SYNLETT

Spotlight 185

This feature focuses on a reagent chosen by a postgraduate,

highlighting the uses and prepa-

ration of the reagent in current

Tetrabutylammonium Triphenyldifluorosilicate (TBAT)

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Introduction

research

Tetrabutylammonium triphenyldifluorosilicate (TBAT, **1**) is a hypervalent silicate which acts as a potent source of fluoride ions (Figure 1). The reagent has been widely exploited in organic chemistry as a means of carrying out nucleophilic fluorination reactions,¹ activating organosilanes as nucleophiles^{2–7} as well as acting as a coupling reagent in palladium-catalysed reactions.^{8–10}

$\begin{bmatrix} F \\ Ph - Si \overset{\mathsf{u} \mathsf{P}h}{\underset{I}{\mathsf{P}}} Ph \end{bmatrix}^{-} Bu_4 N^+$

Figure 1

TBAT (1) is readily soluble in organic solvents, not appreciably basic, non-hygroscopic and trivial to obtain in anhydrous form. It therefore presents numerous advantages over other fluoride sources such as metal fluoride salts and tetraalkylammonium fluorides (such as TBAF) which often cause problems associated with basicity and the presence of water.¹¹

Abstracts

Nucleophilic fluorination of primary alkyl halides **4** and **5**, secondary alkyl halides, tosylate **6**, mesylates and triflate **8** has been achieved using TBAT as a fluoride source. These reactions produced alkyl fluorides in good yields with minimal contamination from alkene or alcohol byproducts.¹

SYNLETT 2007, No. 2, pp 0339–0340 Advanced online publication: 24.01.2007 DOI: 10.1055/s-2007-968020; Art ID: V18906ST © Georg Thieme Verlag Stuttgart · New York

Preparation

Tetrabutylammonium triphenyldifluorosilicate (TBAT, **1**) is commercially available but can also be prepared according to a simple and high-yielding procedure developed by P. DeShong and co-workers.¹² Triphenylsilanol (**2**) is treated with aqueous hydrofluoric acid (CAUTION) in methanol to produce the intermediate triphenylsilyl fluoride (**3**). This fluoride is then treated with TBAF to produce the hypervalent silicate TBAT (**1**, Scheme 1). Care must be taken when analysing TBAT since the compound is acid-sensitive and has been found to degrade in acidic solvents such as chloroform.¹²

Ph₃SiOH
$$\xrightarrow{aq \text{ HF}}$$
 Ph₃SiF $\xrightarrow{\text{TBAF, THF}}$ Bu₄⁺(Ph₃SiF₂)⁻
2 3 (99%) 1 (95%)

Scheme 1





12 (81%)

14 (96%)

17 (79%)

CH₂Ph

20 (51-94%)

,Ph

OTMS

HO

Ph

TBAT (0.1 equiv)

THF 0 °C

Tetrabutylammonium triphenyldifluorosilicate (TBAT) has been employed as a fluoride source to generate in situ carbanions from organosilanes **10**, **13** and **15**; these anions have been reacted with a number of electrophiles including imine **16**, aldehyde **11** and ketones, in moderate to high yields. Tetrabutylammonium triphenyldifluorosilicate (TBAT) can be used in catalytic quantities in the reaction of organosilane compounds with aldehydes.²

The allylfluorosilicate species produced by reaction of TBAT with allyl silanes have been reacted with *N*-acylhydrazones **18** in the presence of indium(III) trifluoromethanesulfonate to produce allyl adducts **20** with good diastereoselectivity. Tetrabutylammonium triphenyldifluorosilicate (TBAT) is unique in this role as a fluoride source since it is the only fluoride source which is compatible with activation of the electrophile (**18**) with a Lewis acid.^{3,4}

A route to multisubstituted indolizidines 22 has been developed, the key step involving the fluoride ion induced intramolecular reaction of 2,3-dihydro-4-pyridinones 21 with a pendant allylsilane. Tetrabutylammonium triphenyldifluorosilicate (TBAT) was found to be the most effective fluoride source in these reactions, leading to the highest yields and minimal side products.⁶

The diastereoselective Michael addition of lactone **23** to the enone system **27** has been carried out using TBAT as a fluoride source. The formation of trimethylsilyl enol ether **24** was achieved by the reaction of lactone **23** with a-trimethylsilyl ester **26** in the presence of catalytic TBAT. Activation of this intermediate **24** (also with TBAT) and reaction with enone **27** produced ketone **25** diastereoselectively in good yield in a single reaction pot.⁷

It has been established that hypervalent silicate compounds can undergo Pd(0)-catalysed cross-coupling reactions and are a viable alternative to toxic stannanes or boronic acid derivatives which can be difficult to prepare. Tetrabutylammonium triphenyldifluorosilicate (TBAT) has proved to be a good phenyl source in Pd(0)-catalysed cross-coupling reactions with allylic ester **28**,⁸ aryl halides **31**¹⁰ and aryl triflates **32**.¹⁰



P٢

С

11

Ph

10







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