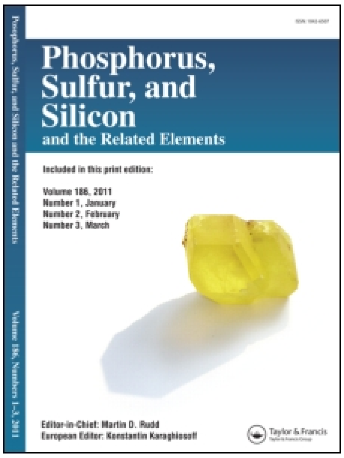

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SILYL-NITROGEN COMPOUNDS,[1] 11: SYNTHESIS AND CHARACTERISATION OF TETRASILAPHOSPHA AND TETRASILA-ARSA TETRAZENES

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SILYL-NITROGEN COMPOUNDS,[1] II: SYNTHESIS AND CHARACTERISATION OF TETRASILA-PHOSPHA AND TETRASILA-ARSA TETRAZENES

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Lithylated bis(trimethylsilyl)hydrazines, $Li_2N_2(SiMe_3)_2$ and $LiHN_2(SiMe_3)_2$ react with $(Me_3Si)_2NECl_2$ (E = P or As) to form hetero atom incorporated tetrazenes, 1,3,4,4-tetrakis(trimethylsilyl)-2-phospha-1-tetrazene $(Me_3Si)_2N—N(SiMe_3)—P{=}NSiMe_3$ and 1,1,4,4-tetrakis-(trimethylsilyl)-2-arsa-2-tetrazene $(Me_3Si)_2N—N{=}As—N(SiMe_3)_2$. The former thermolyses primarily into trisila-phosphatriazene $(Me_3Si)_2N—P{=}NSiMe_3$ and tetrasilahydrazine $(Me_3Si)_4N_2$, whereas, the latter forms tris(trimethylsilyl)hydrazine $(Me_3Si)_3N_2H$. Phosphatetrazene interacts with CH_3OH in an oxidative addition reaction to form [tris(trimethylsilyl)-hydrazino]-(trimethylsilylimino)-(methoxy)-phosphorane, $(Me_3Si)_2N—N(SiMe_3)—PH(OCH_3)({=}NSiMe_3)$, whereas, arsatetrazene undergoes cleavage reaction to yield $(Me_3Si)_3N_2H$.

Key words: Tetrasila-2-phospha-1-tetrazene; tetrasila-2-arsa-2-tetrazene; synthesis; characterization; thermolysis; oxidative addition.

INTRODUCTION

Organic tetrazenes have been known for quite sometime[2] but the inorganic tetrazenes N_4H_4[3,4] and its silylated, germylated or stannylated derivatives were reported relatively recently.[5–8] Scherer and Glässel have already reported[9] a number of Silyl-organyl-phosphatetrazenes but in continuation of our investigations on silyl-nitrogen compounds,[1,7] an attempt has now been made to isolate and characterise new inorganic derivatives, 1,3,4,4-tetrakis(trimethylsilyl)-2-phospha-1-tetrazene $(Me_3Si)_2N—N(SiMe_3)—P{=}NSiMe_3$ and 1,1,4,4-tetrakis-(trimethylsilyl)-2-arsa-2-tetrazene $(Me_3Si)_2N—N{=}As—N(SiMe_3)_2$.

RESULTS AND DISCUSSION

An important ingredient of reactions of lithylated bis-(trimethylsilyl)hydrazines (**1**) with bis(trimethylsilyl)-aminodichlorophosphine $(Me_3Si)_2NPCl_2$ is appearance of yellowish green colour due to the formation of phosphazene derivative. The reaction provides 1,3,4,4-tetrakis(trimethylsilyl)-2-phospha-1-tetrazene $(Me_3Si)_2N—N(SiMe_3)—P{=}N(SiMe_3)$, (**2**) as a yellowish green liquid distilling at 60°C/10^{-3} Torr. On the other hand, a reaction of (**1**) with bis(trimethylsilyl)-

