FACILE PREPARATION OF SILYL AZIDES WITH DIPOLAR APROTIC SOLVENTS

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SUMMARY

The reaction of sodium azide with chlorosilanes in hexamethylphosphoric triamide or dimethylformamide at room temperature affords a high yield preparation of silyl azides, *e.g.* Me_3SiN_3, $Me_2Si(N_3)_2$, $PhMeSi(N_3)_2$ and $Ph_2Si(N_3)_2$. For characterization, the azides may be converted to silylphosphinimines, $R_3Si-N=PPh_3$.

Despite current interest in metal azides[1], especially those of silicon[2-9], as azide transfer agents, preparative routes to these compounds remain far from satisfactory. The recently reported *Organic Syntheses* method[7], while a high yield procedure, requires purification of diglyme (diethylene glycol dimethyl ether), and some rather cumbersome techniques.

In searching for a convenient synthesis of silyl azides, we decided to concentrate of the metathesis of the readily available chlorosilanes and sodium azide. Pronounced solvent effects are common in formally S_N2 type reactions, and we were conscious of the ability of dipolar aprotic solvents to solvate small cations and leave highly reactive, yclept "naked", anions[10]. This reactivity may be harnessed when rate-determining attack by an inorganic anion is involved. Noting that the reaction of sodium azide with 1-butyl bromide was subject to a pronounced solvent effect; relative rates: H_2O, 1; $CH_3CONHMe$, 1.25; $HCONMe_2$, 410; CH_3CN, 740; $(Me_2N)_3P \rightarrow O$, 30,000[11], we thought that the latter solvent, hexamethylphosphortriamide (HMPT) would be an excellent medium for silyl azide preparations.

Such was the case. The reaction of chlorosilanes with sodium azide in HMPT is apparently quantitative. Addition of an equimolar quantity of Me_3SiCl to a reddish-orange slurry of NaN_3 in HMPT (150 ml/mole) caused discharge of the color. The addition funnel was replaced by a still head and a cloudy liquid fraction, b.p. 90–102° was collected. Redistillation afforded an 84% yield of trimethylsilyl azide exhibiting a single NMR resonance (δ 0.18 ppm).

As shown by Table 1, other solvents are less suitable than HMPT for the preparation of trimethylsilyl azide. Only HMPT requires no period of reflux, and its high boiling point allows facile product separation by direct distillation. This expensive solvent may be recovered by filtration of the pot residue from sodium chloride and vacuum distillation.

Table 2 shows the range of silyl azides prepared with dipolar aprotic solvents.

TABLE 1

EFFECT OF SOLVENT ON THE YIELD OF TRIMETHYLSILYL AZIDE

Solvent	Solvent (ml)/ NaN$_3$/mole	Reflux (h)	Yield (%)
None		72	0
THF + 2 mole % AlCl$_3$	70	24	15
TMED^a	70	4	0^b
DMF	125	5	54
HMPT	150	0	84

^{a} N,N,N',N'-Tetramethylethylenediamine. ^{b} Clear, colorless product, b.p. 94–97°; decomposed on standing overnight.

For high-boiling azides, e.g. Ph$_2$Si(N$_3$)$_2$, DMF or pyridine is a useful alternative to HMPT.

Certain limitations of the dipolar aprotic solvents should be noted.

(1). Mixed chlorosilyl azides can not be prepared by the HMPT solvent method. An attempted preparation of Me$_2$Si(N$_3$)Cl from one mole each of Me$_2$SiCl$_2$ and NaN$_3$ in HMPT gave only Me$_2$Si(N$_3$)$_2$ and recovered Me$_2$SiCl$_2$. This is in marked contrast to the Me$_2$SiCl$_2$ + Me$_2$NH reaction, which afforded Me$_2$Si(NMe$_2$)Cl in good yield[12].

TABLE 2

PREPARATION OF SILYL AZIDES WITH DIPOLAR APROTIC SOLVENTS

Chlorosilane (moles)	NaN$_3$ (moles)	Silyl azide	Yield (%)	B.p. (°C/mm)	Solvent
Me$_3$SiCl (1)	1	Me$_3$SiN$_3$	84	95–97 760	HMPT
Me$_2$SiCl$_2$ (1)	1	Me$_2$Si(N$_3$)$_2$	79	144–145 760	HMPT
Ph$_2$SiCl$_2$ (0.5)	1	Ph$_2$Si(N$_3$)$_2$	71	121–123 0.1	DMF
MePhSiCl$_2$ (0.15)	0.3	MePhSi(N$_3$)$_2$	85	83–84 0.2	DMF

(2), H–, Me$_2$N–, and CH$_2$=CH– functionality on silicon is incompatible with the azide/chloride metathesis. Reaction of HSi(Me)Cl$_2$ with NaN$_3$ in HMPT evolved a pyrophoric gas (MeSiH$_3$) and produced no characterizable product. The reaction of (CH$_2$=CH)CH$_3$SiCl$_2$ with NaN$_3$ gives a product which infallibly detonates upon attempted distillation, while Me$_2$Si(NMe$_2$)Cl + NaN$_3$ affords an uncharacterizable product containing no NMe$_2$ group.

Silyl azides may be characterized by a sharp infrared absorption band at 2140 cm^{-1}, or by formation of the crystalline triphenylphosphinimine derivative[13]. Reaction of R$_3$SiN$_3$ with Ph$_3$P in refluxing toluene or mesitylene affords R$_3$SiN=PPh$_3$; the reaction may be easily monitored by measuring nitrogen evolution. Table 3 gives yields and physical constants on phosphinimines prepared.

