

Title: **Modern Approaches to Halogen Exchange Reaction in Aromatic Compounds: Rethinking the Classical Finkelstein Reaction.**

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Halogenated compounds are highly important in many scientific disciplines, among which chemistry, pharmacology and medicine stand out. The usefulness of this compound family has traditionally been related to its reactivity profile. For example, while the highly reactive iodo derivatives are often desired for cross-coupling applications, in other situation the less reactive organochlorine species may help avoid undesired side-reactions. Unfortunately, the halide required in each case is not always the one that is commercially accessible. Therefore, developing halogen exchange methodologies that convert inexpensive halogenated compound to obtain more important but less accessible ones, represents a very important goal of synthetic chemistry.

Even though this type of processes, exemplified by the oft-employed Finkelstein reaction, has been very useful in aliphatic systems, their extrapolation to the C(sp²)-based cores has represented a major challenge. However, significant advances have been achieved thanks to the advent of new types of Ar-X bond activation, such as transition metals catalysis. In this report, a bibliographic search has been carried out to show how the field has evolved from the early halogen exchange processes with (super)stoichiometric amount of metal to the current methods which can be performed using a catalytic amount of metal and even in some cases absent it.

In the Introduction section, the classical Finkelstein process is introduced, along with selected early stoichiometric metal-enables halogen exchange processes in aromatic system, including copper-based Ullmann-type reactivity. In the main section, modern catalytic approaches are discussed, starting with the seminal Buchwald method for Cu-catalyzed aromatic Finkelstein reaction. Finally, additional approaches to halogen exchange are discussed, including the usage of photo-activation of Ar-X bonds by UV radiation.

Keywords: Halogenated compounds, Halogen Exchange, Aryl halide, Vinyl halide, transition metal catalysis, Finkelstein reaction, Aromatic Finkelstein reaction, Photo-activation.