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

DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE
CORVALLIS, OREGON

Tetramethyldisiloxane-1,3-diol

BY GLENNARD R. LUCAS AND ROBERT W. MARTIN

RECEIVED FEBRUARY 29, 1952

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.

Acknowledgments.—The authors wish to express their appreciation to Messrs. J. C. Brown for analytical data and to P. V. Steenstrup for his help.

---

(1) R. Robinson and F. S. Kipping, *Proc. Chem. Soc.*, **28**, 245 (1912).

(2) R. Robinson and F. S. Kipping, *J. Chem. Soc.*, **101**, 2156 (1912).

(3) P. A. Digiorgio, Abstract of paper presented Am. Chem. Soc. meeting, April, 1946, Atlantic City.

(4) N. W. Cusa and F. S. Kipping, *J. Chem. Soc.*, 2205 (1932).

(5) R. O. Sauer, THIS JOURNAL, **68**, 138 (1946).

NEW PRODUCT DEVELOPMENT LABORATORY
GENERAL ELECTRIC COMPANY
PITTSFIELD, MASS.

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}

BY J. D. McCULLOUGH AND J. D. BRITTON

RECEIVED MAY 19, 1952

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

---

(1) E. Zintl and U. Croatto, *Z. anorg. Chem.*, **242**, 79 (1939).

(2) U. Croatto, *Ricerca Sci.*, **12**, 830 (1942).

(3) U. Croatto and A. Mayer, *Gazz. chim. ital.*, **73**, 199 (1943).

(4) U. Croatto, *ibid.*, **73**, 257 (1943).

(5) U. Croatto, *ibid.*, **74**, 20 (1944).

(6) U. Croatto and M. Bruno, *ibid.*, **76**, 246 (1946).

(7) U. Croatto and M. Bruno, *Proc. Intern. Congr. Pure and Applied Chem.* (*London*), **11**, 69 (1947).

(8) U. Croatto and M. Bruno, *Gazz. chim. ital.*, **78**, 83 and 95 (1948).

(9) J. D. McCullough, THIS JOURNAL, **72**, 1386 (1950).

(10) Maria Bruno, *Ricerca Sci.*, **20**, 645 (1950).

TABLE I

LATTICE CONSTANTS FOR AIR-IGNITED SOLID SOLUTIONS OF TRIVALENT RARE EARTH OXIDES IN CERIC OXIDE

Values in parentheses are one-half the true lattice constants for the "C" form

Ce^{IV}-Sm^{III}		Ce^{IV}-Gd^{III}		Ce^{IV}-Y^{III}	
Atomic % Sm	Lattice constant, Å.	Atomic % Gd	Lattice constant, Å.	Atomic % Y	Lattice constant, Å.
0	5.411 ± 0.001	0	5.411 ± 0.001	0	5.411 ± 0.001
10.0	5.423 ± .001	9.92	5.415 ± .002	9.99	5.411 ± .002
20.0	5.433 ± .002	23.1	5.423 ± .003	25.0	5.405 ± .002
34.9	5.441 ± .002	42.8	5.432 ± .003	39.9	5.395 ± .002
49.9	5.453 ± .002	67.0	(5.428 ± .003)	60.0	(5.374 ± .003)
64.8	5.462 ± .003	83.1	(5.420 ± .003)	75.0	(5.355 ± .003)
80.0	(5.466 ± .001)			90.0	(5.324 ± .002)
90.0	(5.466 ± .002)				
100	(5.461)[a]	100	(5.407 ± .002)	100	(5.304 ± .001)

[a] Value given by Iandelli,[13] corrected to true ångstrom units and divided by 2.

use in the studies of the oxidation of praseodymium carried out by Prandtl and Rieder[11] and by Marsh.[12]

Experimental

Materials.—The starting materials used were $(NH_4)_2Ce(NO_3)_6$ (99.99%), Pr_6O_{11} (99.8%), Sm_2O_3 (99%), Gd_2O_3 (98%) and Y_2O_3 (99%). The cerium compound was a product of the G. F. Smith Chemical Co., Columbus, Ohio, and the oxides were products of the Research Chemicals Inc., Burbank, California.

Procedure.—Stock solutions of the rare earths were prepared by dissolving weighed samples of the starting materials and diluting to the desired volume. The cerium compound was dissolved in water. The oxides were ignited 2–3 hours at 850–900° before weighing and dissolved in nitric acid. Except as noted later, the general procedure was the same as that described in the earlier work.[9]

Hydrogen Reduction.—Reduction of the praseodymium–yttrium solid solutions was accomplished by heating the samples for 4 hours at 800° in a stream of pure, dry hydrogen gas. Although this treatment converts pure Pr_2O_3 to the "A" hexagonal form, the presence of only 5% Y_2O_3 stabilizes the "C" cubic form. The preparation of pure Pr_2O_3 in the "C" form may be accomplished by reducing Pr_6O_{11} in a platinum boat in a quartz tube. The heating should be done cautiously with a bunsen flame just long enough to complete the reduction which is indicated by the strong yellow color of the "C" form. Heating for too long a period or to too high a temperature causes transition to the gray-green "A" form.[13]

Air Ignition.—After decomposing the precipitated hydroxides at lower temperatures, all samples were ignited in air for approximately 5 hours at 1100–1200°. Small nickel boats were found to be satisfactory containers for the samples in the high-temperature furnace.