TABLE 3

SILYLPHOSPHINIMINES FROM SILYL AZIDES AND TRIPHENYLPHOSPHINE

Silyl azide	Solvent	Silylphosphinimine	Yield (%)	M.p. (°C)	Ref.
Me_3SiN_3	Mesitylene	$Me_3SiN=PPh_3$	94	74–76	2
$Me_2Si(N_3)_2$	Toluene	$Me_2Si(N=PPh_3)_2$	87	153–155	a
$Ph_2Si(N_3)_2$	Toluene	$Ph_2Si(N=PPh_3)_2$	87	191–192	13
$MePhSi(N_3)_2$	Toluene	$MePhSi(N=PPh_3)_2$	76	171–172	a

a This work.

EXPERIMENTAL

Trimethylsilyl azide (recommended procedure)

A flame-dried, 3-neck, 500 ml flask was charged with 71.5 g (1.1 M) f sodium azide (Fisher Scientific) and 150 ml of HMPT (Eastman White Label). Trimethylchlorosilane (108.6 g, 1.0 mole, Union Carbide Silicones) was added with stirring over a one hour period at such a rate that the red-orange color of the reaction slurry was not dissipated. At the completion of the addition, the dropping funnel was replaced by a partial-reflux still head, and the fraction b.p. 90–102°, a cloudy liquid, was collected. The pot residue was filtered, and the filtrate reused as solvent in subsequent preparations. The cloudy liquid was purified by distillation through a 12" Widmer column. A fraction, b.p. 95–97° (760 mm), 97 g, corresponded to a 84% yield of Me_3SiN_3; IR (7% in CCl_4): 2140, 1695, 1330, 1259 cm^{-1}; NMR (15% in CCl_4): δ 0.18 ppm, singlet. A forerun, b.p. 90–95°, was more than 75% Me_3SiN_3 by NMR.

Trimethylsilyl azide (Alternate procedure, DMF solvent)

The reaction was carried out as above with the substitution of dimethylformamide (Eastman White Label, dried over Linde Molecular Sieves) for HMPT. At the completion of the addition the mixture was heated at reflux 5 h, then filtered under N_2, and worked up as above. Two distillations through the Widmer column were required before a clear distillate was obtained. The yield was 54%.

Dimethyldiazidosilane*

The recommended procedure was employed with 129.1 g (1 mole) of dimethyldichlorosilane (Union Carbide Silicones) and 1 mole of NaN_3. The temperature was maintained below 5° during the addition, then the mixture was stirred 18 h at room temperature. The usual workup afforded 70 g (56%) of Me_2SiCl_2, b.p. 69–70°, and 56 g (79%) of $Me_2Si(N_3)_2$, b.p. 144–145° [13].

Methylphenyldiazidosilane (Recommended procedure for high-boiling silyl azides)

A mixture of 0.30 moles of NaN_3 and 75 ml of DMF was treated over a 30 min period with 28.7 g (0.15 M) of methylphenyldichlorosilane (Peninsular ChemResearch,

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* *Note added in proof.* Dimethyldiazidosilane is known to explode unpredictably. Exercise caution (W. Wolfsberger and H. Schmidbauer, *J. Organometal. Chem.*, 28 (1971) 301.)

distilled b.p. 77°/10 mm), causing a mild exothermic reaction and formation of a pink color. At the completion of the addition the mixture was stirred 30 min, then filtered under a positive pressure of N_2. The filtrate was evaporated at reduced pressure. Distillation of the residue afforded 25.9 g (85%) of methylphenyldiazidosilane, b.p. 83–84° (0.2 mm); NMR (CCl_4): δ 0.68, 5H s; δ 7.48 ppm, 5H m; (Found: C, 41.01; H, 3.69; N, 40.90. $C_7H_8N_6Si$ calcd.: C, 41.16; H, 3.95; N, 41.15%.) If the filtrate was not freed of solvent expeditiously it was observed to darken and evolve gas, probably via reaction of $Si-N_3$ with $HC=O^+$.

Reaction of methyldichlorosilane with sodium azide

Addition of 34.8 g (0.3 M) of $MeHSiCl_2$ (Alfa Inorganics) to an ice-salt bath cooled slurry of 0.6 mole of NaN_3 in 75 ml of HMPT caused evolution of a pyrophoric gas which was collected in a trap at $-78°$. The condensate (4.0 g, 30%) was identified as $MeSiH_3$ on the basis of its characteristic NMR spectrum[14] and IR absorptions at 2395, 2180, and 1255 cm^{-1}.

Bis(triphenylphosphinimino)methylphenylsilane:

Methylphenyldiazidosilane (2.0 g, 10 mmoles) and triphenylphosphine (5.2 g, 20 mmoles) were heated at reflux with 10 ml of toluene for 16 h. The mixture was cooled and the solvent evaporated at reduced pressure. The cream-colored residue was extracted with refluxing Et_2O. Concentration and cooling of the extracts afforded 5.0 g (76%) of $PhMeSi(N=PPh_3)_2$. An analytical sample (from Et_2O) has m.p. 171–172°. NMR (10% $DCCl_3$): δ 0.13, 3H s; δ 7.13–7.87 ppm, 35H m. IR (5% $CHCl_3$): 3080, 3000, 2035, 1600, 1485, 1458, 1280, 1110, 1063, 930, 820, and 690 cm^{-1}. (Found: C, 77.66; H, 5.74; N, 4.03. $C_{43}H_{38}N_2P_2Si$ calcd.: C, 77.92; H, 5.78; N, 4.23%.)

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