine	di(cyclohexyl)amine	(10)
4.1.1.8	3-phenylpropylamine	di(3-phenylpropyl)amine	(11)
4.1.2.1	di(<i>n</i> -pentyl)amine	tri(<i>n</i> -pentyl)amine	(8)
4.1.3.1	$R_3N + R'_3N$	$R_2R'N + R'_2RN$	(12)
4.1.4.1	ethanethiol	C_2H_4	(1)
4.1.4.2	ethylamine	C_2H_4	(5)
4.1.4.3	diethylsulfide	$C_2H_4 + C_2H_5SH$	(1)
4.1.4.4	diethylamine	$C_2H_4 + C_2H_5NH_2$	(13)
4.1.4.5	triethylamine	$C_2H_4 + (C_2H_5)_2NH$	(14)
4.1.4.6	diisopropylamine	$C_3H_6 + (C_3H_7)NH_2$	(14)
4.1.4.7	<i>n</i> -butylamine	butenes	(4, 15)
4.1.4.8	<i>n</i> -butylthiol	butenes	(16)
4.1.4.9	<i>n</i> -pentylamine	pentenes	(5, 6, 7, 8)
4.1.4.10	tert-pentylamine	methylbutenes	(5, 6)
4.1.4.11	di(<i>n</i> -pentyl)amine	$C_5H_{10} + C_5H_{11}NH_2$	(8)
4.1.4.12	2-(<i>n</i> -octyl)amine	octenes	(9)
4.1.4.13	cyclohexylamine	cyclohexene	(8)
4.1.4.14	cyclohexanol	cyclohexene	(8)

Table 4.1: cont... Reactions involving alkyl amines, thiols, and alcohols.

Reaction	Reactant	Product	Citation
4.1.5.1	<i>n</i> -butanol	<i>n</i> -butanone	(17, 18, 19)
“	“	C ₃ + CO	(17, 18)
4.1.5.2	2- <i>n</i> -octanol	2- <i>n</i> -octanone	(9)
4.1.5.3	<i>n</i> -butylamine	<i>n</i> -butanenitrile	(4)
4.1.5.4	<i>n</i> -pentylamine	<i>n</i> -pentanenitrile	(6)
4.1.5.5	<i>neo</i> -pentylamine	<i>neo</i> -pentanenitrile	(5, 6)
4.1.6.1	ethanethiol	C ₂ H ₆	(1, 2)
4.1.6.2	<i>n</i> -butylamine	C ₂ H ₆	(15)
4.1.6.3	<i>n</i> -butanethiol	<i>n</i> -butane	(16)
4.1.6.4	<i>n</i> -pentylamine	<i>n</i> -pentane	(5, 6, 7, 8)
4.1.6.5	<i>neo</i> -pentylamine	<i>neo</i> -pentane	(5)
4.1.6.6	cyclohexylamine	cyclohexane	(8)
4.1.6.7	cyclohexanol	cyclohexane	(8)
4.1.7.1	1-butene	2-butenes	(4, 15, 16)
“	cis-2-butene	trans-2-butene	(4, 15, 16)
4.1.7.2	1-pentene	2-pentenenes	(5, 6, 7, 8)
“	cis-2-pentene	trans-2-pentene	(5, 6, 7, 8)
4.1.7.3	2-methyl-1-butene	2-methyl-2-butene	(5, 6)

In general, the selectivity for dehydrogenated species is favored by low pressures and inert atmosphere, while saturated hydrocarbons are favored by higher pressure and hydrogen atmosphere. However, changing the hydrogen pressure does not significantly influence the conversion of aliphatic amines (8), indicating that the rate determining step in C-N bond cleavage does not involve hydrogen.

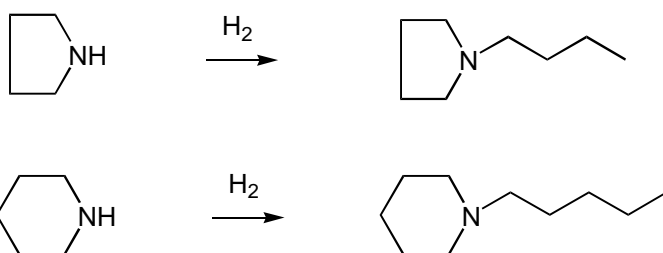
The isomerization reactions of olefins, reported in Scheme 4.1.7, are thought to be secondary reactions. That is, once the primary olefin is generated via β -elimination, it subsequently participates in isomerization. Later, in Scheme 5.3, we show a possible mechanism for how these reactions occur on acid-base sites.

