

SYNLETT Spotlight 123

Antimony Pentachloride

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

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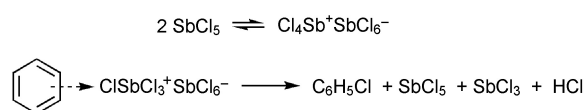
Introduction

Inorganic compounds are well-known in organic synthesis due to their many applications. One of these compounds is antimony pentachloride (SbCl_5), which has a trigonal bipyramidal configuration in the gaseous state.¹ Examination of the Raman spectra^{2,3} points to retention of

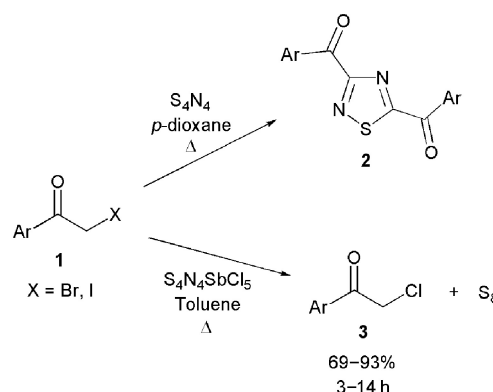
the trigonal bipyramidal configuration in both the liquid and the solid state. This reagent has several applications and can be used as a Lewis acid, as a chlorination agent for olefins and aromatic compounds, and as a Diels–Alder catalyst.

Abstracts

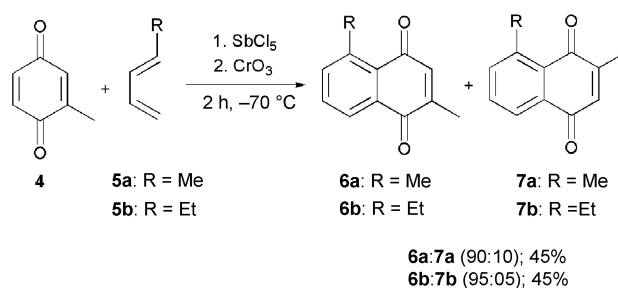
(A) Chlorination of aromatic compounds by antimony pentachloride⁴ has received relatively little attention, except as a route to polychlorinated compounds. An investigation of the reaction of SbCl_5 with halobenzenes and toluene indicated that chlorination proceeds by electrophilic substitution, involving an attacking species of low activity. This was evidenced by the almost exclusive *ortho/para* orientation.⁵



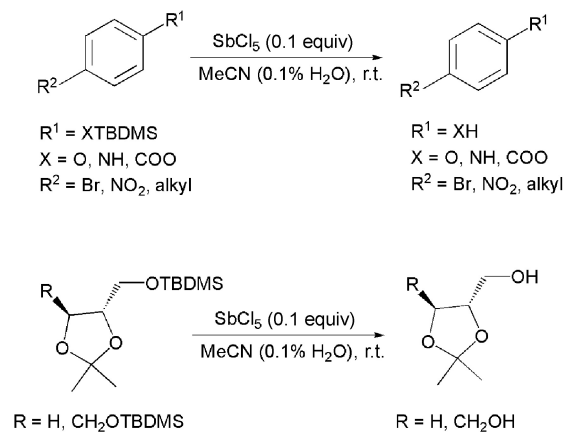
(B) Tetrasulfur tetranitride (S_4N_4) reacts in inert solvents with a wide variety of Lewis acids to give isolable adducts.⁶ The interest in exploiting the potential synthetic utility of the adduct $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$ led to a preliminary result in which treatment of α -bromomethyl ketones **1** with the adduct in toluene at reflux gave the corresponding chloro compounds **3** in good to excellent yields, regardless of the bulkiness of the groups at the α' -position of ketones **1**.⁷



(C) Improved regioselectivity in catalyzed Diels–Alder cycloadditions between non-symmetrical benzoquinones and mono-substituted butadienes can be achieved with SbCl_5 .⁸



(D) SbCl_5 in sub-stoichiometric quantity, in moist acetonitrile, is an efficient and mild system for the deprotection of TBS derivatives of amines, phenols, primary alcohols and aryl carboxylic acids. Yields for this deprotection are good to excellent. High selectivity for OTBS cleavage is noted in the presence of a ketal group.⁹



References

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