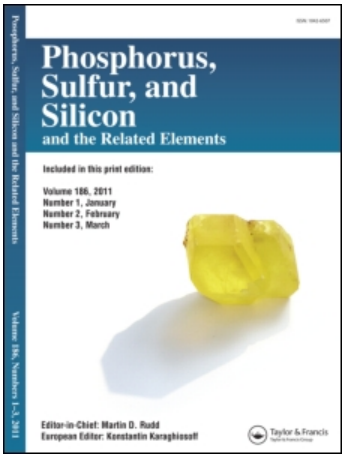

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Radhamani, K. N. and Padma, D. K.(1993) 'A CONVENIENT HIGH YIELD ROOM TEMPERATURE SYNTHESIS OF MIXED TRI(AMINO)SILANES BY TRANSAMINATION OF TRIS(DICYCLOHEXYLAMINO)SILANE AND THEIR CHARACTERIZATION', Phosphorus, Sulfur, and Silicon and the Related Elements, 79: 1, 65 — 68
To link to this Article: DOI: 10.1080/10426509308034398
URL: http://dx.doi.org/10.1080/10426509308034398

Phosphorus, Sulfur, and Silicon, 1993, Vol. 79, pp. 65–68
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A CONVENIENT HIGH YIELD ROOM TEMPERATURE SYNTHESIS OF MIXED TRI(AMINO)SILANES BY TRANSAMINATION OF TRIS(DICYCLOHEXYLAMINO)SILANE AND THEIR CHARACTERIZATION

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(Received November 2, 1992; in final form January 27, 1993)

Tris(dicyclohexylamino)silane, $(DCA)_3SiH$, is prepared by the reaction of trichlorosilane with dicyclohexylamine. This is found to undergo transamination reactions with other secondary amines (R_2NH), such as pyrrolidine, piperidine, hexamethyleneimine, morpholine, N-methylpiperazine and diethylamine to yield mixed tri(amino)silanes of the formula $(DCA)(R_2N)_2SiH$ in quantitative yields. These new derivatives are found to be moisture sensitive and hydrolyze to yield their respective amines, hydrogen and silica. They are found to be stable in an inert atmosphere. They have been characterized by IR, NMR (^1H, ^{29}Si), mass spectroscopy and CHN analysis. ^{15}N NMR for one of the compounds has been done.

Key words: Pyrrolidine; piperidine; hexamethyleneimine; morpholine; N-methylpiperazine; diethylamine.

INTRODUCTION

Tri(amino)silanes are extensively used for the synthesis of various substituted silanes.[1,2] They are employed as catalysts for the addition of $SiHCl_3$ to acrylonitrile to give β-cyanoethyltrichlorosilane and in the preparation of catalysts for urethane foams and elastomers.[3] The potential use of silicon-nitrogen based compounds (polysilazanes) as precursors of silicon nitride and silicon carbonitride[4–9] has prompted the synthesis of new silicon-nitrogen based compounds. Recently, we have reported[10] an elegant synthetic mode for tri(amino)silane of the type, $(R_2N)_3SiH$ by the ammonolysis of Si—Cl bond of trichlorosilane as shown in Equation (1).

$$HSiCl_3 + 6R_2NH \rightarrow (R_2N)_3SiH + 3R_2NH \cdot HCl \qquad (1)$$

Here the aminehydrochloride is filtered and then the product is isolated by evaporation of the solvent. If the reaction is carried out in the presence of a mixture of amines, the compounds isolated are pure single derivative of the amines which has the least steric hindrance.[11] Hence this procedure cannot be used for the preparation of mixed aminosilanes. This drawback has been overcome by transamination (exchange) reactions. As illustrated in Equation (2), the released amine is easily removed.

$$(R_2N)_3SiH + 2R'_2NH \rightarrow (R_2N)(R'_2N)_2SiH + 2R_2NH \qquad (2)$$

Where, $(R_2N)_3SiH$ = tris(dicyclohexyl amino)silane, R'_2NH = pyrrolidine, piperidine, hexamethyleneimine, morpholine, N-methyl piperazine, diethyl amine.

It needs to be pointed out that such transamination reactions are well known with alkylaminosilanes and aminophosphines.[12,13] This study for the first time shows that the presently synthesized tris(dicyclohexylamino)silane, undergoes transamination reactions to yield an interesting variety of mixed tri(amino)silanes.

