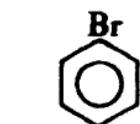


Aryl Halides

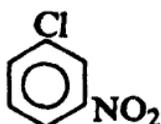
Structure

Aryl halides are compounds containing halogen attached directly to an aromatic ring. They have the general formula ArX, where Ar is phenyl, substituted phenyl.

X= F,Cl,Br,I



Bromobenzene



m-Chloronitrobenzene



p-Iodotoluene



o-Chlorobenzoic acid

An aryl halide is not just any halogen compound containing an aromatic ring. Benzyl chloride, for example, is not an aryl halide, for halogen is not attached to the aromatic ring; in structure and properties it is simply a substituted alkyl halide.

aryl halides differ so much from the alkyl halides in their preparation and properties. Aryl halides as a class are comparatively unreactive toward the nucleophilic substitution reactions so characteristic of the alkyl halides.

The presence of certain other groups on the aromatic ring, however, greatly increases the reactivity of aryl halides; in the absence of such groups, reaction can still be brought about by very basic reagents or high temperatures.

The nucleophilic aromatic substitution can follow two very different paths: the bimolecular displacement mechanism, for activated aryl halides; and the elimination-addition mechanism, which involves the remarkable intermediate called benzyne.

It will be useful to compare aryl halides with certain other halides that are not aromatic at all: vinyl halides, compounds in which halogen is attached directly to a doubly-bonded carbon .



Vinyl halides, we have already seen, show an interesting parallel to aryl halides. Each kind of compound contains another functional group besides halogen: aryl halides contain a ring, which undergoes electrophilic substitution; vinyl halides contain a carbon-carbon double bond, which undergoes electrophilic addition. In each of these reactions, halogen exerts an anomalous influence on reactivity and orientation. In electrophilic substitution, halogen deactivates, yet directs ortho,para; in electrophilic addition, halogen deactivates, yet causes Markovnikov orientation. In both cases we

attributed the influence of halogen to the working of opposing factors. Through its inductive effect, halogen withdraws electrons and deactivates the entire molecule toward electrophilic attack. Through its resonance effect, halogen releases electrons and tends to activate but only toward attack at certain positions.

The parallel between aryl and vinyl halides goes further: both are unreactive toward nucleophilic substitution and, as we shall see, for basically the same reason. Moreover, this low reactivity is caused partly, at least by the same structural feature that is responsible for their anomalous influence on electrophilic attack: partial double-bond character of the carbon-halogen bond.

aryl halides are of "low reactivity" only with respect to certain "sets of familiar reactions typical of the more widely studied alkyl halides.

Physical properties

1- the physical properties of the aryl halides are much like those of the corresponding alkyl halides. Chlorobenzene and bromobenzene, for example, have boiling points very nearly the same as those of *i*-hexyl chloride and *w*-hexyl bromide

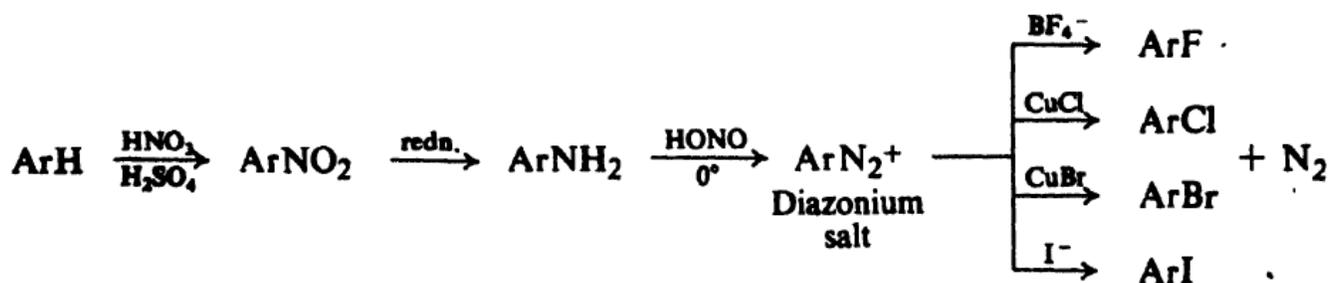
2- like the alkyl halides, the aryl halides are insoluble in water and soluble in organic solvents.

