On the Synthesis and NMR Analysis of Tetrabutylammonium Triphenyldifluorosilicate

Christopher J. Handy, Yiu-Fai Lam, and Philip DeShong*

Department of Chemistry and Biochemistry, The University of Maryland, College Park, Maryland 20742

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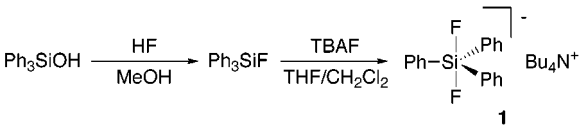
Introduction

Since the initial report of the synthesis of tetrabutylammonium triphenyldifluorosilicate (TBAT, **1**, Scheme 1),[1] this and related hypervalent silicates have been shown to be versatile reagents with numerous synthetic applications.[2−16] Our group has reported on the use of TBAT in nucleophilic displacement reactions,[1] as a fluoride source for silicon−carbon bond cleavage,[17] and as a phenylation reagent in palladium-catalyzed cross coupling reactions.[18,19] Recently, the Denmark group at the University of Illinois contacted us concerning discrepancies in the initial characterization of TBAT. Accordingly, we have performed additional studies concerning both the synthesis of TBAT and its behavior in various NMR solvents and report the following clarifications regarding the original synthetic procedure. In the intial publication, we were not aware of and did not stress the importance of several of these factors.

Results and Discussion

Synthesis of TBAT. Analytically pure TBAT (**1**) is obtained by the previously published synthetic procedure, provided careful attention is given to the following details. The previously reported synthesis of TBAT begins with reaction of triphenylsilanol and aqueous hydrofluoric acid in methanol. The resulting intermediate, triphenylsilyl fluoride, is then converted to **1** using a 1.0 M solution of tetrabutylammonium fluoride (TBAF) in THF. Experience has shown that impurities initially present in the triphenylsilanol are carried through the synthesis. Attempts to remove these impurities through repeated recrystallization of the final product are tedious and often unsuccessful. Therefore, it is recommended that the starting silanol be recrystallized (hexanes/ethyl acetate) prior to transformation to the fluoride.

Scheme 1



Furthermore, the stoichiometry of the reagents in the second step is of the utmost importance. Critical is the need to avoid use of excess TBAF. As noted in the previously published procedure, the stoichiometry is 1.0 equiv of Ph_3SiF to 0.98 equiv of TBAF. In the previously reported procedure, the amount of TBAF to be used is based on the assumption that the crude fluoride contains 4% water. To ensure correct stoichiometry in the second step, we recommend the use of anhydrous triphenylsilyl fluoride, which may be obtained by recrystallization of the crude fluoride from methanol/water followed by drying under vacuum.

A second matter of concern in this step is that commercially available solutions of TBAF (1.0 M in THF) contain varying amounts of bifluoride ion (FHF^-), observable by ^{19}F NMR spectroscopy.[20] Since excess fluoride and bifluoride have been implicated in the decomposition of pentacoordinate fluorosilicates,[21] it is essential that these impurities not contaminate the final product. Consequently, addition of excess or contaminated TBAF is to be avoided.[22]

Following the azeotropic removal of water from the reaction mixture and isolation of the crude product, recrystallization affords analytically pure TBAT. We have found two acceptable solvent systems for recrystallization: ethyl acetate yields TBAT as fine needles, while methylene chloride/hexanes gives TBAT as large blocks.[23]

NMR Analysis of TBAT. Contrary to our previously published results, ^1H and ^{19}F spectra should not be acquired using deuteriochloroform ($CDCl_3$) as the NMR solvent. Solutions of TBAT in $CDCl_3$ give one spectrum immediately following preparation and an entirely different spectrum upon standing at room temperature for several hours. This behavior is attributed to trace amounts of acid in the $CDCl_3$ that act to accelerate the

* To whom correspondence should be addressed. Phone: 301-405-1892. Fax: 301-314-9121. E-mail: pd10@umail.umd.edu.

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(22) We recommend ^{19}F spectroscopy to check the purity of the 1.0 M solution of TBAF in THF prior to its use in the synthesis, as varying amounts of bifluoride and other contaminants are often present in commercially available solutions purchased from Acros and Aldrich. Alternatively, the Denmark group recommends preparation of 1.0 M TBAF in THF from crystalline TBAF purchased from Fluka. These prepared solutions contain <1% bifluoride and are stable indefinitely.

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decomposition of TBAT. This extreme sensitivity of TBAT toward acid has been confirmed by adding HCl to solutions of TBAT in both DMSO and acetonitrile. We therefore recommend dimethyl sulfoxide-d_6 (DMSO-d_6) as the NMR solvent for routine ^{1}H and ^{19}F analysis of TBAT.

