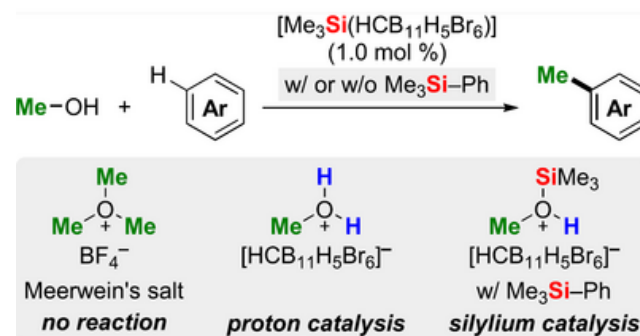


Catalytic protocol for direct methylation of arenes with methanol

Start Time: Sunday, February 5, 2023

End Time:



Catalytically Generated Meerwein's Salt-Type Oxonium Ions for Friedel–Crafts C(sp²)–H Methylation with Methanol

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The group of UniSysCat group leader [Martin Oestreich](#) developed a new catalytic protocol which is important for the industrial methylation of aromatic compounds such as benzene and especially toluene, but also electron-deficient arenes under sustainable reaction condition via a Friedel–Crafts-type direct C(sp²)–H methylation.

Counteranion-stabilized silylium or arenium ions, which form the so-called Meerwein's salt-like oxonium ions initiate the underlying reaction utilizing methanol as the active methylating agents. Such silylated methyloxonium ions comprise stronger electrophiles than their protonated congeners, allowing the Friedel–Crafts alkylation to proceed more efficiently and at a lower reaction temperature, which is of high relevance for a sustainable industrial production. The regeneration of these superelectrophiles within the catalytic cycle is accomplished by the addition of a tetraorganosilane additive, i.e., trimethyl(phenyl)silane or tetraethylsilane. The latter release a silylium ion through protodesilylation by the Brønsted acidic "Wheland" intermediate, which acts as productive "proton-into-silylium ion" generator. This method allows even the C–H methylation of electronically deactivated aryl halides with methanol. In addition, this protocol can be also applied to nonactivated primary as well as π -activated benzylic alcohols and also dialkyl ethers could be used as alkylating agents.

Read more <https://doi.org/10.1021/jacs.2c13341>