4.2. Reactions of aliphatic ring compounds

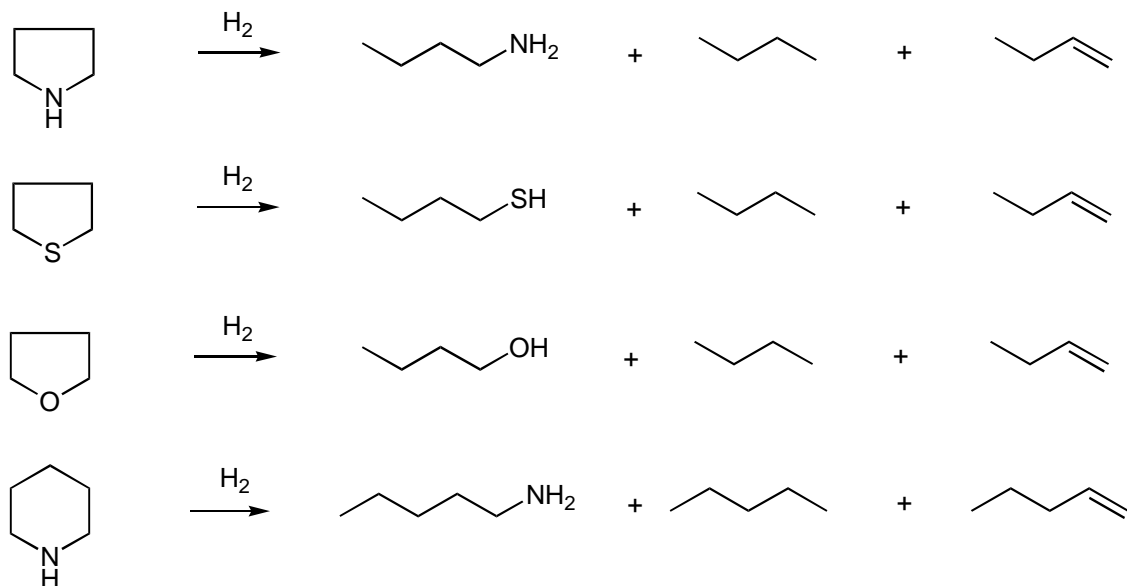
Schemes 4.2.1 through 4.2.3 summarize the basic reactions of the aliphatic heteroatom ring molecules, and Table 4.2 lists the references. Scheme 4.2.1 reports some of the condensation products which have been observed. Note that free hydrocarbon ends on these species could not have been produced by condensation reactions acting alone. It is thus logical to assume that an elimination reaction (and hydrogenation of the so formed olefin) has occurred, leading to the formation of e.g. *n*-pentylamine from piperidine. This intermediate then combines with a second reactant molecule (here piperidine) via a condensation reaction to create the observed product, in this case N-(*n*-pentyl)-piperidine. The usual decomposition products of aliphatic rings are summarized in Scheme 4.2.2. In these situations, intermediate alkyl species are thought to be highly reactive and are thus infrequently seen. The presence of monoolefins and saturated hydrocarbons is common.

Scheme 4.2.: Reactions of aliphatic ring compounds.

4.2.1. Condensation reactions.



4.2.2. Formation of alkyl heteroatomics, alkanes, and alkene from aliphatic rings.



Scheme 4.2.: cont... Reactions of aliphatic ring compounds.

4.2.3. Production of diolefins from aliphatic rings.

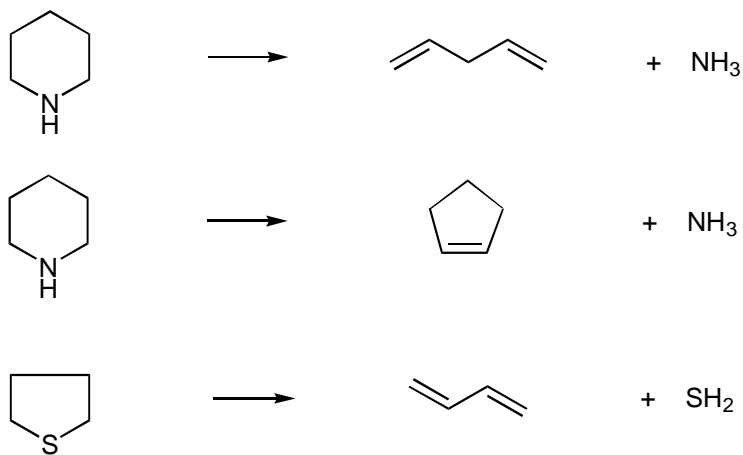


Table 4.2: Reactions of aliphatic ring compounds.

