

A New Synthesis of Trimethylsilyl Esters of Phosphorus(III) Acids

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Abstract—Trimethylsilyl esters of P(III) acids were synthesized in high yields (89–94%) by the reaction of hydrophosphoryl compounds with hexamethyldisilazane at 20°C in the presence of ZnSO₄ and diethylamine. The reaction is complete in 4 h, it does not require specially prepared solvents or an inert atmosphere, and can be proposed as a new synthetically useful and easy-to-perform method for the synthesis of trimethylsilyl esters of P(III) acids.

Keywords: dialkyl phosphites, ethyl phenylphosphonite, diphenylphosphine oxide, hexamethyldisilazane, dialkyl trimethylsilyl phosphites, ethyl trimethylsilyl phenylphosphonite, trimethylsilyl diphenylphosphinite, diethyl(trimethylsilyl)amine, reagent catalyst, ZnSO₄

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INTRODUCTION

Trimethylsilyl esters of P(III) acids **1** are synthetically important precursors for the Michaelis–Arbuzov reaction [1, 2]. Their use in synthesis leads to higher yields of the target P(V) derivatives as with related alkyl esters of P(III) acids [1–3]. At present, a few synthetic approaches to trimethylsilyl ethers **1** have been proposed, the most popular of which involve the reactions of hydrophosphoryl compounds **2** in the presence of triethylamine [4–6] or of their salts with trimethylchlorosilane [5–7], as well as the reactions of hydrophosphoryl compounds **2** with hexamethyldisilazane (**3**) [10–13] or a mixture of hexamethyldisilazane (**3**) with trimethylchlorosilane [12, 13]. However, these methods are all not without drawbacks: they require the use of an inert atmosphere and anhydrous solvents [4–9] or heating to 110–120°C [10–15].

Previously [16], continuing our research [17, 18] on the synthesis of trimethylsilyl esters of P(III) acids **1**, we showed that the reaction of diethyl phosphite (**2a**) with disilazane **3** is reversible. The equilibrium of this

reaction shifts toward the target diethyl trimethylsilyl phosphite (**1a**) in the presence of ZnCl₂ (**4**) as a reagent catalyst which, along with catalyzing the reaction of phosphite **2a** with disilazane **3**, can absorb ammonia released during the reaction and thus make it irreversible. The reaction occurs with self-heating and results in the complete conversion of phosphite **2a** to diethyl trimethylsilyl phosphite (**1a**) with the final yield of 76% [16] (Scheme 1).

However, ZnCl₂ proved to have its own drawbacks: the formation of suspensions during processing the reaction mixture, making it difficult to filter off the precipitate, as well as incomplete precipitation of inorganic components that are partially distilled with the product; as a result, repeated distillation is required, which ultimately reduces the yield.

RESULTS AND DISCUSSION

In the present work we explored the use of zinc sulfate (**5**), which is insoluble in organic solvents and, like ZnCl₂ (**4**), capable of absorbing ammonia, thus driving the reaction. Preliminary experiments established

Scheme 1. Reaction of diethyl phosphite (**2a**) with hexamethyldisilazane (**3**) in the presence of ZnCl₂ (**4**).