3- The isomeric dihalobenzenes, have very nearly the same boiling points: between 173 and 180 for the dichlorobenzenes, 217 to 221 for the dibromobenzenes, and 285 to 287 for the diiodobenzenes

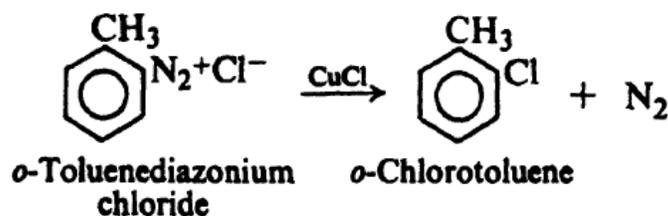
4- the melting points of these same compounds show a considerable spread; in each case, the para isomer has a melting point that is some 70-100 degrees higher than the ortho or meta isomer.

PREPARATION OF ARYL HALIDES

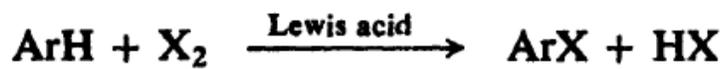
1. From diazonium salts.



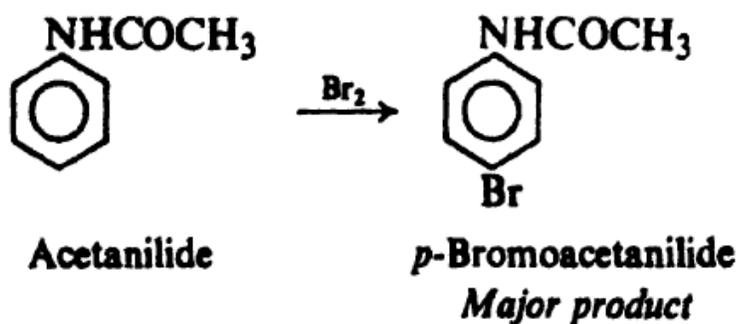
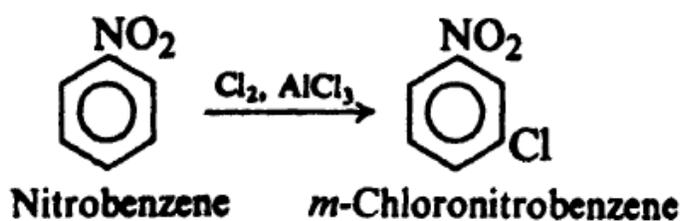
Example:



2. Halogenation.



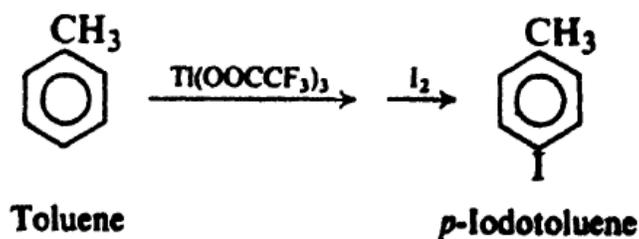
Examples:

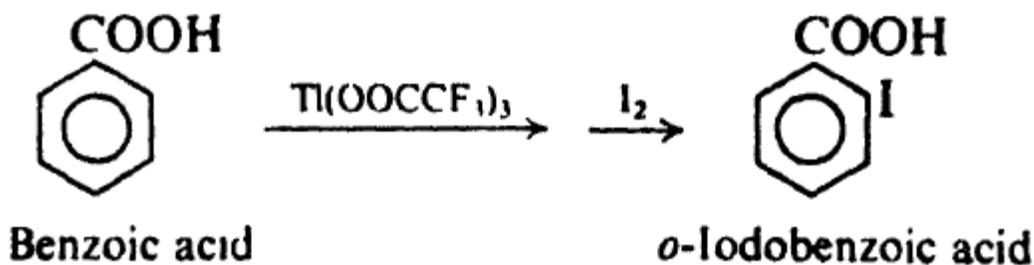


3. From arylthallium compounds.



Examples:





(a) Direct halogenation of the aromatic ring is more useful than direct halogenation of alkanes; although mixtures may be obtained (e.g., ortho + para), attack is not nearly so random as in the free-radical halogenation of aliphatic hydrocarbons.

Furthermore, by use of bulky thallium acetate as the Lewis acid, one can direct bromination exclusively to the para position.

(b) Alkyl halides are most often prepared from the corresponding alcohols; aryl halides are not prepared from the phenols. Instead, aryl halides are most commonly prepared by replacement of the nitrogen of a diazonium salt.

The preparation of aryl halides from diazonium salts is more important than direct halogenation for several reasons:-

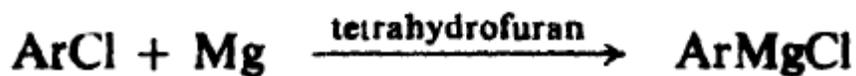
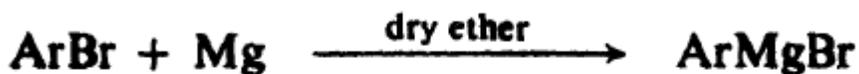
First of all, fluorides and iodides, which can seldom be prepared by direct halogenation, can be obtained from the diazonium salts.