Oxidation of Praseodymium.—A simpler and more reliable method for the oxidation of Pr^{III} to Pr^{IV} was developed. This makes use of a heavy-wall pure silver tube (1/4" o.d., 1/8" i.d. by 8" long) closed at one end and silver soldered into a standard fitting at the other. Several samples contained in small quartz tubes may be oxidized at the same time The system is first flushed free of air by alternate evacuation and admission of oxygen from a cylinder and finally subjected to the full pressure of the cylinder at approximately 2000 p.s.i. (135 atmospheres). The silver tube is then heated to 650° for 4 hours. The tube may be quenched, or cooled slowly, as desired. The oxygen pressure should not be released, however, until the tube has cooled since otherwise PrO_2 might decompose. The newer method has the advantage of being faster, of permitting the oxidation of several samples at once and of oxidizing Pr_2O_3 when in the "A" form. The latter caused some trouble in the method previously employed.

X-Ray Diffraction.—Powder diffraction photographs of all samples were prepared after grinding in an agate mortar. Filtered copper radiation was used in a Norelco Powder Camera having a nominal radius of 5.73 cm. All lattice constants were determined by extrapolation of measurements in the back-reflection region, referred to the wave lengths $CuK_{\alpha 1} = 1.5405$ Å. and $CuK_{\alpha 2} = 1.5443$ Å.

Results and Discussion

The experimental results are given in Tables I and II. In order to simplify comparison of results, the lattice constants for all solid solutions in the "C" form have been divided by two in order to put them on the same scale as the fluorite phase lattice constants. Values resulting from this treatment are in general shown in parentheses in the tables but the dividing line between the fluorite and "C" forms is quite arbitrary.

TABLE II

LATTICE CONSTANTS FOR SOLID SOLUTIONS IN THE PRASEODYMIUM OXIDE–YTTRIUM OXIDE SYSTEMS

Values in parentheses are one-half the true lattice constants for the "C" form

Atomic % Y	Reduced in hydrogen Pr^{III}-Y^{III}	Ignited in air Pr^{IV}-Pr^{III}-Y^{III}	Heated in oxygen Pr^{IV}-Y^{III}
0	(5.570 ± 0.002)	5.468 ± 0.001	5.394 ± 0.002
5.0	(5.561 ± .003)	5.463 ± .002	
10.0	(5.545 ± .015)	5.465 ± .010	
14.9			5.398 ± .003
19.9	(5.527 ± .006)	5.448 ± .006	
30.0			5.398 ± .004
35.0	(5.480 ± .001)	5.423 ± .005	
50.0	(5.437 ± .004)	(5.395 ± .002)	(5.385 ± .005)
65.0	(5.397 ± .003)	(5.367 ± .002)	
70.0			(5.355 ± .005)
80.0	(5.358 ± .005)	(5.344 ± .003)	
85.1			(5.330 ± .003)
87.5	(5.355 ± .002)	(5.344 ± .002)	
90.0	(5.329 ± .001)	(5.327 ± .001)	
100	(5.304 ± .001)	(5.304 ± .001)	(5.304 ± .001)

One of the interesting features of the present study is the gradual and continuous change from the face-centered cubic fluorite structure shown by pure CeO_2 and PrO_2 to the "C" type body-centered cubic structure shown by the trivalent rare earth oxides. This is shown best in the systems Ce^{IV}–Y^{III} and Pr^{IV}–Y^{III}. On the diffraction photographs of samples in these systems, lines characteristic of the "C" structure appear when as little as 15 atomic per cent. of yttrium is present and gradually increase in relative intensity with increasing yttrium content. This effect is shown with decreasing tendency in going to the systems Ce^{IV}–Gd^{III} and Ce^{IV}–Sm^{III} and was not in evidence in the systems Ce^{IV}–Nd^{III} and Ce^{IV}–Pr^{III}. This indicates that ordering of the vacant anion sites re-

---

(11) W. Prandtl and G. Rieder, *Z. anorg. Chem.*, **238**, 225 (1938).

(12) J. K. Marsh, *J. Chem. Soc.*, 5 (1946).

(13) Aldo Iandelli, *Gazz. chim. ital.*, **77**, 312 (1947).

quired by the "C" structure is favored by the trivalent ions of smaller radius. The continuous transition from the fluorite structure to the "C" type M_2O_3 structure is possible because of the close similarities of the two structures.[14]

Although the previous studies indicated rather definite upper solubility limits of around 60–70 atomic per cent. of the trivalent oxides in the tetravalent oxides, only the Ce^{IV}–Gd^{III} system shows an indication of a limit in the present work. Due to tendencies toward supersaturation in this case, however, it is possible to explore the entire range of solid solutions and it is difficult to determine just where the solubility limit is.

