ation of the nickel thiocyanate complex is practically independent of the amine used in its formation.

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Tetramethyldisiloxane-1,3-diol

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A number of diorganosilane diols and tetraorganodisiloxane-1,3-diols have been prepared where one or more of the organic groups are larger than methyl.[1–4] However silane diols containing only methyl groups are very susceptible to condensation and have not been reported. We have now found that tetramethyldisiloxane-1,3-diol (I), the dimer of dimethylsilanediol, can be obtained in 60% yield by adding dimethyldichlorosilane to excess cold water maintained near neutrality by simultaneously adding ammonia. The compound is a snow-white crystalline solid, m.p. 67–68°, which may be stored, when pure, at room temperature without decomposition. The compound dissolves in water, but crystallizes from a cold aqueous solution upon the addition of salt.

The structure of the compound was shown by elemental analysis and determination of molecular weight and active hydrogens. On heating alone or in an inert solvent a mole of water is eliminated per mole of disiloxanediol with the formation of dimethylpolysiloxanes. Refluxing the compound with *n*-butanol and an acidic catalyst resulted in rapid dehydration and slow alcoholysis to form dimethyldibutoxysilane.

Experimental

Preparation of Tetramethyldisiloxane-1,3-diol.—Fifteen liters of water was placed in a flask equipped with a high speed stirrer and surrounded by an alcohol–Dry Ice cooling bath. Brom thymol blue and phenolphthalein indicators were added and the water was cooled to 2°. Ten moles of dimethyldichlorosilane was slowly added from a dropping funnel with rapid stirring. The dimethyldichlorosilane hydrolyzed almost instantly and the hydrogen chloride generated was neutralized with gaseous ammonia bled in from a cylinder through a glass tube which dips well below the surface of the water. The addition of the chlorosilane and ammonia was adjusted so that color of solution was in the blue range, *p*H 6.5–8.5. The addition of the silane required 48 minutes during which time the reaction temperature was kept at 0 to 2° and bath temperature at −30 to −40°. Five thousand grams of salt was added, and the reaction mixture was allowed to stand 24 hours at 10°. The crystalline mass which separated was filtered and taken up in two liters of boiling hexane. Upon cooling the hexane solution to 10° 494 g. of tetramethyldisiloxane-1,3-diol separated as snow-white needles. A sample for analysis was recrystallized from hexane, m.p. 67–68°.

Anal. Calcd. for $C_4H_{14}O_3Si_2$: C, 28.91; H, 8.49; Si, 33.78; mol. wt., 166.27; hydroxyl, 20.4. Found: C, 28.9, 29.2; H, 8.3, 8.5; Si, 33.61 (average of 12 determinations); mol. wt., 176 (in phenol), 171 (in camphor), 170 (in dioxane); hydroxyl (Zerewitinoff), 20.2.

Condensation of (I).—Refluxing of 16.6 g., 0.10 mole, of (I) in 100 ml. of dry benzene containing 1 g. of *p*-toluenesulfonic acid in a flask equipped with a Birdwell–Sterling water trap resulted in the formation in 20 minutes of a maximum 1.8 ml. of water. This is the theoretical amount required for complete dehydration to form dimethylpolysiloxanes.

Alcoholysis of (I).—Fifty-hour refluxing of 16.6 g., 0.10 mole, of (I) in a dry solution of 0.5 g. of *p*-toluenesulfonic acid in 100 ml. of *n*-butanol and 25 ml. of benzene resulted in the separation of 4.8 ml. of water of which 1.8 ml., 0.10 mole, separated in the first few minutes. No water was formed by refluxing the reactants in the absence of (I). Independent experiments showed that the rapid elimination of 0.1 mole of water was largely due to self-condensation of (I) and that the slow elimination of water that followed was due to the alcoholysis of the condensation products. Complete alcoholysis of 0.1 mole of (I) to dimethyldibutoxysilane would yield 5.4 ml. of water as compared to 4.8 ml. obtained. A larger run, in which the reaction mixture was neutralized and distilled, resulted in the isolation of dimethyldibutoxysilane (b.p. 190–200°; Si found 13.7 and 13.4, theory 13.73) together with a probable mixture of the latter with 1,3-dibutoxytetramethyldisiloxane,[5] b.p. 200–216°; Si found 17.7 and 17.6, theory 20.15.

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NEW PRODUCT DEVELOPMENT LABORATORY
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X-Ray Studies of Rare Earth Oxide Systems. II. The Oxide Systems Ce^{IV}–Sm^{III}, Ce^{IV}–Gd^{III}, Ce^{IV}–Y^{III}, Pr^{IV}–Y^{III} and Pr^{III}–Y^{III}

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Solid solutions of the trivalent rare earth oxides La_2O_3, Ce_2O_3, Pr_2O_3, Nd_2O_3 and Sm_2O_3 in the tetravalent rare earth oxides CeO_2 and PrO_2 have been studied by a number of investigators.[1–10] Although the separate studies have involved the use of X-ray powder photographs, density determinations and measurement of electric conductivities, complete studies of all of these systems have not as yet been reported. All of the systems studied show a homogeneous region with the fluorite structure from the pure tetravalent oxide to about 60 atom per cent. of the trivalent oxide. The deficiency of oxygen caused by substitution of M^{III} for M^{IV} in the fluorite structure leads to random vacancies in the anion lattice. This contention is supported by the relative intensities of the X-ray diffraction lines[1,9] and by the correlation of density measurements with the lattice constants.[1,7]

The present communication reports an extension of the X-ray studies to some trivalent rare earth ions of smaller radius. Yttrium has been included because of its great similarity to the rare earth elements of higher atomic number and because of its

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