Tetrahedron Letters,Vol.25,No.15,pp 1631-1632,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

ON THE NON-EXISTENCE OF TRIMETHYLSILYL TETRAFLUOROBORATE IN ACETONE AND ACETONITRILE : THE GENERATION OF BORON TRIFLUORIDE IN WEAKLY COORDINATING SOLVENTS

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Summary: The recently proposed preparation of trimethylsilyl tetrafluoroborate[1] actually gives trimethylfluorosilane and boron trifluoride coordinated to acetone or acetonitrile.

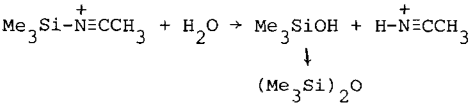
We are currently studying[2,3] *the interaction of highly electrophilic silicon species* (Me_3SiX, X = I, Br, OSO_2CF_3, ClO_4) with nucleophiles, such as hexamethylphosphoramide, dimethyl formamide and acetonitrile. Our aim is to produce more effective silylation agents for organic synthesis. The recent report[1] on the apparent generation of a new, highly electrophilic species, trimethylsilyl tetrafluoroborate was therefore of considerable interest. The reagent was produced by the reaction of silver tetrafluoroborate with trimethylchlorosilane in acetonitrile or acetone. The reaction was suggested to be:

$$Me_3SiCl + AgBF_4 + CH_3CN \rightarrow Me_3Si\overset{+}{N}{\equiv}CCH_3 + AgCl\downarrow + BF_4^-$$

The proposed course of the reaction was surprising on a number of grounds. The silicon-fluorine bond is extremely strong[4] (E_m = 594 kJ mol^{-1}), and therefore trimethylfluorosilane might be expected to be a major product. This is confirmed by the early report of Lawton and Levy[5] that an analogous attempt at the synthesis of triphenylsilyl tetrafluoroborate gave triphenylfluorosilane in moderate yields.

$$Ph_3SiCl + NaBF_4 + (CH_3)_2C{=}O \rightarrow Ph_3SiF + BF{\cdot}O{=}C(CH_3)_2 + NaCl$$

In addition, the proposed trimethylsilyl tetrafluoroborate was used, in one example,with water as the nucleophile[1]. Under such circumstances rapid hydrolysis would result.



$$Me_3Si\text{-}\overset{+}{N}{\equiv}CCH_3 + H_2O \rightarrow \underset{\displaystyle (Me_3Si)_2O}{\underset{\downarrow}{Me_3SiOH}} + H\text{-}\overset{+}{N}{\equiv}CCH_3$$

We have therefore examined the nmr spectra of the products of reaction of silver tetrafluoroborate with trimethylchlorosilane in deuterioacetone and deuterioacetonitrile, and can confirm that trimethylfluorosilane is produced quantitatively in each case.

$$Me_3SiCl + AgBF_4 + CH_3C{\equiv}N \rightarrow Me_3SiF + BF_3{\cdot}N{\equiv}CCH_3$$

$$Me_3SiCl + AgBF_4 + (CH_3)_2C{=}O \rightarrow Me_3SiF + BF_3{\cdot}O{=}C(CH_3)_2$$

The presence of trimethylfluorosilane as the only silicon-containing product was confirmed by comparison of the ^{29}Si and ^{19}F spectra with an authentic sample of trimethylfluorosilane (^{29}Si nmr : doublet $J = 274H_3$ $\delta 32.9$ ppm in acetone-d_6 relative to internal TMS; ^{19}F, δ-156 ppm relative to internal $CFCl_3$, lit. -158 ppm[6]. The ^{19}F nmr spectra of the reaction mixtures showed, in addition to Me_3SiF a singlet (δ-147 in $(CD_3)_2CO$ and δ-141 in CD_3CN, lit. -143 ppm[7]) attributable to coordinated BF_3. The presence of two separate ^{19}F peaks and the observation of silicon-fluorine coupling shows that the equilibrium,

$$BF_3 + Me_3Si\overset{*}{F} \rightleftharpoons BF_2\overset{*}{F} + Me_3SiF$$

is slow on the nmr time scale.

As trimethylfluorosilane is not a highly electrophilic silicon species we suggest that the effective catalyst in the reported solvolyses[1] is BF_3 weakly coordinated to acetone or acetnotrile. Corey[8] has shown that BF_3 is a useful catalyst in related solvolyses. Although this reaction fails to give a new silicon-based reagent it could provide a useful route to BF_3 coordinated to solvents other than diethyl ether. The trimethylfluorosilane coproduct is not very reactive and unlikely to interfere in any reactions.

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(Received in UK 10 February 1984)