

# Notes on aryl halides

[Science](#), [Chemistry](#)



**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 S<sub>N</sub>Ar) 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<sup>-</sup> 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:

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- benzyne cannot form if both ortho positions are occupied by other groups 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 Br<sub>2</sub>/CCl<sub>4</sub> KMnO<sub>4</sub> AgNO<sub>3</sub> 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<sup>-1</sup> C - F str. 750 - 850 cm<sup>-1</sup> C - Cl str. 500 - 680 cm<sup>-1</sup> C - Br str. 200 - 500 cm<sup>-1</sup> C - I str. Important peak frequencies 1500, 1600 cm<sup>-1</sup> 3000 - 3100 cm<sup>-1</sup> aromatic C - C str. aromatic C - H str. Reaction with Lithium Metal: Transmetallation - most successful with ArBr and ArI 4