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Studies on Reactivity patterns of Si-N and Si-H bonds in Tri(amino)silanes: Explored via NMR Spectroscopy

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Abstract:

A brief study on the reactivity of Si-N and Si-H bonds of tri(amino)silanes has been done. Replacing the weaker with Si-N bonds with strong Si-O bonds favours the formation of various alkoxy silanes. Si-H hydrogen in tri(amino)silanes can be used for reduction reactions involving P=O bonds. In both cases the compounds were isolated and identified by ^{29}Si NMR and ^{31}P NMR. The reaction of the tri(amino)silanes with phosphine shows that this type of reaction offers very good scope in the preparation of different substituted phosphines. The hydrogen attached to the silicon can be used for the selective reduction of various functional groups.

Keywords: Tri(amino)silane, ^{31}P NMR, ^{29}Si NMR.

Introduction:

It has been known that alkylsilanes and alkoxysilanes when activated by KF as catalysts are efficient and selective agents for the heterogeneous reduction of carbonyl groups [1]. The conversion of the sulphoxide to sulphides and phosphine oxides to phosphine using silanes have been reported [2]. Tri(amino)silanes especially $SiH(N(CH_3)_2)_3$ have been used as a versatile starting material for the preparation of various substituted silanes. The difference in reactivity of secondary and tertiary alcohols with tri(amino)silanes has been used to separate these mixtures quantitatively [3]. In the presence of catalysts, the reaction with alcohols is directed towards the high yield syntheses of alkoxysilanes [4]. As hydrolysis of tri(amino)silanes results in the liberation of hydrogen and the cleavage of Si-N bonds. In the present study the reducing activity of these tri(amino)silanes has been investigated in presence of Potassium fluoride. In tri(amino)silanes the silicon-nitrogen and silicon-hydrogen bonds permits their use in the preparation of various substituted silanes. It has been reported that organosilanes can be especially being used as adhesives which can find application in dentistry [5]. Silane coupling treatment is considered as a highly effective method for boosting interfacial bonding strength between fibers and matrices. This treatment offers a dual advantage by facilitating both physical and chemical bonding, thereby significantly enhancing the adhesion [6]. Triphenyl phosphine finds a variety application in sensitizers, light stabilizers, flame retardants, antistatic agents, rubber antioxidants [7,8,9,10].

Experiments

Part-1:

a) Methanolysis

Tris(morpholino)silane was prepared as reported earlier [11]. Methanolysis of tris(morpholino)silane in 1:1, 1:3 and l:4 molar ratio's have been carried out. 145 mg of tris(morpholino)silane was dissolved in a dry solvent (benzene/hexane) in an inert atmosphere, to this 0.06 ml of dry methanol was added and kept for stirring for the reaction to complete. As soon as the methanol was added, an exothermic reaction took place with effervescence. The experiment was repeated for the all molar ratios.

Part-2:

a) Reduction of phosphine oxide

Reductions were carried out by taking the reactants, triphenyl phosphine oxide, potassium fluoride and tris(diethylamino)silane, in 1: 1: 2.5 molar ratios, in a 50 ml flask with side-arm flushed with dry nitrogen without any solvent. The reaction mixture was heated on a water bath for about 12 hours, after which the mixture was concentrated under vacuum and the ^{31}P NMR of the crude product was recorded. The reaction mixture was further heated for another 12 hours and the mixture was extracted with chloroform. The chloroform was removed on a water bath. The solid product was identified ^{31}P NMR and melting point.

Results and discussion: (part1)

The products obtained in the above reaction were identified by ^{29}Si NMR, which agrees well with that reported for tetramethoxy silane [12]. Fig1 (a) and (b) shows the ^{29}Si NMR spectrum of the product obtained in 1:1, 1:3 and 1:4 molar ratios (the product obtained is the same in both 1:1 and 1:3 molar ratio).

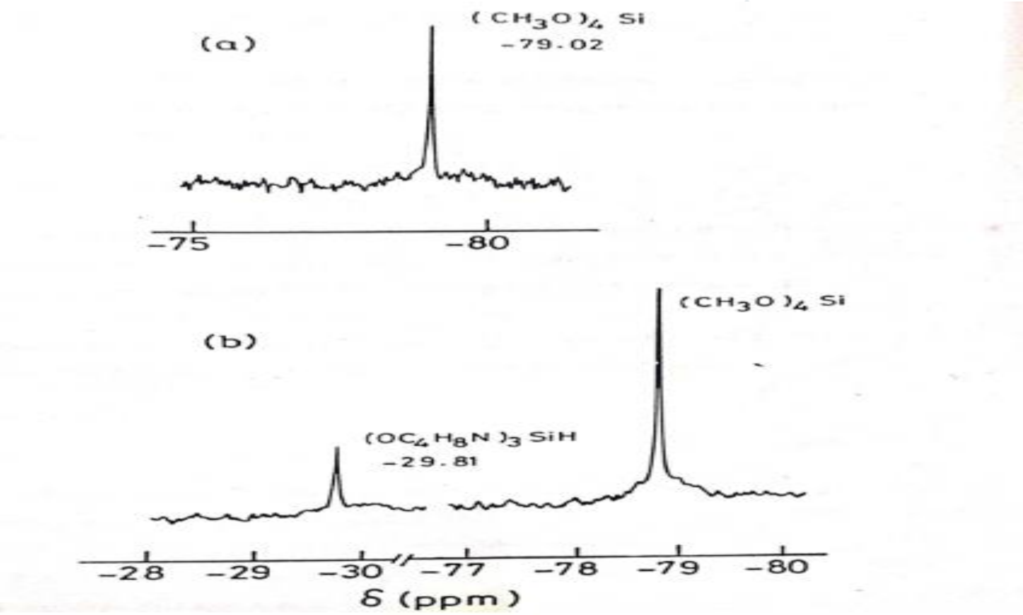


Fig 1: a) & b) ^{29}Si NMR spectra of the methanolysis product of $(OC_4H_8N)_3SiH$

a) CH_3OH: $(OC_4H_8N)_3SiH$= 4:1 (molar ratio)

b) CH_3OH: $(OC_4H_8N)_3SiH$ = 1:1 (molar ratio)