A particularly interesting characteristic of the ^{1}H NMR spectrum of TBAT is the long relaxation times of the aromatic protons relative to the relaxation times of the tetrabutylammonium cation protons. A solution of TBAT in DMSO-d_6 subjected to an inversion recovery experiment illustrates this phenomenon. Measurement of the T_1 values gives relaxation times of approximately 2 s (τ_{null}/ln 2) for the aromatic protons, thus indicating that it is necessary to set the delay time between pulses to approximately 8 s in order to obtain accurate integration of the aromatic region of the spectrum.

Unfortunately, solutions of TBAT in DMSO-d_6 are not practical for ^{13}C and ^{29}Si NMR spectral analysis, presumably due to extremely slow relaxation of the corresponding nuclei. In these two cases, we recommend preparation of a concentrated solution of TBAT in freshly distilled $CDCl_3$ (approximately 0.25 M) followed by immediate spectral analysis. As in the previous case, it is necessary to adjust the instrument delay time to 4 s (^{13}C) and 10 s (^{29}Si) in order to obtain accurate spectral data. Furthermore, the optimal conditions for obtaining the ^{13}C spectrum of TBAT are a 30° pulse with inverse gated proton decoupling to eliminate NOE.

Conclusion

With the several precautions mentioned above, synthesis of analytically pure TBAT can be accomplished. However, the sensitivity of TBAT toward acid and the long relaxation times of its aromatic protons complicate the subsequent NMR spectral analysis.

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Supporting Information Available: ^{1}H and ^{19}F spectra of TBAT in DMSO-d_6, ^{13}C and ^{29}Si spectra of TBAT in $CDCl_3$, ^{1}H spectrum of TBAT in $CDCl_3$ illustrating its decomposition, and stacked plot from the inversion recovery experiment. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) TBAT is synthesized as follows. (i) Synthesis of triphenylsilyl fluoride: Triphenylsilanol was recrystallized from hexanes/ethyl acetate prior to use. A solution of triphenylsilanol (25.0 g, 90.4 mmol) in methanol (90 mL) in a polypropylene bottle was prepared and cooled to 5 °C. Aqueous HF (13 mL of a 49% solution, 360 mmol) was slowly added. The reaction mixture was allowed to warm to room temperature, followed by stirring for an additional 30 min. Distilled water (50 mL) was added to induce further precipitation of product. The resulting slurry was vacuum filtered and rinsed with water (4 × 75 mL). The crude product was recrystallized (methanol/water) and dried under vacuum for 24 h to afford 23.9 g (85.9 mmol, 95%) of triphenylsilyl fluoride as fine white crystals, mp (corr.) 62−63 °C. Spectral data matched that which was previously reported.[1] (ii) Synthesis of tetrabutylammonium triphenyldifluorosilicate (TBAT, **1**): Triphenylsilyl fluoride (23.9 g, 85.9 mmol) was dissolved in CH_2Cl_2 (100 mL). Tetrabutylammonium fluoride (84 mL of a 1.0 M solution in THF, 84 mmol) was added in one portion, and the reaction mixture was concentrated at reduced pressure. The resulting white paste was dissolved in 750 mL of ethyl acetate. Approximately 250 mL of the ethyl acetate was distilled off under N_2 to azeotropically remove water. Additional ethyl acetate (250 mL) was then added and distilled off, resulting in a solution of TBAT in approximately 500 mL of ethyl acetate. The solution was allowed to cool to room temperature, then stored at −20 °C for 12 h. After filtration, crude TBAT (43.6 g, 80.7 mmol, 94%) was obtained as small white flakes. Recrystallization of the crude product from ethyl acetate (2 L) afforded TBAT (39.2 g, 72.6 mmol, 86%) as long colorless needles: mp (corr) 155−156 °C; ^{1}H NMR (DMSO-d_6) δ 7.86 (dd, 6H, 6.7, 1.5), 7.06−7.13 (m, 9H), 3.11−3.15 (m, 8H), 1.51−1.57 (m, 8H), 1.29 (sextet, 8H, 7.3), 0.92 (t, 12H, 7.3); ^{13}C NMR ($CDCl_3$) δ 150.2 (t, 41), 137.1, 126.5, 126.3, 56.9, 23.2, 19.1, 13.6; ^{19}F NMR (DMSO-d_6) δ (CF_3CO_2H = −76.2) −96.0 (J_{Si-F} = 252 Hz); ^{29}Si NMR ($CDCl_3$) δ −106.3 (J_{Si-F} = 252 Hz); IR data was identical to that reported in ref 1.