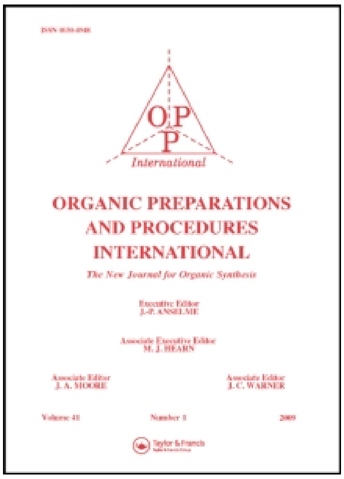

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# UNSYMMETRICALLY ALKOXYLATED DISILAZANES

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# UNSYMMETRICALLY ALKOXYLATED DISILAZANES

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Unsymmetrically methoxylated and ethoxylated alkyldisilazanes (III) have been prepared by an extension of the method of Weibrecht and Rochow[2] as shown in the following equations:

$$(1)\quad (CH_3)_2SiCl_2 + ROH \xrightarrow[25°]{\text{hexane}} \underset{\text{(I)}}{RO\text{-}Si(CH_3)_2Cl} + HCl$$

$$(2)\quad SiCl_4 + 3R'OH \xrightarrow[25°]{\text{hexane}} \underset{\text{(II)}}{(R'O)_3SiCl} + 3HCl$$

$$(3)\quad I + II + 3NH_3 \xrightarrow[70°]{\text{hexane}} 2NH_4Cl + \underset{\text{(III)}}{(R'O)_3Si\text{-}NH\text{-}Si(CH_3)_2OR}$$

$$(1)\quad R = CH_3$$

$$(2)\quad R' = C_2H_5 \text{ or } CH_3$$

It should be noted that the ready exchange of alkoxy groups and halogen bonded to silicon[3] makes the presence of some dimethyldimethoxysilane among the products of reaction (1) very probable. Similarly, in reaction (2) a mixture of alkoxychlorosilanes would also be expected. Only the most probable product is shown in reaction (2).

## Experimental

In a typical preparation of 1,1-dimethyl-1,3,3,3-tetramethoxydisilazane, 2 moles of dimethyldichlorosilane were added to 1 l. of dry n-hexane in a 3 l., 3-necked, round bottom flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. In like manner in another reaction vessel, 2 moles of $SiCl_4$ were added dropwise to the flask containing the dimethyldichlorosilane, and six moles of methanol to the flask containing $SiCl_4$. Hydrogen chloride evolution began immediately. After all of the methanol had been added, the reaction mixtures were refluxed for 1.5 hrs. and in each case the reaction vessels were flushed with dry nitrogen to remove traces of hydrogen chloride. The methoxydimethylchlorosilane and trimethoxychlorosilane which were presumably the major products of these reactions were not isolated. Rather, ammonia gas was added directly to the combined hexane solutions described above, and ammonium chloride precipitation was observed immediately. The reaction was highly exothermic. The hexane solution was separated from the ammonium chloride by suction filtration. Ammonia gas was again added to the filtered hexane solution. This process was repeated until no further precipitation of ammonium chloride occurred, indicating completion of the reaction. In each case, the ammonium chloride was washed with hexane and the hexane fractions were combined. The liquid boiling above 95° at atmospheric pressure corresponded to a 73% yield of crude disilazanes. This liquid was fractionally distilled at 10 mm.

pressure, using a 15-inch, insulated column packed with glass helices. A small amount of a substance collected at 47° was shown by n.m.r. to be the symmetrical compound, 1,3-dimethoxy-1,1,3,3-tetramethyldisilazane. A small amount of another substance, boiling at 92-95°, was identified as hexamethoxydisilazane. Although constant boiling mixtures of the various disilazanes were obtained, it was possible to isolate 1,1-dimethyl-1,3,3,3-tetramethoxydisilazane, bp. 82-84°/10 mm., (bp., 205°/740 mm.) in 35-40% yield.

Anal. Calc'd for $C_6H_{19}NSiO_4$: C, 32.10; H, 8.49; Si, 25.00; N, 6.24; MW, 225. Found: C, 32.26; H, 8.70; Si, 25.01; N, 6.31; MW, 231.

Proton nmr spectrum: $(SiCH_3)$ (s), $\delta = 0.09$; $(OCH_3)$ (s), $\delta = 3.50$; $(OCH_3)$ (s), $\delta = 3.60$. $(CH_3):(OCH_3)$ Found: 1/1.99. Calc'd: 1/2.

It should be noted that the formation of the symmetrically alkoxylated disilazanes is probably only one-half as likely as the formation of the unsymmetrical compound. Since there are two possible symmetrical compounds and only one unsymmetrical product, one-half of the crude disilazane mixture should theoretically be the unsymmetrical compound. (73% x 0.50 = 36.5%). This compares favorably with the 35-40% yields obtained. The same reasoning applies to the formation of 1-methoxy-1,1-dimethyl-3,3,3-triethoxydisilazane described below.

When the reaction mixture for the preparation of 1-methoxy-1,1-dimethyl-3,3,3-triethoxydisilazane was treated in exactly the same manner as described above, an approximately 75% yield of the crude, mixed disilazanes was obtained. Fractional distillation at 10 mm. pressure yielded a small amount of 1,3-dimethoxy-1,1,3,3-tetramethyldisilazane. The distillation residue was shown by vpc to contain hexaethoxydisilazane. Constant boiling mixtures were again obtained. However, 1-methoxy-1,1-dimethyl-3,3,3-triethoxydisilazane was obtained in 42% yield as a fraction boiling at 90-92°/10 mm., (bp., 215°/740 mm.).

Anal. Calc'd for $C_9H_{25}NSiO_4$: C, 42.64; H, 9.94; N, 5.25. Found: C, 42.71; H, 9.96; N, 5.29.

Proton nmr spectrum: ($SiCH_3$) (s), $\delta = 0.09$; ($OC_2H_5$) (t), $\delta = 1.24$; ($SiOCH_3$) (s), $\delta = 3.50$; ($OC_2H_5$) (q), $\delta = 3.90$. ($CH_3$):($OC_2H_5$):($OCH_3$) Found: 2/3/1. Calc'd: 2/3/1.

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