Reaction	Reactant	Product	Citation
4.2.1.1	pyrrolidine	N-(<i>n</i> -butyl)pyrrolidine	(8)
4.2.1.2	piperidine	N-(<i>n</i> -pentyl)piperidine	(5, 20)
4.2.2.1	pyrrolidine	<i>n</i> -butylamine	(8)
“	“	butenes	(8)
“	“	<i>n</i> -butane	(8)
4.2.2.2	tetrahydrothiophene	<i>n</i> -butanethiol	(16)
“	“	butenes	(16)
“	“	<i>n</i> -butane	(16)
4.2.2.3	tetrahydrofuran	<i>n</i> -butanol	(17, 18, 19)
“	“	butenes	(17, 18, 19)
“	“	<i>n</i> -butane	(17, 18, 19)
4.2.2.4	piperidine	<i>n</i> -pentylamine	(20, 21, 22)
“	“	pentenes	(5, 20, 21, 22)
“	“	pentane	(5, 20, 21, 22)
4.2.3.1	piperidine	pentadienes	(23)
4.2.3.2	piperidine	cyclopentene	(8)
4.2.3.3	tetrahydrothiophene	butadiene	(16)
4.2.3.4	tetrahydrofuran	butadiene	(19)

Scheme 4.2.3 reports some diene species which have been produced from aliphatic rings.

The formation of dienes is infrequent, but their identification backs up our position that the heteroatom removal step is likely occurring via an elimination mechanism. In this case two C=C bonds are formed, once for each C-X (X = N, S, O) bond broken.

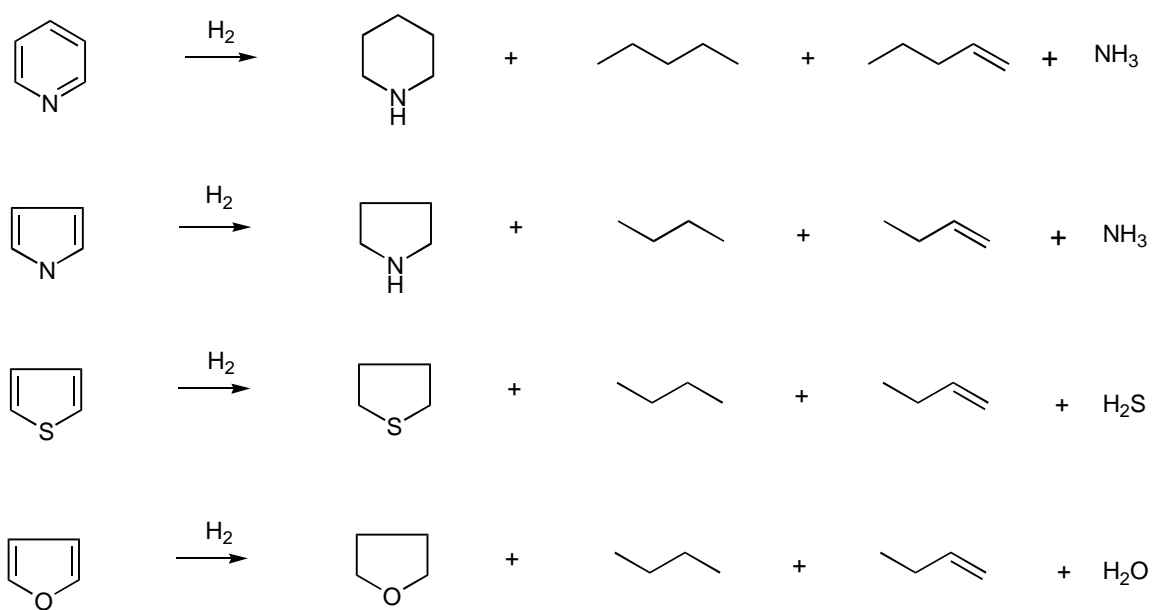
4.3. Reactions of aromatic heterocyclic hydrocarbons.

Scheme 4.3 reports common reactions of aromatic heterocycles. Here, the hydrogenation reactions of the heteroatomic ring are usually the first to occur, and the so formed aliphatic ring structure may then react according to the examples for aliphatic rings given in Schemes 4.1 and 4.2. Thus the typical products are hydrogenated aliphatic rings, alkyl species, monoolefins and saturates. Occasionally, dienes are observed in the products, as well as condensation products typical of the aliphatic ring, which are summarized in Scheme 4.3.2.