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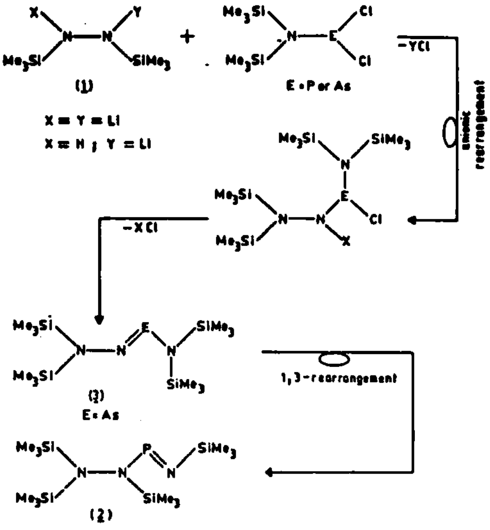
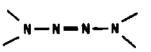
aminodichloroarsine $(Me_3Si)_2NAsCl_2$ provides an arsatetrazene, 1,1,4,4-tetrakis(trimethylsilyl)-2-arsa-2-tetrazene $(Me_3Si)_2N{-}N{=}As{-}N(SiMe_3)_2$, (**3**), an orange red liquid distilling at 80°C/10^{-3} Torr. The reaction appears to involve 1,2-anionic rearrangement[10] followed by a pathway implying intermediate formation of 2-tetrazene isomer which in case of phosphorus incorporated derivative undergoes 1,3-migration of silyl group[8] to form 2-phospha-2-tetrazene as shown in Scheme I. The assumption of 2-phospha-2-tetrazene intermediate is supported by the isolation of 2-arsa-2-tetrazene and by the successful trapping of $(Me_3Si)_2N{-}N{=}P{-}NEt_2$ in the reaction of (**1**) with Et_2NPCl_2 containing non-migratory ethyl group.[11]

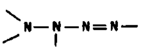


SCHEME I

It is reported[8] that tetrazenes, which can show position isomerism, have been found to exhibit 2-tetrazene constitution in all its silylated, germylated and

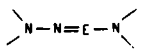


2-Tetrazene

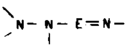


1-Tetrazene

stannylated inorganic tetrazenes as well as alkyl-tetrazenes. Analogously, both phospha- and arsa-tetrazenes may also be expected to prefer 2-tetrazene constitution. However NMR studies (discussed subsequently) of (**2**) favour



2-Tetrazene
E = P or As



1-Tetrazene
E = P or As

2-phospha-1-tetrazene constitution and of (**3**) favour 2-arsa-2-tetrazene constitution. Constitution of (**2**) agrees with that reported for silylated organophosphatetrazenes.[9] Reasons for preference of 2-phospha-1-tetrazene isomeric form over 2-phospha-2-tetrazene and otherway round for arsa-tetrazene and tetrazenes[8] are still not clear. An already reported[9] observation in silylated organo-phosphatetrazenes that 2-phospha-1-tetrazene isomer is more stable than 2-phospha-2-tetrazene due to preferred stability of imino nitrogen atom through *t*-butyl group —P═N—CMe_3 and its easier dimerisation when Me_3C is replaced by Me_3Si group —P═N—$SiMe_3$, does not find favour in our investigations. With all the positions occupied by Me_3Si groups inclusive of imino nitrogen, we have observed that the compound is quite stable up to 100°C.

Proton decoupled ^{31}P NMR spectrum of (**2**) shows an extremely low field absorption at 327.6 ppm which is characteristic of 2-coordinated phosphorus(III) azenes.[9] Its ^1H NMR shows three signals (δ values in Experimental section) in the ratio 2:1:1 corresponding to $(Me_3Si)_2N$, Me_3SiNN and $Me_3Si{=}NP$ protons which are indicative of 2-phospha-1-tetrazene constitution. Furthermore, ^1H NMR up to −80° reveals no change in the spectrum which indicates that an isomer equilibrium arising from Me_3Si migration appears unlikely.

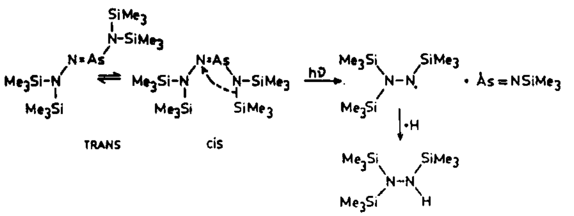
The 2-phospha-1-tetrazene constitution is also supported by ^1H decoupled ^{29}Si NMR showing signals in the intensity ratio 2:1:1 at 13.96, 10.97 and 4.99 d ppm corresponding to $(Me_3Si)_2N$, Me_3SiNN and $Me_3SiN{=}P$ silyl groups. The latter signal due to the more shielded silylimino group $Me_3SiN{=}P$ appears as a doublet with $^2J_{Si-P}$ 28.2 Hz. This agrees with the coupling constant reported[12] for silylimino group in phospha-triazene $(Me_3Si)_2N{-}P{=}NSiMe_3$.