Second, where direct halogenation yields a mixture of ortho and para isomers, the ortho isomer, at least, is difficult to obtain pure.

On the other hand, the ortho and para isomers of the corresponding nitro compounds, from which the diazonium salts ultimately come, can often be separated by fractional distillation

REACTIONS OF ARYL HALIDES

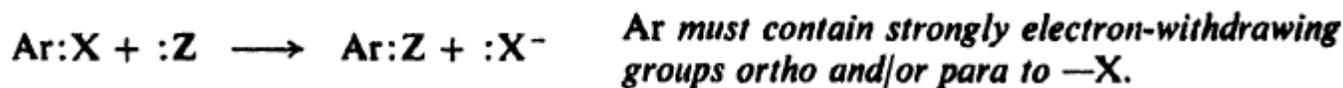
1. Formation of Grignard reagent.



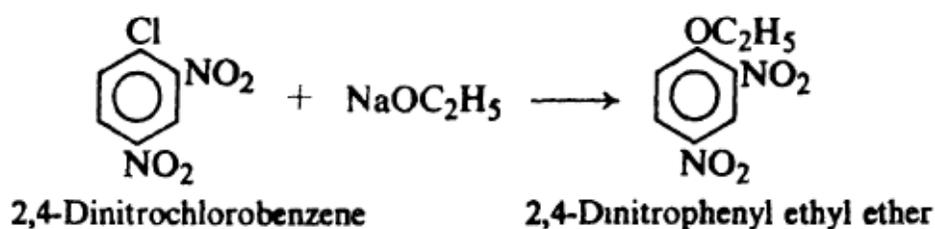
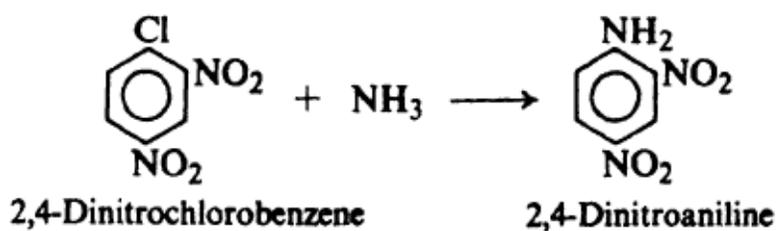
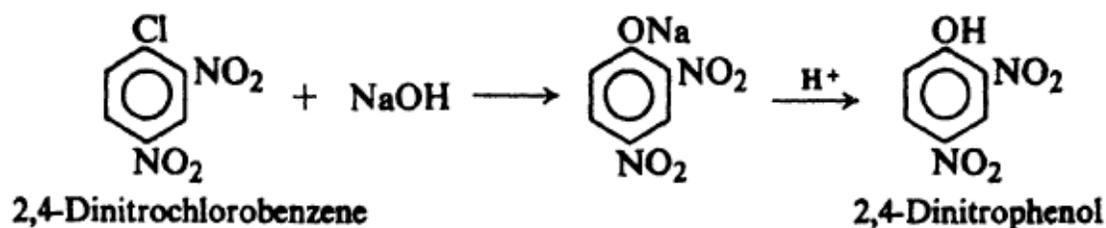
2. Substitution in the ring. Electrophilic aromatic substitution

X: Deactivates and directs ortho,para in electrophilic aromatic substitution.

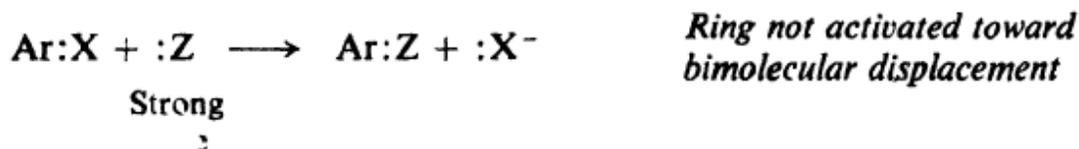
3. Nucleophilic aromatic substitution. Bimolecular displacement



