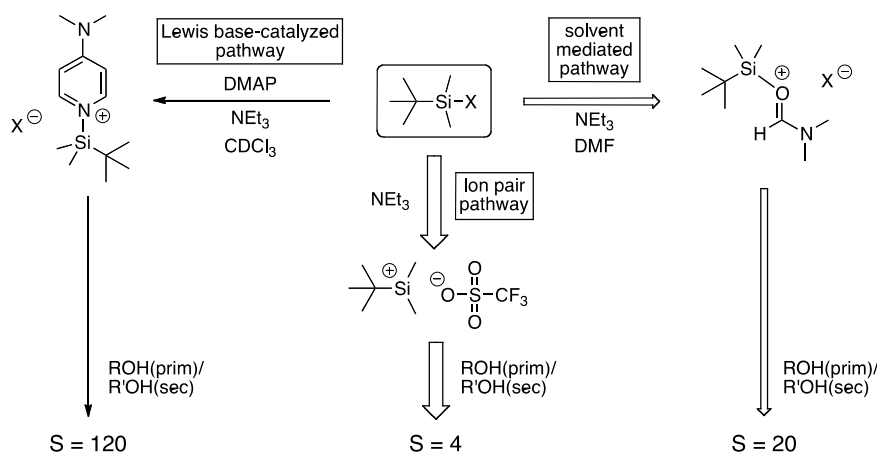


The Silylation of Alcohols

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The selective silylation of alcohols represents one of the most powerful tools in the manipulation of polyfunctional molecules. The selectivity S can readily be quantified as the ratio of silylation rates of structurally similar primary and secondary alcohols.¹ Using selected reagents for transfer of the *tert*-butyldimethylsilyl (TBS) group we show that the underlying reaction mechanisms are highly variable, and include at least three different limiting scenarios. For the most reactive silyltriflate reagents the reaction rates show hardly any Lewis base catalysis and are characterized by low S values. Less reactive reagents such as silyl chlorides and cyanides react most readily in a Lewis basic solvent such as DMF, which is actively involved in promoting the reaction.² Much slower absolute reaction rates (and highest substrate selectivities S) are found for this latter group of reagents in apolar organic solvents. The reactions can then be promoted quite effectively by Lewis base catalysts.



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2. Zhang, C.; Patschinski, P.; Stephenson, D. S.; Panisch, R.; Wender, J. H.; Holthausen, M. C.; Zipse, H. *Phys. Chem. Chem. Phys.* **2014**, *16*, 16642.