

Removal of the TCBOC group can be accomplished with the supernucleophilic cobalt(i)-phthalocyanine anion in methanol or acetonitrile^[3, 7, 8] and with zinc in glacial acetic acid (see Table 3); the yields of amine component are 66–94%. N-Terminal deprotection by lithium cobalt(i)-phthalocyanine also proceeds smoothly in the case of benzyl esters.

Table 3. Removal of the TCBOC group from compounds (4) by lithium cobalt(i)-phthalocyanine in methanol (method A) or acetonitrile (method B) or with zinc in glacial acetic acid (method C) at 20°C.

(4)	Method	Reaction time	Yield of (3) [%]
(4g) TCBOC-Val-OMe	A	1 min	87
(4h) TCBOC-Val-OCH ₂ Ph	A	1 min	93
(4d) TCBOC-Val-Ala-Phe-OrtBu	B	1 h [a]	94
(4g) TCBOC-Val-OMe	C	3 h	66
(4d) TCBOC-Val-Ala-Phe-OrtBu	C	3 h	73

[a] The actual deprotection reaction only takes 5 min.

Experimental

Synthesis of (2): Anhydrous chloretone (1) (178 g, 1.0 mol) dissolved in anhydrous dichloromethane (400 ml) is treated at -20°C with phosgene (140 ml, 2.0 mol). Pyridine (105 ml, 1.5 mol) in dichloromethane (70 ml) is added dropwise at -20°C and the mixture is then stirred for 12 h at 20°C. Subsequent washing of the ether solution at 0°C with water (caution: vigorous evolution of gas owing to liberation of excess phosgene), 2 N sulfuric acid, and water followed by distillation affords 214 g (89%) of (2), b. p. 77–81°C/12 torr.

Synthesis of (4a): Valine (11.7 g, 0.1 mol), dissolved in water (200 ml) and 1 N sodium hydroxide solution (250 ml), is treated with diethyl ether (100 ml) and then emulsified at 0°C with (2) (33.8 g, 0.14 mol) in dioxane (140 ml) for 1 h. The aqueous phase is washed with diethyl ether, acidified with 5 N hydrochloric acid, and extracted into ethyl acetate. After washing with water, compound (4a) (26 g, 82%) crystallizes from the extract; the product is recrystallized from hexane; m. p. 102°C.

Deprotection of (4d) (method B): A solution of lithium cobalt(i)-phthalocyanine^[3, 7, 8] (2.5 g, 2.8 mmol) in acetonitrile (15 ml), phenol (600 mg, 6 mmol), and (4d) (500 mg, 0.84 mmol) are stirred together at 20°C under N₂ for 1 h. Water (20 ml) and 1 N HCl (2 ml) are added to the dark green mixture; the dark blue precipitate is centrifuged off, and the residue is washed with 1% citric acid and water. The supernatant liquors (pH 4.0) are washed with ether, rendered alkaline with Na₂CO₃ and extracted with ethyl acetate. Evaporation of the extract affords (3d) (310 mg, 94%) (identification by ¹H-NMR, IR).

Deprotection of (4d) (method C): Compound (4d) (595 mg, 1.0 mmol) is dissolved in 95% acetic acid (10 ml) and zinc dust (ca. 1 g) is added portionwise over 3 h to the stirred solution. Zinc is then filtered off, washed with water, and the filtrate and washings washed with ether. After rendering alkaline with caustic soda solution and extraction with ethyl acetate, (3d) (286 mg, 73%) is obtained from the extract by evaporation (identification by ¹H-NMR, IR).

CAS Registry numbers:

(2), 66270-36-8; (3a), 72-18-4; (3d), 66270-37-9; (4a), 66270-38-0; (4b), 66270-39-1; (4c), 66270-40-4; (4d), 66270-41-5; (4e), 66270-42-6; (4f), 66270-43-7; (4g), 66270-44-8; (4h), 66270-45-9

- [1] E. Wünsch in Houben-Weyl: Methoden der organischen Chemie. 4th Edit. Thieme, Stuttgart 1974, Vol. 15.
 [2] H. Eckert, G. N. Schrauzer, I. Ugi, Tetrahedron 31, 1399 (1975).
 [3] H. Eckert, I. Ugi, Angew. Chem. 88, 717 (1976); Angew. Chem. Int. Ed. Engl. 15, 681 (1976); H. Eckert, I. Ugi, to be published.
 [4] J. Grimshaw, J. Chem. Soc. 1965, 7136.
 [5] R. B. Woodward, K. Heusler, S. Gosteli, D. Naegeli, W. Oppolzer, R. Ramage, S. Ranganathan, H. Vorbrüggen, J. Am. Chem. Soc. 88, 852 (1966).
 [6] L. A. Carpino, K. N. Parameswaran, R. K. Kirkley, J. W. Spiwak, E. Schmitz, J. Org. Chem. 35, 3291 (1970).
 [7] H. Eckert, Synthesis 1977, 332; H. Eckert, I. Ugi, H.-J. Kabbe, DOS 26 19 247 (1977), Bayer AG.
 [8] H. Eckert, I. Lagerlund, I. Ugi, Tetrahedron 33, 2243 (1977).

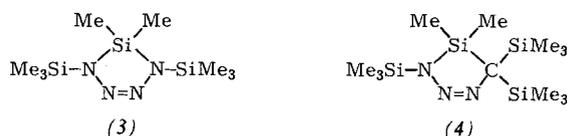
Preparation and Some Reactions of Dimethyl(trimethylsilylimino)silane, Me₂Si=N₂SiMe₃^[1]

By Nils Wiberg and Gerhard Preiner^[*]

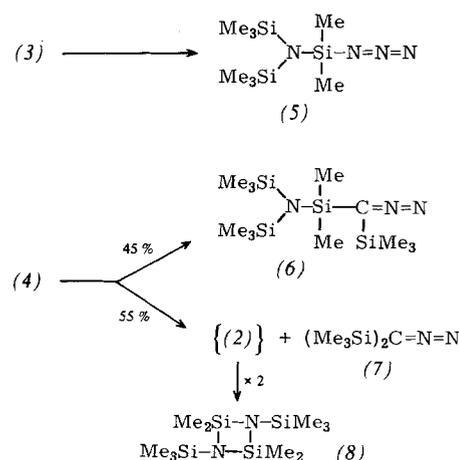
Having synthesized the silaethene (1)^[2], we have now found a facile entry to iminosilane (2)—a representative of the poorly characterized, highly reactive compounds containing a Si=N double bond which have not yet been isolated^[3].



Our study was prompted by observation of differing behavior on thermolysis of the "isosteric" heterocycles (3) and (4):



While thermolysis of (3) at 180°C leads quantitatively via isomerization to the aminosilyl azide (5)^[4], compound (4) (readily accessible from (1) and Me₃SiN₃; metastable below -5°C)^[2, 5] is not converted exclusively into (6) (analogous to (5)); fragmentation also occurs, affording the iminosilane (2), which dimerizes to (8) in the absence of a trapping reagent, and the diazomethane derivative (7)^[5].



[*] Prof. Dr. N. Wiberg, Dipl.-Chem. G. Preiner
 Institut für Anorganische Chemie der Universität
 Meiserstrasse 1, D-8000 München 2 (Germany)