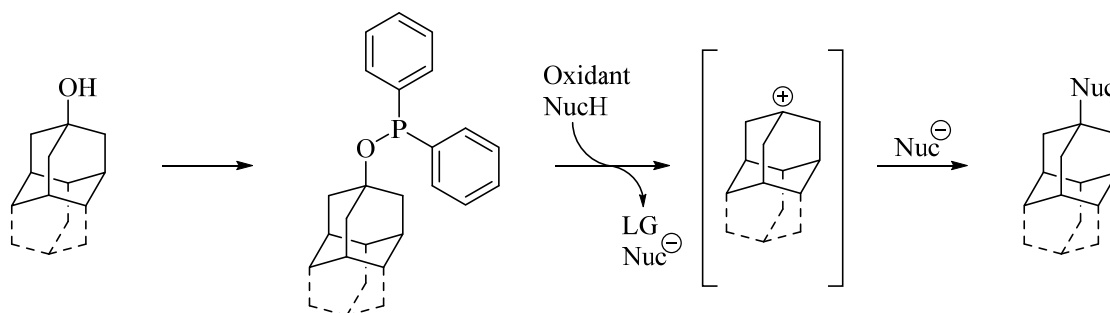


ALKOXYDIPHENYLPHOSPHINITES AS CARBOCATION SYNTHONS

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Alcohols are one of the most common classes of organic compounds and they are often used as starting materials for functional group transformations. Substitution reactions on alcohols are often carried out in acidic media (S_N1) or with prior conversion to more suitable leaving groups like halides or sulfonate esters (S_N1 or S_N2). Due to limitations of these reaction pathways, different methods for *in situ* activation of alcohols have been developed throughout the last decades. Nevertheless restrictions in the substrate scopes are common, often due to steric hindrance.[1,2] We present a modified procedure of the Mitsunobu reaction, including prior conversion of tertiary (diamondoid) alcohols to alkoxydiphenylphosphinites that can be activated by mild oxidants like DIAD. Protonation of the betaine intermediate by even weakly acidic nucleophiles releases a phosphonohydrazine as leaving group together with a carbocation that is trapped by the deprotonated nucleophile.



Scheme 1: Substitution of sterically demanding alcohols *via* oxidative activation of their diphenylphosphinites.

Because of promising preliminary results with 1-adamantanol and 4-diamantanol for C-C, C-N, C-S, C-O and C-X bond formations, we envision to apply this kind of transformation to other challenging alcohols.

[1] O. Mitsunobu, M. Yamada, T. Mukaiyama, *B. Chem. Soc. Jpn.* **1967**, *40*, 935-939.

[2] Q. Yang, Q. Wang, Z. Yu, *Chem. Soc. Rev.* **2015**, *44*, 2305-2329.