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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≡CX (X = halide) as a synthon for 'R–C≡C^{+} (i.e. electrophilic acetylene) is an umpolung of the normal more common acetylide, R–C≡C^{-} (i.e. nucleophilic) reactivity.

Source:
PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1174

