

# [Notes on aryl halides](https://assignbuster.com/notes-on-aryl-halides/)

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## PHYSICAL PROPERTIES:

Boiling points – similar to those of alkyl halides; same trends ? Melting point – Among disubstituted aryl dihalides, para isomer has unusually high MP; ~70 – 100 °C higher than ortho and meta isomers ? Solubility behavior – insoluble in water; soluble in nonpolar organic solvents – para isomer is less soluble than ortho or meta in any given solvent ? can be readily purified by recrystallization

## Consider:

### REACTIONS:

* Electrophilic aromatic substitution (EAS) – recall directing power (o, p director) but ring is deactivated toward EAS.

Nucleophilic Aromatic Substitution (NAS or SNAr) ipso substitution ? an atom or group other than H is replaced in the reaction Reaction Mechanisms For NAS: A. BIMOLECULAR DISPLACEMENT: addition-elimination mechanism; occurs under mild conditions \*\*\*the aromatic ring must contain strongly electron – withdrawing or electron – attracting groups 2 3/22/2012

### Observations:

* Element effect (Bunnett): Aryl halides do not show much difference in reactivities toward NAS via bimolecular displacement.
* Aryl fluorides are most reactive.

Addition - fast removal of the halogen as X- is not the rate determining step .

The Benzyne Mechanism: Elimination-addition mechanism - occurs under forcing or vigorous conditions Evidence for the benzyne mechanism:

* scrambling of the label - reaction mechanism:
* benzyne cannot form if both ortho positions are occupied by other groups 3 3/22/2012

Wurtz-Fittig Reaction 3. O-bromoanisole and m-bromoanisole give the same product under the reaction conditions.

## ANALYSIS:

Chemical tests: Test Reagent Br2/CCl4 KMnO4 AgNO3 Result

### OTHER REACTIONS OF ARYL HALIDES

* Metallation Reactions for aryl halides without reactive groups Grignard Reaction:
* IR Spectroscopy C-X absorptions lie in the fingerprint region ? not useful for analysis 1000 – 1350 cm-1 C – F str. 750 – 850 cm-1 C – Cl str. 500 – 680 cm-1 C – Br str. 200 – 500 cm-1 C – I str. Important peak frequencies 1500, 1600 cm-1 3000 – 3100 cm-1 aromatic C – C str. aromatic C – H str. Reaction with Lithium Metal: Transmetallation – most successful with ArBr and ArI 4