Thus, we have built up to the reactions of the simplest aromatic heterocycles, based upon reactions observed for intermediates of their decomposition. It is relevant to note that the hydrogenation reactions of heterocyclic rings are thought to occur on different catalytic sites from those responsible for reactions of aliphatic species. This point is exemplified by the conversion of piperidine over alumina and alumina/phosphate catalysts, while pyridine displayed no reaction under the same conditions (23). The ‘dual function’ hydroprocessing catalyst, having hydrogenation and hydrogenolysis capabilities, is indeed much discussed in the literature (22).

Scheme 4.3: Reactions of aromatic heterocyclic compounds.

4.3.1. Hydrogenation of aromatics to form aliphatic rings, alkanes, and alkenes.



Scheme 4.3: cont... Reactions of aromatic heterocyclic compounds

4.3.2. Secondary reactions of aromatic heterocycles. Formation of condensation products.

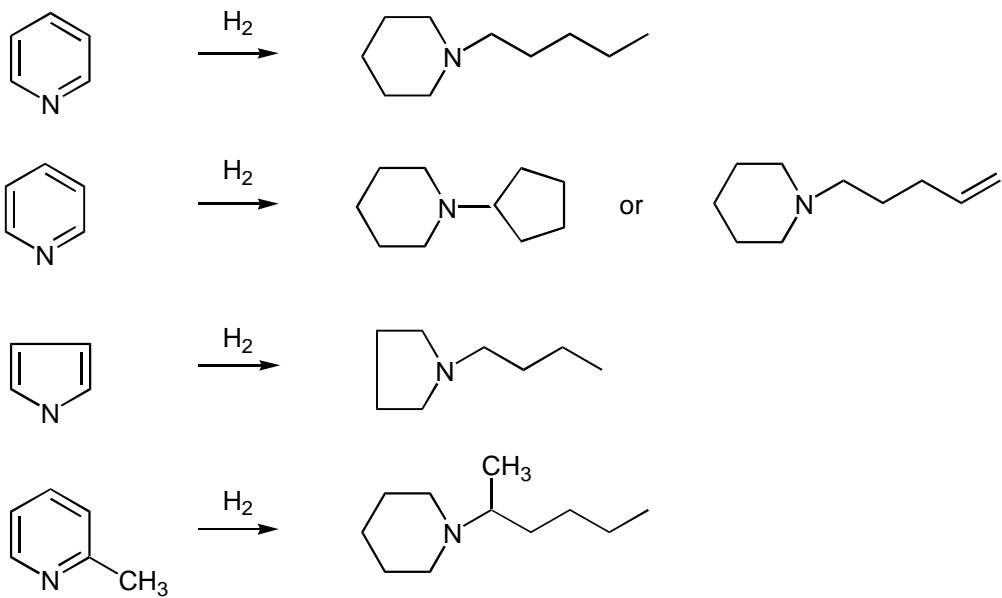


Table 4.3: Reactions of aromatic heterocyclic compounds.

Reaction	Reactant	Product	Citation
4.3.1.1	pyrrole	pyrrolidine	(8, 24)
“	“	<i>n</i> -butylamine	(8, 24)
“	“	butadiene	-
“	“	2-butenes	(8, 24)
“	“	butane	(8, 24)
4.3.1.2	thiophene	tetrahydrothiophene	(25)
“	“	<i>n</i> -butanethiol	-
“	“	butadiene	(25)
“	“	butenes	(17, 25, 26)
“	“	butane	(17, 25, 26)
4.3.1.3	furan	tetrahydrofuran	(17, 18, 19)
“	“	<i>n</i> -butanol	(17)
“	“	butenes	(17, 18, 19)
“	“	butane	(17, 18, 19)
“	“	butanone	(17, 18)
“	“	C ₃ + CO	(17, 18, 19)
4.3.1.4	pyridine	piperidine	(5, 27, 28)
“	“	<i>n</i> -pentylamine	(29)
“	“	pentenes	(5, 27, 28, 29)
“	“	pentane	(5, 27, 28, 29)
4.3.1.5	2-methylthiophene	tetrahydro-2-methylthiophene	(8, 17)
“	“	pentenes	(8, 17)
“	“	pentane	(8, 17)
4.3.1.6	2-methylpyridine	2-methylpiperidine	(30)

Table 4.3: cont... Reactions of aromatic heterocyclic compounds.