RESULTS AND DISCUSSSION

These transamination reactions are very sensitive to the steric hindrance of the amine concerned. Therefore the bulkiness of dicylohexylamino group has been exploited in the present synthesis. The IR data indicate that the stretching and bending vibrations of the Si—H bond occurs in the region 2116 to 2134 cm^{-1} and 822 to 855 cm^{-1}, repectively for all the derivatives prepared, and for tris(dicyclohexylamino)silane the νSi—H occurs at 2212 cm^{-1}, this suggets a weakening of the Si—H bond in these derivatives. It is interesting to note that the νSi—N in these derivatives (669–687 cm^{-1}) occurs in the same region as in the case of tris(dicyclohexylamino)silane (672 cm^{-1}). The marginal strengthening of the Si—N bond is due to a greater overlap of the *d* orbital of silicon atom with the *p* orbital of the nitrogen atom of the less bulkier amino groups. This argument holds good even in the case of tri(amino)silane derivatives. The bulkier amino derivative, tris(dicyclohexylamino)silane shows νSi—H at 2212 cm^{-1} while for the less bulkier tri(amino)derivatives, e.g., $(C_4H_8N)_3SiH$, it appears at 2102 cm^{-1} indicating the weakening of νSi—H in derivatives having less bulky groups[10] (on hydrolysis the intensity of the Si—N and the Si—H band decrease and finally disappear in the spectrum indicating the cleavage of both these bonds during hydrolysis giving rise to SiO_2 and the respective amines). This fact is borne out in the ^1H NMR spectra, wherein the Si—H protons of the less bulky amino derivatives resonate in a very narrow range of about 4.34 to 4.53 ppm[10] while the bulky tris(dicyclohexyl-amino)silane resonates at 5.69 ppm. ^{29}Si NMR can be used as a very good tool for characterizing the tri(amino)silanes. The $\{^1H\}^{29}Si$ NMR spectra of these monohydrides indicate that the resonance of the silicon appears in the region −33 to −40 ppm with respect to the external standard (TMS) and is more shielded in these derivatives when compared to alkyl and aryl monohydrides reported (0–30 ppm).[14] In the ^{29}Si NMR spectra the proton attached to silicon couples with it thereby showing the splitting of the silicon resonance and it is found that a linear correlation exists between the ^1J Si—H and νSi-H showing that both are governed by similar type of effects such as bulkiness and basicity of the coordinating amines. The ^{15}N NMR of $((C_6H_{11})_2N)(C_6H_{12}N)_2SiH$ shows two nitrogen resonances and it provides the evidence that the electronic environment of two of the nitrogen atoms are equivalent while for the other nitrogen it is not even though the basicities of the unsubstituted amines (hexamethyleneimine pKa = 11.29, dicyclohexyl-amine pKa = 11.25)[15,16] are not very different. The ^{15}N chemical shift shows that one of the nitrogen atoms is more deshielded than the other two. The two peaks appear at −313.7 and −343.4 ppm and this region agrees well with that reported for tris(ethylamino)silane (−343.9 ppm).[17] Perhaps the orientation of the

nitrogen lone pair plays a dominant role. Thus, the above results indicate that stable mixed amino silanes are easily prepared by transamination in good yields and high purity.

EXPERIMENTAL

All reagents were of AR grade, purified and dried by standard procedures. n-Hexane and benzene (caution! potential carcinogen) were distilled and stored over sodium wire. The spectral instruments used were as follows: IR: Hitachi 270-50 spectrometer; ^{1}H NMR: Bruker ACF 200, ^{29}Si and ^{15}N NMR: Bruker AMX-400, MS: Finnigan Matt 8230, CHN analysis Heraeus CHN-O RAPID. All operations were performed under a dry oxygen free nitrogen atmosphere using standard schlenk techniques.

Synthesis of tris(dicyclohexylamino)silane. 11.85 ml (0.06 mole) of dicyclohexylamine was taken in 100 ml of 1:1 benzene/n-hexane in a 250 ml dried side-arm flask flushed with nitrogen and it was cooled to Ca 5°C. To this was added 2 ml (0.01 mole) of trichlorosilane in 50 ml in the same solvent mixture over a period of 15 minutes with constant stirring. After the addition, the mixture was brought to room temperature and it was kept for another 12 hours for continuous stirring. At the end, the mixture was filtered under an inert atmosphere and it was washed with the same solvent mixture. The filtrate was concentrated under vacuum. The solid product was identified as tris(dicyclohexylamino)silane, $((C_6H_{11})_2N)_3SiH$. Characteristic data for tris(dicyclohexylamino)silane obtained are as follows: ^{29}Si NMR: −26.45 ppm; ^{1}J Si—H: 313.90 Hz; ^{1}H NMR: δSi—H, 5.69 ppm; IR (cm^{-1}): νSi—H, 2212; νSi—N, 672. CHN analysis calculated for $C_{36}H_{67}N_3Si$: C 75.92, H 11.78, N 7.38%; obtained C 75.20, H 11.32, N 7.69%.

