A SHORT COURSE OF ORGANIC CHEMISTRY

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FUNCTIONAL GROUPS

Many of the reactions of organic compounds do not involve the carbon skeleton at all but are confined to the substituent. Such substituents are called *functional groups* because they determine in large part the chemical properties and function of the molecule.

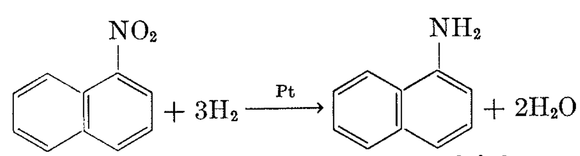
A study of functional groups is especially profitable because the reactions of a functional group tend to be about the same, regardless of the nature of the rest of the molecule. For example the compound 2-nitropropane can be reduced to 2-aminopropane by means of hydrogen and a platinum catalyst. The reaction is essentially a reaction of the functional group and nothing very important happens to the rest of the molecule.

$$\underset{\text{2-Nitropropane}}{CH_3\text{—}\underset{\underset{NO_2}{|}}{CH}\text{—}CH_3} + 3H_2 \xrightarrow{\text{Pt}} \underset{\text{2-Aminopropane}}{CH_3\text{—}\underset{\underset{NH_2}{|}}{CH}\text{—}CH_3} + 2H_2O$$

Similarly,

$$CH_3CH_2NO_2 + 3H_2 \xrightarrow{\text{Pt}} CH_3CH_2NH_2 + 2H_2O$$

and



1-Nitronaphthalene   1-Aminonaphthalene

If we let R stand for any alkyl or aryl (aromatic) group, all of the foregoing reactions can be summarized by a single general equation.

$$R{-}NO_2 + 3H_2 \xrightarrow{Pt} R{-}NH_2 + 2H_2O$$

A change in R will make the reaction go faster or slower, but it will usually not change the kind of product. It is therefore sufficient to know the behavior of the nitro group ($-NO_2$) to know the behavior of a vast number of nitro compounds, and this situation keeps the interesting aspects of organic chemistry from being lost in a discouraging forest of facts that can only be memorized and not correlated.

The functional groups introduced in this chapter will be encountered later in our detailed discussion of various substances of industrial or biological importance. The student should return to this chapter for a review of the chemistry of each functional group as it is met in later chapters.

THE HYDROXYL GROUP—ALCOHOLS AND PHENOLS

If an alkyl halide is treated with aqueous (not alcoholic) sodium hydroxide solution, it is hydrolyzed to the corresponding hydroxy compound or *alcohol*. The hydroxide ion in this general reaction displaces the halide ion, Cl^-, Br^-, or I^-.

$$HO^- + CH_3Cl \xrightarrow[H_2O]{heat} HO{-}CH_3 + Cl^-$$

Methanol or methyl alcohol, b.p. 64.7°

$$HO^- + CH_3CH_2Br \xrightarrow[H_2O]{heat} CH_3CH_2{-}OH + Br^-$$

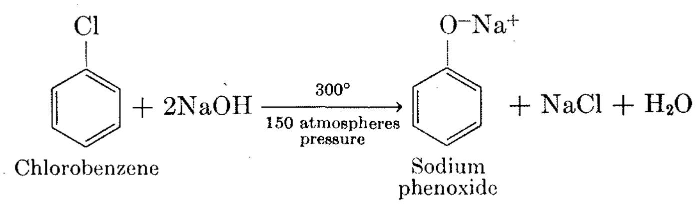
Ethanol or ethyl alcohol, b.p. 78.4°

In general, where R is any alkyl group and X is chlorine, bromine, or iodine, the following reaction can be carried out:

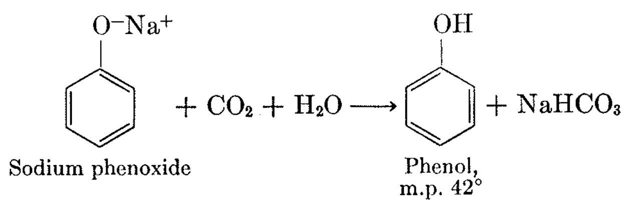
$$HO^- + R{-}X \xrightarrow[H_2O]{heat} R{-}OH + X^-$$

An alkyl halide (R—X); An alcohol (R—OH)

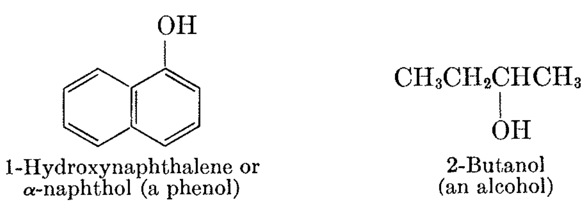
Phenol, or hydroxybenzene, can be made similarly by treating chlorobenzene with sodium hydroxide solution, but very much more drastic reaction conditions are required.



Note in the case of phenol and other hydroxyaromatic compounds that the product is the sodium salt rather than the free hydroxy compound or phenol. This is because phenols, unlike alcohols, are weakly acidic and react with the alkali used in the reaction. The phenol can be liberated from its sodium salt by reaction with carbonic acid (carbon dioxide and water).



The word *phenol* is used as a general term for any hydroxyaromatic compound as well as being the name of a specific compound, hydroxybenzene. *Alcohol* is the general term for hydroxyalkanes as well as being a term loosely used to indicate beverage or grain alcohol, CH_3CH_2OH.



The reason for classifying alcohols and phenols separately even though they are hydroxy compounds is the difference in their acidities. Alcohols are *very* weak acids, about like water, and the "salt" of an alcohol is not made by reacting the alcohol with sodium hydroxide but by reacting it with metallic sodium.

$$2CH_3OH + 2Na \longrightarrow \underset{\text{Sodium methoxide}}{2CH_3O^-Na^+} + H_2$$

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