Mass spectral analysis of (**2**) shows a molecular ion with a relatively higher intensity (60% 70 eV; 75% 20 eV) at *m*/*z* 365. The observed isotopic pattern agrees with that calculated for $C_{12}H_{36}N_3PSi_4$ (Experimental). Prominent fragments corresponding to phosphatriazene and phosphadiazene have been observed at *m*/*z* 278 $(m\text{-}Me_3SiN)^+ = [(Me_3Si)_2N{-}P{=}NSiMe_3]^+ = m'$ and 191 $(m\text{-}Me_3SiN{=}NSiMe_3)^+ = (Me_3SiP{=}NSiMe_3)^+$, respectively. Valuable metastable transitions for establishing fragmentation pathways have also been observed at 335 (*m*-Me), 221 (*m*′-2Me), 195 (*m*′-3Me and 93 $(m'\text{-}Me_3SiNMe_2)$.

Contrary to phosphazene (**2**), the arsazene (**3**), 1,1,4,4-tetrakis(trimethylsilyl)-2-arsa-2-tetrazene exhibits 2-tetrazene constitution analogous to silylated, germylated, stannylated and alkyl tetrazenes.[8] This is indicated in its ^1H NMR which shows two kinds of silyl protons with relative area (1:1) and the spectrum does not change up to −80°, thereby, opposing the occurrence of Me_3Si shift. However, the compound appears to exhibit thermal *trans*/*cis* rearrangement at higher temperatures. The reaction product at room temperature contains 100% *trans*-isomer with proton resonance signals at 0.26 and 0.16 ppm (1:1) in ether. The *cis*-isomer appears on heating and shows new proton resonance signals at 0.24 and 0.15 ppm (1:1) in ether.

Mass spectral analysis of (**3**) shows molecular ion with lower intensity (7%, 70 eV; 15%, 20 eV) at *m*/*z* 409. The loss of trimethylsilylnitrene $Me_3Si{-}\dot{N}{:}$ from the molecular ion is very significant and represents the base peak at *m*/*z* 322. Fragments corresponding to direct or successive loss of CH_3 and Me_3Si radicals are quite prominent.

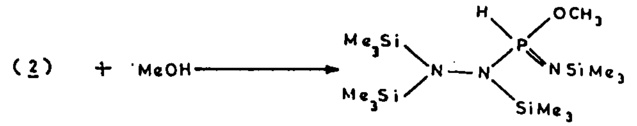
Phosphatetrazene (**2**) is stable when pure but arsatetrazene (**3**) is quite sensitive to daylight. Compound (**3**) loses its orange red colour on exposure to daylight and ^1H NMR shows the formation of tris(trimethylsilyl)hydrazine $(Me_3Si)_3N_2H$. Photolytic decomposition of (**3**) appears to occur via transformation into *cis*-derivative which is likely to undergo 1,3-migration of silyl group[8] followed by



SCHEME II

radical decomposition as shown in Scheme II. The hydrazyl radicals abstract protons to form $(Me_3Si)_3N_2H$. This is also supported by thermolysis of (**3**).

The 2-phospha-1-tetrazene structural feature of (**2**) is further supported by its reaction with MeOH. Compound (**2**) combines with MeOH with oxidative addition at the phosphorous atom to form [tris(trimethylsilyl)hydrazino)]-(trimethylsilylimino)-(methoxy)phosphorane, (**4**). ^1H NMR of (**4**) in C_6D_6 shows



(**4**)

resonance signals at 0.35, 0.27, 0.42 and 0.30 d ppm in the ratio 1:1:1:1 corresponding to silyl protons $Me_3SiN—Si$, $SiN—SiMe_3$, Me_3SiNP and $Me_3SiN{=}P$, respectively. Two separate (1:1) signals for the $(Me_3Si)_2N$ protons may be attributed to hindered rotation about N—N. The doublet at 0.30 ppm due to $Me_3SiN{=}P$ protons has a coupling constant $^4J_{H—P}$ 0.6 Hz. Furthermore, a doublet at 3.37 ppm due to methoxy group $P—OCH_3$ has a coupling constant $^3J_{H—P}$ 13.4 Hz. Another doublet corresponding to P—H group is observed at 6.81 ppm with a large coupling constant $^1J_{H—P}$ 593.2 Hz.

The ^1H-decoupled ^{31}P NMR spectrum shows a signal in the expected region at 11.42 ppm. Partially ^1H coupled ^{31}P NMR spectrum shows two quartets at 3.415 and 21.830 ppm with $^1J_{P—H}$ 593.1 Hz and $^3J_{P—H}$ 13.4 Hz. The IR spectrum of the pure sample shows ν(P—H) at 2300 cm^{-1} and ν(P=N) at 1250 cm^{-1} supporting the presence of these functional groups in (**4**).