As it clear from the Fig.1 a) & b) that in 1:4 molar ratio the complete conversion of tris(morpholino)silane to tetramethoxy silane. But the reactions, in 1:1 and 1:3 molar ratios show the presence of a small amount of starting material. The ^{1}H NMR of the solution showed the presence of a small amount of free amine. The high bond energy of the Si-O bond permits the cleavage of the Si-N and Si-H bonds in the tri(amino)silanes. From this, the reaction can be written as:

$$(OC_4H_8N)_3SiH + 4\ CH_3OH \xrightarrow{1:4 molarratio} > (CH_3O)_4Si + 3OC_4H_8NH + H_2$$

$$4(OC_4H_8N)_3SiH + 12CH_3OH \xrightarrow{1:3 molarratio} > 3(CH_3O)_4Si + (OC_4H_8N)_3SiH+ \\ +9OC_4H_8NH + 3H_2$$

a) Reduction of phosphine oxide

Results and Discussion

Tri(amino)silanes when activated by potassium fluoride in the absence of solvent, quantitatively reduces triphenyl phosphine oxide to phosphine. Fig. 2 (a) shows the ^{31}P NMR of the compound obtained after 12 hours of heating, which agrees well with the reported value. This spectrum shows two peaks, corresponding to triphenyl phosphine oxide and phosphine.

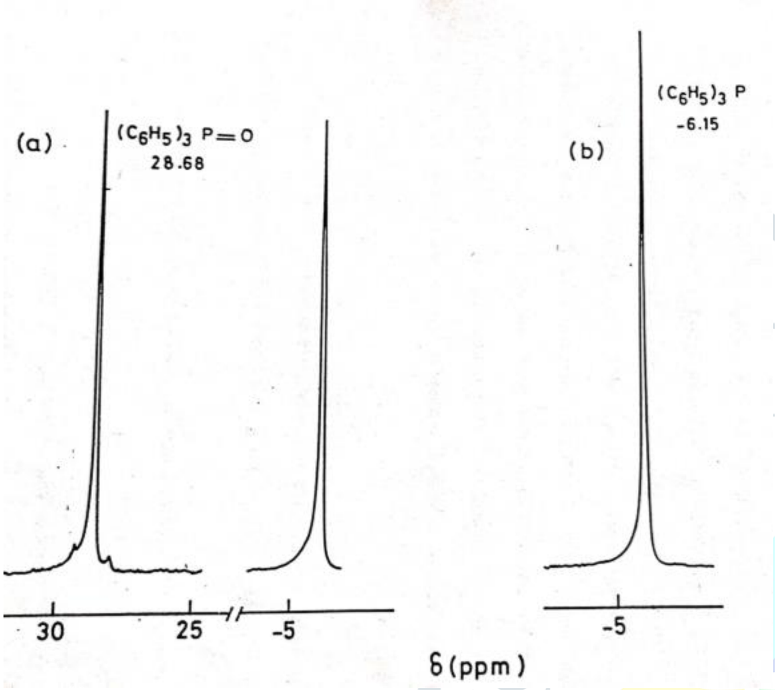
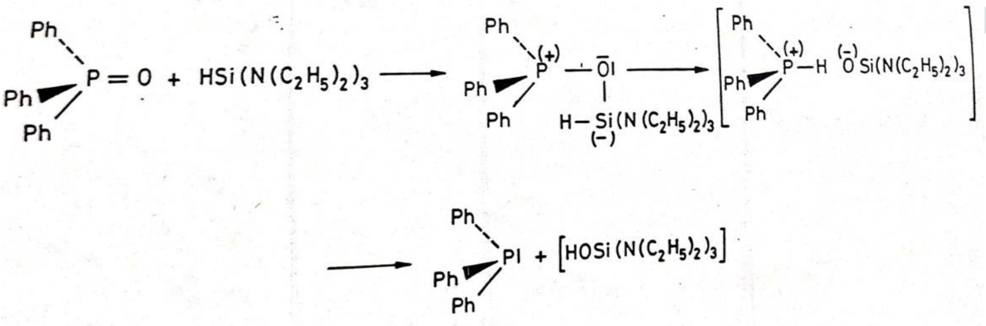


Fig. 2 (b) shows the NMR recorded after 24 hours. This shows the presence of only one compound in the product, viz. triphenyl phosphine indicating the complete conversion of the triphenyl phosphine oxide to triphenyl phosphine. Potassium fluoride is an efficient and selective catalyst for the heterogeneous reduction of P=O bonds. The reaction probably follows the path as shown in the reaction scheme 1, similar to that observed for alkylsilanes [13].



Reaction scheme 1

Conclusion

The weak nature of Si-N bonds can be used for synthesizing different compounds with Si-O bonds. The hydrogen atom attached to silicon in tri(amino)silanes can be used for selective reduction of various functional groups. The reaction tri(amino)silanes with phosphine shows that this type of reaction offers very good scope in the preparation of different substituted phosphines.

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