

umpolung

Any process by which the normal alternating donor and acceptor reactivity pattern of a chain, which is due to the presence of O or N heteroatoms, is interchanged. Reactivity umpolung is most often achieved by temporary exchange of heteroatoms (N, O) by others, such as P, S and Se.

The original meaning of the term has been extended to the reversal of any commonly accepted reactivity pattern. For example, reaction of $R-C\equiv CX$ (X = halide) as a synthon for ' $R-C\equiv C^+$ ' (i.e. *electrophilic* acetylene) is an umpolung of the normal more common acetylide, $R-C\equiv C^-$ (i.e. *nucleophilic*) reactivity.

1994, 66, 1174