Mass spectrum of the sample shows molecular ion with relatively low intensity (2% 70 eV; 15% 15 eV) at m/z 397. The observed isotopic pattern agrees with that calculated for $C_{13}H_{40}N_3OPSi_4$ (Experimental). A prominent fragment indicating the loss of silylnitrene $Me_3Si—\dot{N}$: from the molecular ion is observed at m/z 310. Another distinct fragment indicating the loss of amine $(Me_3Si)_2NCH_3$ is observed at m/z 222. Other important fragments have been observed at 293$[(Me_3Si)_3N_2P{=}NH]^+$, 248 $[(Me_3Si)_3N_2H)]^+$ and 150$[Me_3Si{=}P(H)OMe)]^+$.

In contrast to phosphatetrazene (**2**), the arsatetrazene (**3**) undergoes cleavage on reaction with MeOH. The reaction mixture (1:1) shows the presence of $(Me_3Si)_3N_2H$, Me_3SiNH_2 and the unreacted arsatetrazene. A 1:3 reaction occurs primarily according to the equation:

$$(Me_3Si)_4N_3As + 3MeOH \rightarrow (Me_3Si)_3N_2H + Me_3SiNH_2 + As(OMe)_3$$

Besides that, small amounts of bis(trimethylsilyl)hydrazine $(Me_3Si)_2N_2H_2$ (arising due to protololysis of trisilahydrazine) and bis(trimethylsilyl)amine $[2Me_3SiNH_2 \rightarrow (Me_3Si)_2NH + NH_3]$ are also present.

Preliminary investigations indicate that 1,3,4,4-tetrakis(trimethylsilyl)-2-phospha-1-tetrazene, (**2**), is quite reactive and undergoes a variety of reactions, such as, oxidative addition, addition at P═N-ylid, complexation, partial and complete desilylation leading to the parent hydride H_4N_3P.[13]

EXPERIMENTAL

General comments

All investigations were carried out on a vacuum line and in the absence of air and moisture. All reactants were handled in a dry nitrogen atmosphere. Bis(trimethylsilyl)hydrazine,[14] butyl lithium,[15] dilithium bis(trimethylsilyl)hydrazine,[16] mono-lithium bis(trimethylsilyl)hydrazine,[16] bis(trimethylsilyl)aminodichlorophosphine[17] and bis(trimethylsilyl)aminodichloroarsine[18] were prepared as reported in literature. Diethyl ether and tetrahydrofuran were dried over sodium benzophenoneketyl. Carbon tetrachloride and methanol were rigorously dried before use. *n*-Hexane was dried over P_2O_5 and kept over sodium wire. NMR spectra were recorded on Varian EM 390 and Jeol FX 90 Q instruments, IR spectra on a Perkin Elmer 621 spectrometer and mass spectra on Varian MAT CH7 and VG Micromass MM70/70F.

^{1}H NMR of Me_3Si protons, δ(ppm) in benzene (Et_2O): $(Me_3Si)_2N_2H_2$, 0.117 (0.066); $(Me_3Si)HN$—$NH(SiMe_3)$, 0.041 (0.000); $(Me_3Si)_3N_2H$, 0.13, 0.11 (2:1) (0.09); $LiN(SiMe_3)_2$, 0.128 (0.047); $(Me_3Si)_2NPCl_2$, 0.300d, $^4J_{H—P}$ 2.5 Hz; $Li_2N_2(SiMe_3)_2$, 0.210 (0.000); $LiN_2H(SiMe_3)_2$, −0.030 in THF (0.053 and 0.023, 1:1), Me_3SiCl, 0.208 (0.400); $(Me_3Si)_2NH$, 0.09 (0.05); Me_3SiNH_2, 0.045 (0.023) and $(Me_3Si)_2NAsCl_2$, 0.22 ppm.