Synthesis of mixed tri(amino)silanes, $((C_6H_{11})_2N)(R_2N)_2SiH$. In a typical reaction tris(dicyclohexylamino)silane and another secondary amine was taken in 1:2 molar ratio in 50 ml of 1:1 (v/v) benzene-hexane mixture in a 100 ml side-arm flask flushed with nitrogen. The reaction mixture was stirred continuously for 12 hours. A slight exothermic reaction was found to occur as soon as the addition started. At the end, the solvent mixture was removed in vacuum. The product formed was purified either by fractional crystallization or distillation under reduced pressure. The overall reaction is as follows.

$$(DCA)_3SiH + 2R_2NH \rightarrow (R_2N)_2DCASiH + 2DCA$$

[R_2N = (1) pyrrolidino-, (2) piperidino-, (3) hexamethyleneimino-, (4) N-methylpiperazino- and (5) diethylamino-, DCA = dicyclohexylamino-,]

Characteristic data for the mixed amino derivatives. No; compound; bp/mp ([a], bp at 0.7 mm of mercury, [b], mp); νSi—H, νSi—N, δSi—H; ^{1}H MNR (δ in ppm); ^{29}Si (δ in ppm) NMR; ^{1}J Si—H (in Hz).

(1) $((C_6H_{11})_2N)(C_4H_8N)_2SiH$; 167[a]; 2116, 669, 828, 4.54 (s, 1H), 2.99 (m, 8H), 2.65 (m, 2H), 1.69 (m, 12H), 1.66 (m, 8H), 1.24 (m, 8H); −39.69; 221.0.

(2) $((C_6H_{11})_2N)(C_5H_{10}N)_2SiH$; 149[b]; 2128, 682, 843, 4.37 (s, 1H), 2.84 (m, 8H), 2.59 (m, 2H), 1.69 (m, 12H), 1.52 (m, 12H), 1.24 (m, 8H); −36.11; 225.1.

(3) $((C_6H_{11})_2N)(C_6H_{12}N)_2SiH$: 50[b]; 2122, 669, 855, 4.34 (s, 1H), 2.90 (m, 8H), 2.62 (m, 2H), 1.68 (m, 8H), 1.57 (m, 12H), 1.24 (m, 8H); −33.77; 226.9.

(4) $((C_6H_{11})_2N)(OC_4H_8N)_2SiH$: 181[b]; 2128, 681, 837; 4.49 (s, 1H), 3.56 (m, 8H), 2.94 (m, 8H), 2.60 (m, 2H), 1.71 (m, 12H), 1.25 (m, 8H); −35.98; 230.5.

(5) $((C_6H_{11})_2N)(CH_3NC_4H_8N)_2SiH$: 85[b]; 2134, 687, 834; 4.38 (s, 1H), 2.89 (m, 8H), 2.52 (m, 2H), 2.20 (m, 8H), 1.62 (m, 12H), 1.17 (m, 8H); −35.86; 234.1.

(6) $((C_2H_5)_2N)_2((C_6H_{11})_2N)SiH$: 167[a]; 2122, 669, 846; 4.48 (s, 1H), 2.83 (m, 8H), 2.60 (m, 4H), 1.61 (m, 12H), 1.18 (m, 8H), 0.99 (m, 12 H); −35.63; 223.8.

Spectral and analytical data are as follows. With a view to provide additional evidence for this set of compounds, analytical and mass spectral data are recorded for one of the selected sample (3) $((C_6H_{11})_2N)(C_6H_{12}N)_2SiH$.

Analysis [Calcd. (%) for (3) C, 70.99; H, 11.59; N, 10.35.
Found % C, 70.30; H, 11.98; N, 10.371.
Mass spectral data (EI, 70 eV) m/e for $((C_6H_{11})_2N)(C_6H_{12}N)_2SiH$: 405 ($m^+$, $C_{24}H_{47}N_3Si$, 5%), 334(m^+-$C_{19}H_{36}N_3$, 11%), 225 ($(C_6H_{12}N)_2SiH$, 11%), 181 ($(C_6H_{12}N)(C_6H_{11})^+$, 11%), 138 ($C_6H_{11}N_2Si^+$, 100%), 56 ($C_4H_8^+$, 54%).

ACKNOWLEDGEMENTS

We thank CHEMPLAST India Ltd. for free pure samples of trichlorosilane. Spectral facilities of the sophisticated instrument facility, I.I.Sc, Bangalore is gratefully acknowledged.

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