Reaction	Reactant	Product	Citation
4.3.2.1	pyrrole	N-(<i>n</i> -butyl)pyrrolidine	(8)
4.3.2.2	pyridine	N-(<i>n</i> -pentyl)piperidine	(5, 8, 31)
4.3.2.3	pyridine	N-(cyclopentyl)piperidine	(5)
4.3.2.4	2-methylpyridine	N-(2-hexyl)-2-methylpiperidine	(30)

4.4. Heteroatom exchange reactions

Scheme 4.4 summarizes heteroatomic exchange reactions, and the references are listed in Table 4.4. These exchange reactions are likely of the condensation type (nucleophilic substitution), proceeded or followed by hydrogenation/dehydrogenation reactions yielding the listed product. One interesting reaction is the combined cyclization and heteroatom exchange found in the conversion of 1-pent-4-entylamine. This reactant can be considered to be the reactive intermediate formed by the cleavage of the first C-N bond in piperidine. As noted, the cyclization and heteroatom exchanged product thiane is also observed in the conversion of piperidine.

Scheme 4.4: Exchange reactions of heteroatoms.

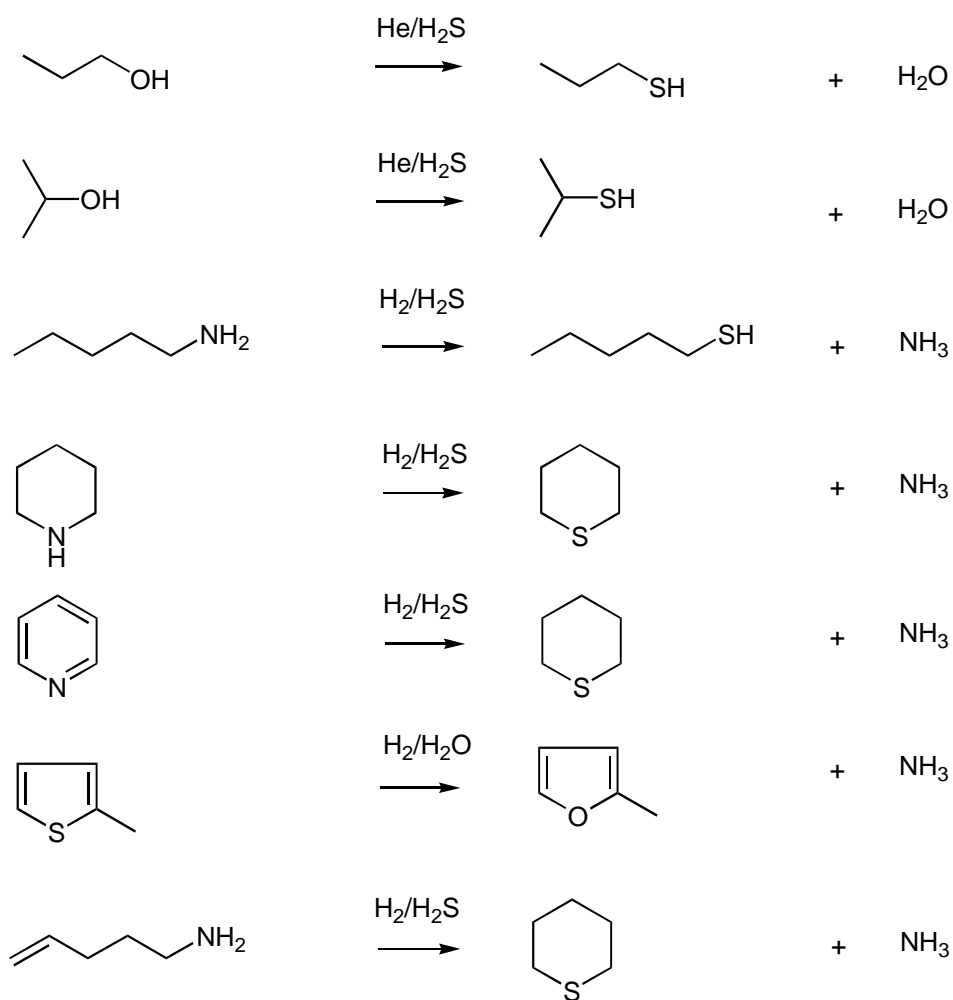


Table 4.4: Exchange reactions of heteroatoms.

Reaction	Reactant	Product	Citation
4.4.1	<i>n</i> -propanol	<i>n</i> -propanethiol	(32)
4.4.2	<i>iso</i> -propanol	<i>iso</i> -pentanethiol	(32)
4.4.3	<i>n</i> -pentylamine	<i>n</i> -pentanethiol	(5, 6)
4.4.4	<i>neo</i> -pentylamine	<i>neo</i> -pentanethiol	(6)
4.4.5	1-pent-4-enylamine	thiane	(33)
4.4.6	piperidine	thiane	(5, 33)
4.4.7	pyridine	thiane	(5)
4.4.8	2-methylthiophene	2-methylfuran	(17)

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