Preparation of 1,3,4,4-tetrakis(trimethylsilyl)-2-phospha-1-tetrazene (**2**). Dilithium 1,2-bis(trimethylsilyl)hydrazine, 200 mmol = 37.5 g, [or monolithium 1,2 bis(trimethylsilyl)hydrazine, 200 mmol = 36.4 g] suspended in 200 ml of Et_2O (or *n*-hexane), was cooled to −40°C and an equivalent amount of bis(trimethylsilyl)aminodichlorophosphine solution in 200 ml of *n*-hexane-Et_2O mixture was added to it dropwise with constant stirring. A light yellow colour appeared at −40°C which then changed slowly to green as the temperature rose gradually to 0°C. Reaction mixture was then stirred at room temperature for 4 h and then filtered to get 396 mmol = 9.3 g (or 196 mmol = 4.6 g) of LiCl. ^{1}H NMR of the green filtrate showed major signals at about 0.37, 0.20 and 0.11 ppm in the intensity ratio of 1:2:1 (75–80% conversion) and two small signals at 0.41 ppm (Me_3SiCl) and 0.047 ppm $(Me_3Si)_2N_2H_2$. Ether, *n*-hexane, Me_3SiCl and $(Me_3Si)_2N_2H_2$ were removed under vacuum at room temperature. The residual green thick liquid was quickly distilled (to avoid frothing which hinders in the distillation process) under high vacuum. A yellowish green liquid distilling at 70–80°C/10^{-3} Torr was redistilled at 60–65°C/10^{-3} Torr to obtain about 100 mmol (50% yield) of pure 1,3,4,4-tetrakis(trimethylsilyl)-2-phospha-1-tetrazene. The yellowish green pure liquid compound (b.p., 60°C/10^{-3} Torr) is stable at room temperature if protected from air and moisture. Found: C, 39.32; H, 9.75; N, 11.62. $C_{12}H_{36}Si_4N_3P$ calcd; C, 39.45; H, 9.86; N, 11.50%.

^{1}H NMR in benzene (Et_2O): δ(ppm) 0.18 (0.21) [s, 18H, $(Me_3Si)_2N$]; 0.36 (0.37) [s, 9H, $(Me_3Si)N$—N] and 0.27 (0.11) [s, 9H, $(Me_3Si)N$═P]. ^{1}H NMR spectrum in *n*-heptene is similar to that in Et_2O and shows signals at δ 0.22, 0.38 and 0.13 ppm (2:1:1). The spectrum was monitored at low temperatures which showed no change up to −80°.

^{31}P NMR: Chemical shift of 60% solution in *n*-hexane (H_3PO_4 external standard) is 327.6 ppm.

^{29}Si NMR (^{1}H-decoupled): chemical shift of pure liquid against TMS (external): δ(ppm) 13.96 [s, 2Si, $(Me_3Si)_2N$]; 10.97 [s, 1Si, $(Me_3Si)N$—N]; and 4.99 [d, 1Si, $(Me_3Si)N$═P, $2J_{Si—P}$ 28.2 Hz].

UV-VIS(*n*-hexane solution): λ_{max} in *nm* (log ε); 282(3.72) $\pi \rightarrow \pi^*$; 350(2.44) $n \rightarrow \pi^*$.

Mass Spectrum (70, 20 eV), *m/z* (assignment; relative intensity 70, 20 eV, %): 365 [$(m)^+$; 60,75], 350 [$(m\text{-}Me)^+$; 100, 65], 335 [$(m\text{-}2Me)^+$; 7,84], 292 [$(m\text{-}Me_3Si)^+$; 8,15], 278 [$(m\text{-}Me_3SiN)^+ = (m') = (Me_3Si)_2N{=}P{=}NSiMe_3)^+$; 52,53], 263 [$(m'\text{-}Me)^+$; 74,100], 248 [$(m'\text{-}2Me)^+$; 48,87], 233 [$(m'\text{-}3Me)^+$; 20,33], 218[$(m'\text{-}4Me)^+$; 17,22], 205 [$(m'\text{-}Me_3Si)^+$; 50,68], 191[$(m'\text{-}Me_3SiN)^+ = m'' = (Me_3SiN{=}P{-}SIMe_3)^+$; 76,71], 176 [$(m''\text{-}Me)$; 48,84], 161[$(m''\text{-}2Me)^+$; 22,29], 146 [$(m''\text{-}3Me)^+$; 42,42], 131 [$(m''\text{-}4Me)^+$; 24,22], 118 [$(m''\text{-}Me_3Si)^+$; 13,24], 99[$(Me_3SiNC)^+$; 3,23], 87[$(Me_3SiN)^+$; 5,25], 73[$(Me_3Si)^+$; 50,32]. Metastable fragments at 335, 221, 195 and 93 have been observed both at 70 and 20 eV. $C_{12}H_{36}Si_4N_3P$: Isotopic pattern(calcd.):

Mass	365	366	367	368	369	370	371
$I_{Max} = 100$	100.000	35.464	19.096	4.585	1.257	0.212	0.266

