Halogenation

10-November

Chlorination with Phosphorus Chlorides:

$$3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3$$

$$3RCOONa + PCl_5 \rightarrow 3RCOCl + NaPO_3 + 2NaCl$$
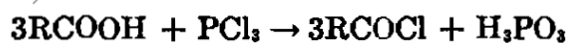
Preparation of Chlorine Derivatives by the Sandmeyer and Gattermann Reactions:

$$RN_2Cl + Cu_2Cl_2 \xrightarrow{HCl} RCl + N_2 + Cu_2Cl_2 \qquad \text{(Sandmeyer)}$$

$$RN_2Cl \xrightarrow[Cu]{HCl} RCl + N_2 \qquad \text{(Gattermann)}$$
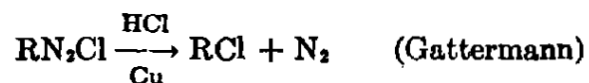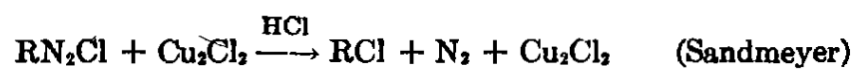
Bromination. In many instances, brominations may be carried out in a manner similar to that employed for the preparation of chlorine deriv-
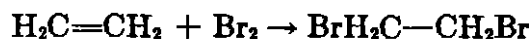
atives. Thus, bromine, bromides, bromates, and alkaline hypobromites may be employed instead of the corresponding chlorine compounds. The Sandmeyer and Gattermann reactions also may advantageously be used for the preparation of bromine compounds.

Reactions involving addition and substitution are common. Bromine dissolved in water is frequently employed, particularly in the bromination of phenols. Potassium bromide is generally added to aqueous bromine solutions to increase the concentration of soluble molecular halogen. Concentrated bromine solutions are thus made available, presumably because of the following equilibrium:

$$Br_2 + KBr \rightleftharpoons KBr_3$$

Bromine, hydrobromic acid, and alkali hypobromites, like the corresponding chlorine compounds, find employment in technical brominations.
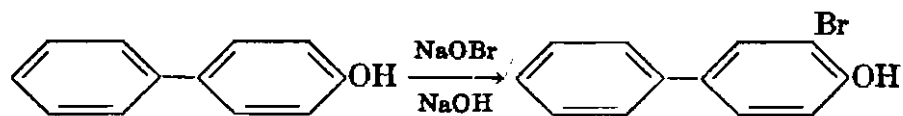
Addition Reaction:

$$H_2C{=}CH_2 + Br_2 \rightarrow BrH_2C{-}CH_2Br$$

Replacement Reaction:

$$C_2H_5OH + \xrightarrow[H_2SO_4]{KBr} C_2H_5Br + KHSO_4 + H_2O$$

Substitution Reaction:

A number of organic carriers for bromine to produce specific types of bromine-containing compounds have been explored through the use of N-bromosuccinimide, N-bromoacetamide, 1,3-dibromo-5,5-dimethylhydantoin, and associated compounds.

Iodination. The methods employed in iodination differ somewhat from those for chlorination or bromination. The relatively weak C-I bond, which is indicated by the low heat of reaction and which distinguishes iodine from other halogens, makes permanent, direct union of carbon to iodine by the replacement of hydrogen possible only in exceptional cases. Such iodinations are reversible in character, as, for instance, the iodination of acetic acid:

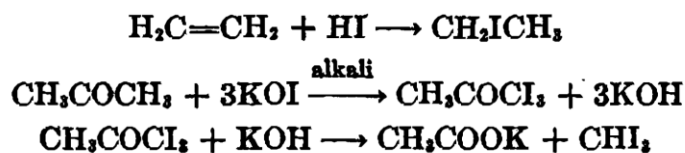$$CH_3COOH + 2I \rightleftharpoons CH_2ICOOH + HI$$
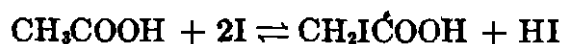
and are governed largely by the conditions employed. The hydrogen iodide tends to effect deiodination of the halogenated compounds and, indeed, is sometimes thus employed. The removal of the hydrogen iodide by such means as oxidation or absorption in alkali is consequently essential for successful iodination. When nitric acid is employed as the oxidant, practically all the iodine enters the organic compound. In the

ordinary direct halogenation in the absence of an oxidizing agent, half the reacting halogen is converted to the hydrogen halide.

Catalysts are only infrequently employed in iodination, phosphorus being the principal accelerator. Iodine monochloride, because of its activity under mild operating conditions, is a useful catalyst for the iodination of amino compounds:

$$I + Cl \rightleftharpoons ICl$$
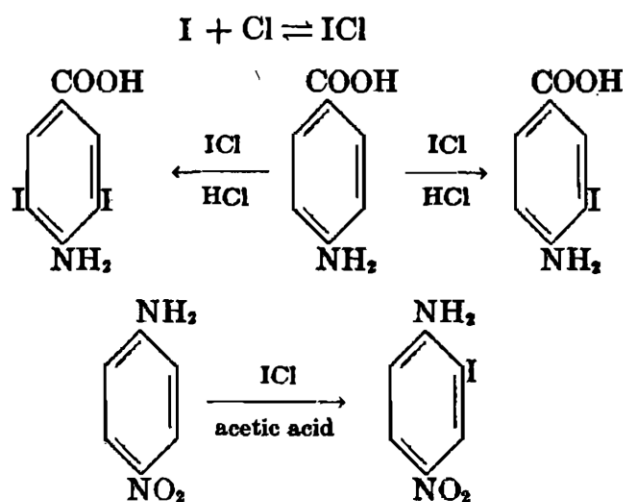
Hydriodic acid and alkali hypoiodites, like the corresponding chlorine and bromine compounds, find employment in iodinations:

$$H_2C=CH_2 + HI \longrightarrow CH_2ICH_3$$

$$CH_3COCH_3 + 3KOI \xrightarrow{\text{alkali}} CH_3COCI_3 + 3KOH$$

$$CH_3COCI_3 + KOH \longrightarrow CH_3COOK + CHI_3$$

Fluorination. Fluorine acts directly on hydrocarbons to produce fluorides, but the reaction is violent and constitutes an explosion hazard. Some reactions can be carried out by careful control of temperature and fluorine concentration, but even then there may be a cleavage of carbon-carbon bonds. The bonds holding the atoms in the fluorine molecule are stronger than in the other halogens; but once the reaction is initiated and fluorine atoms are available, they combine more readily with hydrogen and hydrocarbons than do the halogens of higher molecular weight. Furthermore, the new bonds that are formed are so strong and the heat liberated is so great that precautions must be taken to moderate the reaction so as to keep it under control.

Despite all these problems and the high cost of elemental fluorine, commercial processes of fluorination are being operated and university and industry laboratories are rapidly adding to this technology.