

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 , $\text{Me}_2\text{Si}(\text{N}_3)_2$, $\text{PhMeSi}(\text{N}_3)_2$ and $\text{Ph}_2\text{Si}(\text{N}_3)_2$. For characterization, the azides may be converted to silylphosphinimines, $\text{R}_3\text{Si-N=PPh}_3$.

Despite current interest in metal azides¹, especially those of silicon²⁻⁹, as azide transfer agents, preparative routes to these compounds remain far from satisfactory. The recently reported *Organic Syntheses* method⁷, 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 on the metathesis of the readily available chlorosilanes and sodium azide. Pronounced solvent effects are common in formally $\text{S}_{\text{N}}2$ type reactions, and we were conscious of the ability of dipolar aprotic solvents to solvate small cations and leave highly reactive, cyclic "naked", anions¹⁰. 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; $(\text{Me}_2\text{N})_3\text{P} \rightarrow \text{O}$, 30,000¹¹, we thought that the latter solvent, hexamethylphosphorotriamide (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.* Ph₂Si(N₃)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 Me₂Si(N₃)Cl from one mole each of Me₂SiCl₂ and NaN₃ in HMPT gave only Me₂Si(N₃)₂ and recovered Me₂SiCl₂. This is in marked contrast to the Me₂SiCl₂ + Me₂NH reaction, which afforded Me₂Si(NMe₂)Cl in good yield¹².

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-, Me₂N-, and CH₂=CH- functionality on silicon is incompatible with the azide/chloride metathesis. Reaction of HSi(Me)Cl₂ with NaN₃ in HMPT evolved a pyrophoric gas (MeSiH₃) and produced no characterizable product. The reaction of (CH₂=CH)CH₃SiCl₂ with NaN₃ gives a product which infallibly detonates upon attempted distillation, while Me₂Si(NMe₂)Cl + NaN₃ affords an uncharacterizable product containing no NMe₂ group.

Silyl azides may be characterized by a sharp infrared absorption band at 2140 cm⁻¹, or by formation of the crystalline triphenylphosphinimine derivative¹³. Reaction of R₃SiN₃ with Ph₃P in refluxing toluene or mesitylene affords R₃SiN=PPh₃; 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 ₃ SiN ₃ | Mesitylene | Me ₃ SiN=PPh ₃ | 94 | 74–76 | 2 |
| Me ₂ Si(N ₃) ₂ | Toluene | Me ₂ Si(N=PPh ₃) ₂ | 87 | 153–155 | ^a |
| Ph ₂ Si(N ₃) ₂ | Toluene | Ph ₂ Si(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) of 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 Me₃SiN₃; IR (7% in CCl₄): 2140, 1695, 1330, 1259 cm⁻¹; NMR (15% in CCl₄): δ 0.18 ppm, singlet. A forerun, b.p. 90–95°, was more than 75% Me₃SiN₃ 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 N₂, 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 NaN₃. 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 Me₂SiCl₂, b.p. 69–70°, and 56 g (79%) of Me₂Si(N₃)₂, b.p. 144–145°¹³.

Methylphenyldiazidosilane (Recommended procedure for high-boiling silyl azides)

A mixture of 0.30 moles of NaN₃ and 75 ml of DMF was treated over a 30 min period with 28.7 g (0.15 M) of methylphenyldichlorosilane (Peninsular ChemResearch,

* 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 N₂. 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 (CCl₄): δ 0.68, 5H s; δ 7.48 ppm, 5H m; (Found: C, 41.01; H, 3.69; N, 40.90. C₇H₈N₆Si 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–N₃ with HC=O⁴.

Reaction of methylchlorosilane with sodium azide

Addition of 34.8 g (0.3 M) of MeHSiCl₂ (Alfa Inorganics) to an ice-salt bath cooled slurry of 0.6 mole of NaN₃ 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 MeSiH₃ on the basis of its characteristic NMR spectrum¹⁴ and IR absorptions at 2395, 2180, and 1255 cm⁻¹.

Bis(triphenylphosphinino)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 Et₂O. Concentration and cooling of the extracts afforded 5.0 g (76%) of PhMeSi(N=PPh₃)₂. An analytical sample (from Et₂O) has m.p. 171–172°. NMR (10% DCCl₃): δ 0.13, 3H s; δ 7.13–7.87 ppm, 35H m. IR (5% CHCl₃): 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. C₄₃H₃₈N₂P₂Si calcd.: C, 77.92; H, 5.78; N, 4.23%.)

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