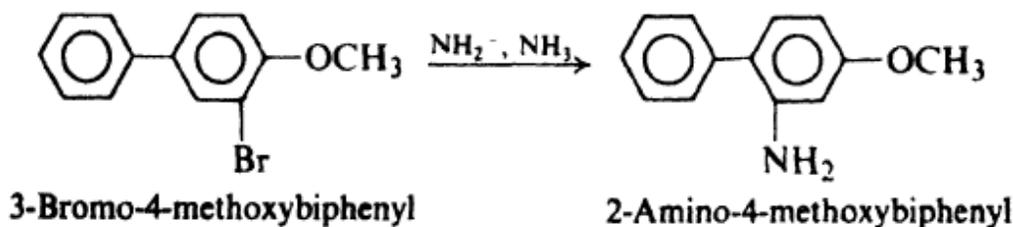
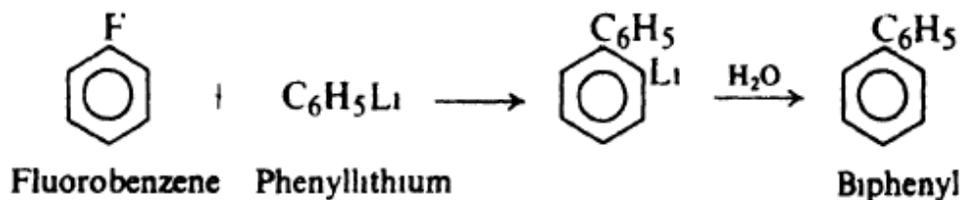
Examples:



4. Nucleophilic aromatic substitution. Elimination-addition.

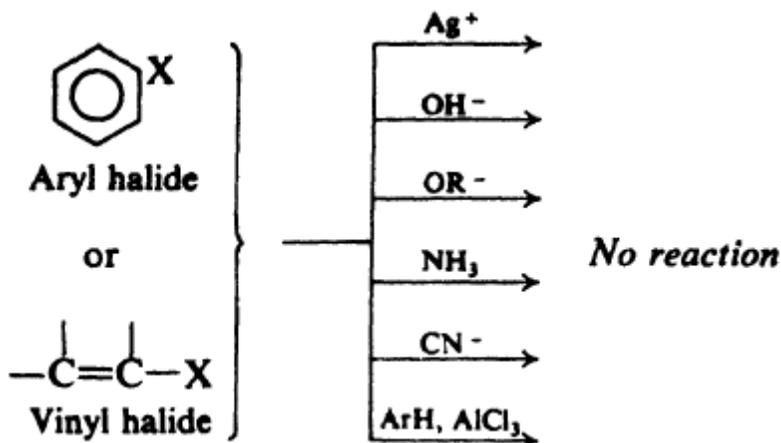


Examples:



Low reactivity of aryl and vinyl halides

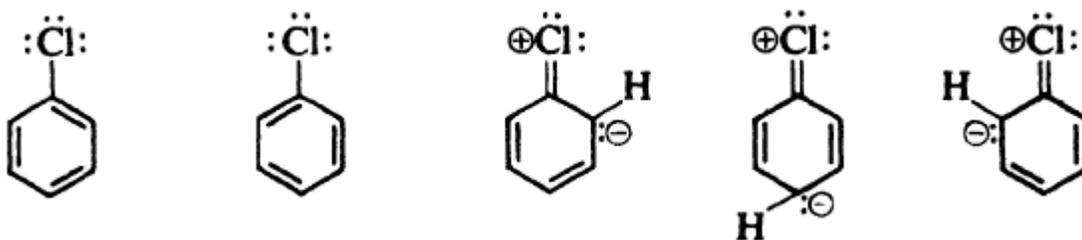
alkyl halide precipitation of insoluble silver halide when it is warmed with alcoholic silver nitrate. The reaction occurs nearly with tertiary, allyl, and benzyl bromides, and within five minutes or so with primary and secondary bromides. Compounds containing halogen joined directly to an aromatic ring or to a doublybonded carbon, however, do not yield silver halide under these conditions. Bromobenzene or vinyl bromide can be heated with alcoholic AgNO₃ for days without the slightest trace of AgBr being detected. In a similar way, attempts to convert aryl or vinyl halides into phenols (or alcohols), ethers, amines, or nitriles by treatment with the usual nucleophilic reagents are also unsuccessful; aryl or vinyl halides cannot be used in place of alkyl halides in the Friedel-Crafts reaction.



Structure of aryl and vinyl halides

The low reactivity of aryl and vinyl halides toward displacement has, like the stabilities of alkenes and dienes been attributed to two different factors:

- (a) delocalization of electrons by resonance; and
- (b) differences in (δ) bond energies due to differences in hybridization of carbon.



vinyl chloride is considered to be a hybrid of two structure



Nucleophilic aromatic substitution: bimolecular displacement

Nucleophilic aromatic substitution is much less important in synthesis than either nucleophilic aliphatic substitution or electrophilic aromatic substitution. the presence of certain groups at certain positions of the ring markedly activates the halogen of aryl halides toward displacement.