Preparation of 1,1,4,4-tetrakis(trimethylsilyl)-2-arsa-2-tetrazene (**3**). Bis(trimethylsilyl)aminodichloroarsine $(Me_3Si)_2NAsCl_2$ (9.36 g, 30.6 mmol), in 40 ml Et_2O, was added dropwise with constant stirring to dilithium 1,2-bis(trimethylsilyl)hydrazine (5.94 g, 30.6 mmol) [or 5.57 g of $Li(H)N_2SiMe_3)_2$] in 40 ml Et_2O at −80°C. The light yellow solution containing white precipitates changed to yellow as the temperature rose followed by dark orange red colour around 0°C. The reaction mixture was stirred at room temperature for 4 h and filtered to isolate LiCl, 2.46 g = 58 mmol [1.18 g = 28 mmol in case of $Li(H)N_2SiMe_3)_2$]. ^1H NMR of the orange red filtrate showed major signals at 0.26 and 0.16 ppm and two very small signals at 0.4(Me_3SiCl) and 0.087 ppm [$(Me_3Si)_3N_2H$]. Ether, Me_3SiCl and $(Me_3Si)_3N_2H$ were removed under vacuum at room temperature to get a dark orange red liqid. Its ^1H NMR in Et_2O (benzene) showed signal at 0.26 (0.35) and 0.16 (0.21)ppm with relative area (1 : 1). The dark orange red liquid could not be crystallised from *n*-pentane or Et_2O solution at low temperatures. Therefore, it was fractionated at $80°C/10^{-3}$ Torr to get an orange red liquid (4.0 g, 8.8 mmol). Distilled product was always contaminated with $(Me_3Si)_3N_2H$ indicating mild decomposition at $80°/10^{-3}$ Torr. Tris(trimethylsilyl)hydrazine was then removed by evacuation at 10^{-3} Torr at room temperature.

Found: C, 35.55; H, 8.90; N, 10.15. $C_{12}H_{36}Si_4N_3As$. Calcd: C, 35.20; H, 8.80; N, 10.27%.

The distilled orange red liquid consisted of a mixture of *trans-cis* isomers in a tentative ratio 2 : 1. The two could not be separated by repeated fractionation under vacuum. ^1H NMR in Et_2O (benzene): δ (ppm) *trans*: 0.26 (0.35) [s, 18H, $2Me_3Si$]; 0.16 (0.21) [s, 18H, $2Me_3Si$]. *cis*: 0.24 (0.33) [s, 18H, $2Me_3Si$]; 0.15 (0.22) [s, 18H, $2Me_3Si$]. ^1H NMR spectrum in Et_2O showed no changes up to −80°.

It is protected from bright daylight due to the loss of orange red colour with the formation of $(Me_3Si)_3N_2H$.

Mass spectrum (70, 20 eV), *m*/*z* (assignment; relative intensity 70, 20 eV, %): 409 [$(m)^+$; 7,15], 394 [$(m\text{-}Me)^+$; 29,20], 322 [$(m\text{-}Me_3SiN)^+$; 100,100], 306 [$(m\text{-}Me_5Si)^+$; 75,48], 276[$(m\text{-}Me_2SiAs)^+$; 9,18], 248 [$(Me_3Si)_3N_2H^+ = m'$; 54,72], 233 [$(m'\text{-}Me)^+$; 24,15], 205 [$(m\text{-}Me_8Si_3)^+$; 25,46], 146 [$(Me_6Si_2)^+$; 32,60], 131 [$(Me_5Si_2)^+$; 60,21], 73[$(Me_3Si)^+$; 56,47].

Preparation of [tris(trimethylsilyl)hydrazino]-(trimethyl-silylimino)-methoxy)phosphorane, (**4**). Compound (**2**), (7.3 g, 20 mmol) was taken in a flask containing 20 ml of Et_2O and methyl alcohol (0.8 ml, 20 mmol), taken in 10 ml of Et_2O, was added dropwise with constant stirring at room temperature. The greenish yellow solution became colourless with the appearance of a slight turbidity. The reaction mixture was stirred at room temperature for ½ h and filtered to get a colourless solution. ^1H NMR of the solution showed major signals at δ 0.32, 0.24, 0.19 and 0.07 ppm. The solution was evacuated to remove Et_2o and other volatile products. The residual liquid was then distilled *in vacuo* and the first fraction distilling at $65\text{–}70°C/10^{-3}$ Torr was collected. It was redistilled at $55\text{–}60°C/10^{-3}$ Torr to get [tris(trimethylsilyl)-hydrazino-(trimethylsilylimino)-(methoxy)phosphorane, (**4**).

