

## A New Method for the Reduction of Isocyanates to Isocyanides

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Both diphenyl-*t*-butylsilyl-lithium and trichlorosilane-triethylamine reduce isocyanates to isocyanides in high yield under mild conditions.

The literature contains few methods for reducing isocyanates to isocyanides, equation (1). While simple phosphines and

$$\text{R-N=C=O} \rightarrow \text{R-N=C} \quad (1)$$

phosphites are effective in certain cases, they suffer the drawback of requiring high temperatures.<sup>1,2</sup> Mukaiyama's reagent,<sup>3</sup> 2-phenyl-3-methyl-1,3,2-oxazaphospholidine, has proved to be

an effective reducing agent at room temperature but is difficult to prepare and store. We report two novel, high yielding methods which effect this reduction utilizing silicon anions as the reducing agent.

Thus, treatment of a solution of diphenyl-*t*-butylsilyl-lithium<sup>3</sup> (10 mmol) in tetrahydrofuran (THF, 10 ml) at 0 °C with an equivalent of the isocyanate (1), (2), or (3) dissolved in THF (10 ml) led, after fractional distillation, to the isolation of the corresponding isonitrile in good yield. However reaction with 4-chlorophenyl isocyanate (4) gave a very poor yield of the isonitrile presumably owing to competing metallation of the aromatic ring (Table 1).

The same reduction can also be achieved, in good yield, using trichlorosilane-triethylamine<sup>4</sup> in dichloromethane. Phenyl isothiocyanate (8) was also reduced albeit in lower yield. In addition, trichlorosilane-triethylamine reduces carbamates (5), (6), and (7) to the corresponding isonitriles, in fair yields, presumably *via* the isocyanates.<sup>5</sup> Dicyclohexylcarbodiimide was not reduced by either trichlorosilane-triethylamine or diphenyl-*t*-butylsilyl-lithium.

We found the trichlorosilane-triethylamine reagent to be preferable to diphenyl-*t*-butylsilyl-lithium on the grounds that it is less basic, more economical, and allows for easier isolation of products.

A typical experimental procedure using trichlorosilane is as follows. To a solution of trichlorosilane (12 mmol) and triethylamine (28 mmol)† in dichloromethane (15 ml) was added the isocyanate, carbamate, or isothiocyanate (10 mmol). The mixture was stirred for 0.5 h at 0 °C in the case of isocyanates, 40 h at 20 °C in the case of carbamates, and 6 h at 20 °C for phenyl isothiocyanate. When the reaction was complete, ammonia was blown through the reaction mixture to precipitate any silicon-containing species, the mixture was

† The use of di-isopropylethylamine gives slightly higher yields.

**Table 1.** Yields of isocyanides obtained from the reductions of a number of isocyanates and carbamates.

		Yield (%) of isocyanide <sup>a</sup>	
		Ph <sub>2</sub> Bu <sup>t</sup> SiLi	Cl <sub>3</sub> SiH
Phenyl isocyanate	(1)	65	70
1-Naphthyl isocyanate	(2)	79	70
Cyclohexyl isocyanate	(3)	73	60
4-Chlorophenyl isocyanate	(4)	14	60
Methyl phenylcarbamate	(5)	—	40
Methyl 1-naphthylcarbamate	(6)	—	15
Methyl cyclohexylcarbamate	(7)	—	50
Phenyl isothiocyanate	(8)	—	15

<sup>a</sup> All compounds gave satisfactory i.r., n.m.r., and mass spectral data.

filtered, and excess of base removed by extraction with NaH<sub>2</sub>PO<sub>4</sub>. The organic phase was filtered through a silica gel plug and concentrated *in vacuo* to yield the product (Table 1).

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