

SYNLETT Spotlight 261

Triethylsilane (TES)

Compiled by Jorge de Almeida Rodrigues Jr



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Jorge de Almeida Rodrigues Jr was born in 1982 in Rio de Janeiro, Brazil. He received his B.Sc. in Chemistry (2006) from the Chemistry Institute of Universidade Federal do Rio de Janeiro, Brazil. He joined the doctorate program in Organic Chemistry of the same institute in 2006, where is currently pursuing his D.Sc. under the supervision of Professor Regina Sandra Veiga Nascimento. His current research focuses on the development of new polymers through the modification of commercial ones, aiming towards application in petroleum industry.

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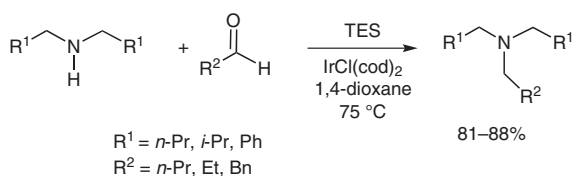
Introduction

Triethylsilane (TES or Et_3SiH) is a versatile reagent in organic chemistry that can be used primarily as a hydride source in a series of reduction reactions, including etherification of carbonyls,¹ aldol reactions,² conversion of aliphatic carboxyl derivatives in hydrocarbons,³ and reduction

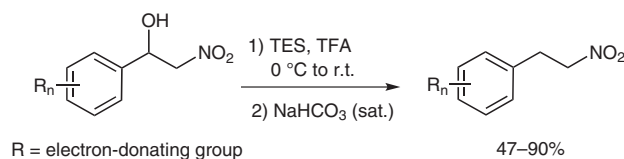
of organic azides to amines⁴ and nitro groups to hydroxylamines or amines.⁵ TES also has great potential for use in radical reactions, performing as an alternative to the toxic Bu_3SnH as hydrogen source.⁶ Recently, TES was shown to be a good reagent for generating hydrogen in situ on catalytic surfaces,⁷ leading to successful hydrogenation reactions without the use of the dangerous hydrogen gas.

Abstracts

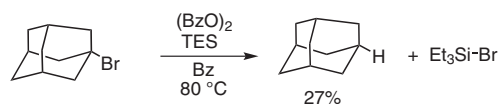
(A) In order to promote the reductive alkylation of secondary amines with aldehydes, the reducing agent TES was used together with an iridium complex as catalyst, in an efficient methodology proposed by Mizuta et al.⁸ Through deuterium labelling experiments, it was also revealed that silane and water, generated during the formation of enamine by the reaction of amine and aldehyde, seem to behave as a hydrogen source.



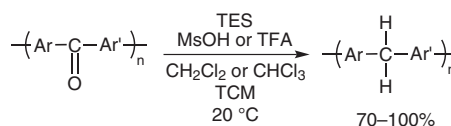
(B) Direct conversion of ring-activated β -aryl- β -hydroxynitro compounds into the corresponding β -arylnitroethanes using TES and trifluoroacetic acid (TFA) was described by Luzzio et al. as a new and useful way to obtain intermediates.⁹ This route presents the advantage of bypassing the formation of nitroolefin in the usual way, avoiding the need to reduce conjugated double bonds, which could lead to mixtures of products.



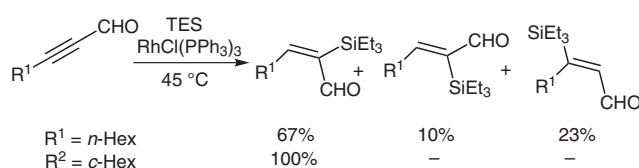
(C) Recently, Longshaw and co-workers, while re-investigating the use of $(\text{TMS})_3\text{CH}$ as mediator of radical reactions, observed that it does not function in this reaction.¹⁰ However, in competition experiments, they noted that TES plays as a more effective reagent for this kind of reaction, since the abstraction of bromine from 1-bromoadamantane is exothermic for Et_3Si , but endothermic for $(\text{TMS})_3\text{C}$.



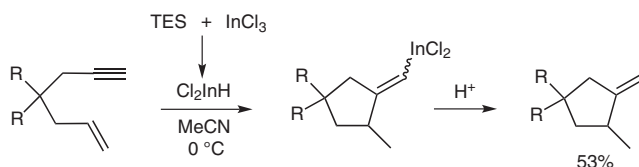
(D) TES was reported as an efficient reagent for reducing aromatic ketone linkages to methylene groups, in order to achieve linear polymers containing benzylic methylene linkages.¹¹ This kind of polymer would be very difficult to obtain through direct synthesis, due to the strong tendency of cross-linking to occur.



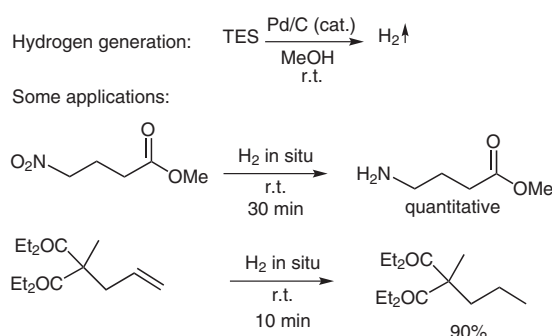
(E) Ynals are quantitatively hydrosilylated with TES, using $\text{RhCl}(\text{PPh}_3)_3$ as catalyst, resulting in enals. In the case of 3-cyclohexylprop-2-ynal, the hydrosilylation is both regio- and stereospecific. The obtained products were used in the synthesis of a series of 1,3-arylsubstituted allenes.¹²



(F) Indium hydride generated from TES and InCl_3 was presented by Hayashi et al. as a promising alternative to Bu_3SnH in radical reactions.⁶ Their work shows an effective intramolecular cyclization of enynes using the proposed system.



(G) A series of hydrogenation reactions was successfully performed by Mandal and McMurray through the in situ generation of hydrogen on a Pd/C catalytic surface, with TES as hydrogen source,¹³ inspired by previous work of Fukuyama and co-workers.¹⁴



References

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