Found: C, 39.35; H, 9.95; N, 10.42. $C_{13}H_{40}N_3OPSi_4$

Calcd: C, 39.29; H, 10.07; N, 10.58%.

^1H NMR in $C_6D_6(CCl_4)$: δ(ppm) 0.35 (0.24) [s, 9H, $(Me_3Si)NSi$], 0.27(0.19) [s, 9H, $SiN(SiMe_3)$], 0.42 (0.32) [s, 9H, $(Me_3Si)NN$], 0.30 (0.07) [d, 9H, $(Me_3Si)N{=}P$; $4J_{P—H}$ 0.6 Hz], 3.37 (3.64) [d, 3H, OCH_3; $^3J_{P—H}$ 13.4 Hz], 6.81[d, 1H, HP; $^1J_{P—H}$ 593.2 Hz].

^{31}P NMR (50% solution in C_6D_6; H_3PO_4 external standard: δ(ppm) Decoupled 11.42(s), Partially ^1H-coupled 3.415 (q; $^1J_{P—H}$ 593.1 Hz), 21.830 (q; $^3J_{P—H}$ 13.4 Hz). Important IR bands (thin film, cm^{-1}): 2300s [ν(P—H)], 1250s [ν(P═N)], 1035[ν(N—N)], 930 [$\nu_{as}(Si_2N)$].

Mass spectrum (70, 15 eV) *m*/*z* (assignment; relative intensity 70, 15 eV, %): 397 [$(m)^+$; 2,15], 396 [$(m\text{-}H)^+$; 1,1], 382 [$(m\text{-}Me)^+$; 6,26], 366 [$(m\text{-}OMe)^+$; 1,1], 325 [Tris*-PH(OMe)(═NH)$^+$; 1,3], 311 [Tris-PH(OH)(═NH)$^+$; 2,9], 310 [Tris-PH(OMe)$^+$; 1,3], 296 [$(m\text{-}Me_3SiNN)^+$; 2,8], 295 [Tris-PH(═O); 2,7], 294 [Tris-PH(═NH)$^+$; 2,5], 293 [Tris-P═NH)$^+$; 2,9], 282 [$(m\text{-}Me_3SiN_3)^+$; 2,8], 281 [$(m\text{-}Me_3SiN_3H)^+$; 2,10], 248 [(Tris H)$^+$; 7,36], 247 [(Tris)$^+$; 2,3], 222[$Me_3SiNPH(OMe)NSiMe_2{}^+$; 9,37], 221 [$Me_3SiNP(OMe)NSiMe_2{}^+$; 3,15], 207 [$Me_2SiNHP(OMe)NSiMe_2{}^+$; 5,11], 176 [$Me_2SiNP(H)NSiMe_2{}^+$; 12,56], 150 [$(PH(OMe)(NSiMe_3)^+$; 16,44], 147 [$(Me_3Si)_2O\text{-}Me^+$; 29,71], 146 [$(Me_3Si)_2NH\text{-}Me^+$; 35,100], 73 [$(Me_3Si)^+$; 100,51].

*Tris = $(Me_3Si)_2N_2SiMe_3^+$.

$C_{13}H_{40}N_3OPSi_4$: Isotopic pattern (calcd.):

Mass	397	398	399	400	401	402	403
$I_{max} = 100$	100.000	36.081	19.515	4.759	1.318	0.225	0.037

Reaction of 1,1,4,4-tetrakis(trimethylsilyl)-2-arsa-2-tetrazene with MeOH. Tetrasila-2-arsa-2-tetrazene (**3**), (1.56 g, 5.1 mmol) in 5 ml Et_2O, was cooled to −10° and treated dropwise with 0.2 ml (5 mmol) CH_3OH diluted with 5 ml Et_2O. The yellowish solution was stirred for $\frac{1}{2}$ h at room temperature. ^1H NMR of the solution showed a large signal at 0.087 ppm $(Me_3Si)_3N_2H$, a prominent signal at 0.03 ppm Me_3SiNH_2 along with smaller signals at 0.05$(Me_3Si)_2NH$, 0.06 ppm $(Me_3Si)_2N_2H_2$ and others due to unreacted (**3**). The mixture was treated with more of CH_3OH (10 mmol) and stirred overnight at room temperature. ^1H NMR showed all the above signals except those due to (**3**). After removal of benzene, the product was fractionated to obtain a mixture of $(Me_3Si)_2NH$ and $As(OMe)_3$ at 125°–130°C. Further distillation of the residual product gave $(Me_3Si)_2N_2H_2$ at 80°C/40 Torr and $(Me_3Si)_3N_2H$ at 80°/10 Torr (0.92 g, 3.7 mmol).

Thermolysis of 1,3,4,4-tetrakis(trimethylsilyl)-2-phospha-1-tetrazene. Tetrasila-2-phospha-1-tetrazene, (**2**), (3.7 g, 10.1 mmol) was dissolved in 10 ml benzene and the solution was sealed in an evacuated glass tube. The sealed tube was heated at 100°C for 24 h and then opened. The gaseous nitrogen was estimated to be 2.1 mmol. ^1H NMR of the thermolysed mixture showed four major signals of almost the same size at δ 0.29, 0.27, 0.25 [$(Me_3Si)_3N_2P$] and 0.22 [$(Me_3Si)_4N_2$]. The mixture was first evacuated at room temperature to a vacuum of about 0.1 Torr and the trapped solution was found to contain small amounts of $(Me_3Si)_2NH$. The residual mixture was fractionated to obtain tetrasilahydrazine (~0.58 g, 1.8 mmol) at 65–75°/0.5 Torr and trisilaphosphatriazene $(Me_3Si)_2N{-}P{=}NSiMe_3$ (~2.1 g, 7.6 mmol) at 60–65°/10^{-2} Torr. ^1H NMR of the undistilled product contained signals due tetrasila-2-phospha-1-tetrazene and other broad signals due to some polymerised product. Thermolysis in a sealed NMR tube was also monitored by ^1H NMR to determine tentative half life of thermolysis.

Thermolysis of 1,1,4,4-tetrakis(trimethylsilyl)-2-arsa-2-tetrazene. Tetrasila-2-arsa-2-tetrazene, (**3**), (0.16 g), 0.4 ml benzene and 2 drops of TMS were taken together in a sealed NMR tube. The tube was placed in a bath at 100°C. ^1H NMR showed the formation of tris(trimethylsilyl)hydrazine (distilled at 80°C/10 Torr) and a waxy material having very broad signals with a maximum at 0.47 ppm which could not be characterised.

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REFERENCES

1. S. K. Vasisht, M. Sood, N. Sood and G. Singh, *J. Organomet. Chem.*, **301**, 15 (1986).
2. P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds", Benjamin, New York (1966).
3. N. Wiberg, H. Bayer and H. Bacchuber, *Angew. Chem. Int. Ed. Engl.*, **14**, 177 (1975).
4. N. Wiberg, H. W. Häring and S. K. Vasisht, *Z. Naturforsch.*, **34B**, 356 (1979).
5. N. Wiberg, S. K. Vasisht, H. Bayer and R. Meyers, *Chem. Ber.*, **112**, 2718 (1979).
6. N. Wiberg, H. Bayer, S. K. Vasisht and R. Meyers, *Chem. Ber.*, **113**, 2916 (1980).
7. N. Wiberg, R. Meyers, S. K. Vasisht and H. Bayer, *Chem. Ber.*, **117**, 2886 (1984).
8. N. Wiberg, *Adv. Organomet. Chem.*, **24**, 179 (1985).
9. O. J. Scherer and W. Glässel, *Chem. Ber.*, **110**, 3874 (1977).
10. R. West, *Adv. Organomet. Chem.*, **16**, 1 (1977).
11. The yellowish green liquid $(Me_3Si)_2N{-}N{=}P{-}NEt_2$ decomposes at room temperature but combines with MeOH at −10°C with addition at $-P{=}N$-ylid to form a colourless liquid $(Me_3Si)_2N{-}N(H){-}P(OMe)(NEt_2)$ distilling at 70°C/10^{-2} Torr.
12. E. Niecke and W. Flick, *Angew. Chem. Int. Ed. Engl.*, **12**, 585 (1973).
13. S. K. Vasisht, P. K. Verma, T. Kaur and K. Usha, Unpublished results.
14. U. Wannagat and H. Niederprum, *Z. Anorg. Allg. Chem.*, **310**, 32 (1961).
15. U. Wannagat, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).
16. N. Wiberg, E. Weinberg and W. Ch. Joo, *Chem. Ber.*, **107**, 1764 (1974).
17. O. J. Scherer and N. Kuhn, *J. Organomet. Chem.*, **82**, C-3 (1974).
18. M. J. S. Gynane, A. Hudson, M. F. Lappert, P. P. Power and H. Goldwhite, *J. Chem. Soc. Dalton Trans.*, **33**, 2428 (1980).