Another point of interest is the inability of praseodymium to be oxidized beyond the tetravalent state in the Pr–Y system. This is worth noting because it was their work on this system which Prandtl and Rieder[11] offered as proof of the ability of praseodymium to be oxidized to Pr^V. This claim was later refuted by Marsh[12] and by one of the present authors.[9] The rigorous oxidizing conditions used in the present work leave little doubt about the extreme reluctance of praseodymium to be oxidized beyond the tetravalent state. It was Prandtl and Rieder's belief that the presence of Y_2O_3 should promote the oxidation of praseodymium to the pentavalent state by forming the compound $YPrO_4$. However, the present study indicated a definite increase in the difficulty of oxidizing praseodymium with increasing yttrium content.

[14] L. Pauling and M. D. Shappell, *Z. Krist.*, **75**, 138 (1930).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA AT LOS ANGELES
LOS ANGELES 24, CALIFORNIA

1,3,5,7,9-Decapentaene and 1,3,5,7,9,11,13-tetradecaheptaene

BY ALEXANDER D. MEBANE

RECEIVED APRIL 21, 1952

In the series of unsubstituted linear polyenes, $H(CH{=}CH)_nH$, the first four members are known. By application of the sodamide–liquid ammonia coupling of allylic halides[1] to pentadienyl and heptatrienyl halides, what are undoubtedly the $n = 5$ and $n = 7$ members of the series have now been prepared. Decapentaene was obtained in 5% yield as cream-colored crystals melting at *ca.* 145°; tetradecaheptaene, in minute yield, only as an impure concentrate.

The ultraviolet absorption spectra (Fig. 1) continue the series defined by those of butadiene, hexatriene[2] and octatetraene.[3] The absorption maxima of the five compounds fall on a smooth curve.[4] The "fine structure" shows a consistent increase as the series is ascended, until in decapentaene and tetradecaheptaene the longest wave length absorption peak has become the most intense one, and the spectrum is clearly approaching, as a limit, a series of equally-spaced discrete absorption "lines" of diminishing intensity. It may be recalled that the absorption spectra of the α,ω-diphenylpolyenes undergo a similar evolution as the series is ascended.[5] The separation between the individual absorption peaks, which in both series ranges from about 1350 to 1550 cm.$^{-1}$, is customarily identified with the stretching frequency of the double bond.

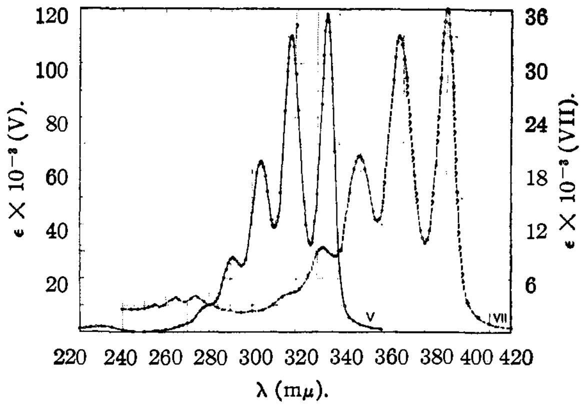

Fig. 1.—Ultraviolet absorption spectra, in "isoöctane," of: V, crystalline all-*trans*-decapentaene; VII, tetradecaheptaene concentrate.

The infrared spectrum of decapentaene (Fig. 2) closely resembles those of hexatriene[2] and octatetraene,[3] except in the extreme lowness of the 7.1-μ peak and the differing appearance of the 6.1–6.6-μ system.[6] The entire absence of the infrared *cis*-peak (14.0 ± 0.5 μ) shows that the all-*trans* stereoisomer was the one isolated in crystalline form. This conclusion was confirmed by the results of catalytic iodine treatment.

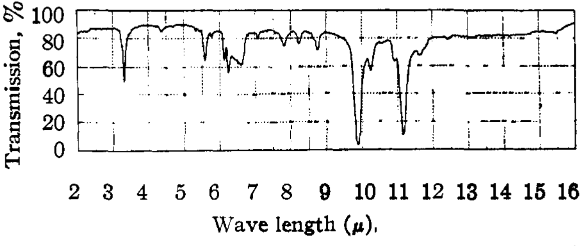

Fig. 2.—Infrared spectrum of all-*trans*-decapentaene (1.7% solutions, 0.2-mm. cell).

In the chromatographic forerun of decapentaene, a *cis*-isomer or isomers (not obtained in solid condition) appeared to be present.

The tetradecaheptaene was obviously not sterically homogeneous, since the absorption maxima at the beginning and end of the chromatographic fraction differed by more than 2 mμ. However, the highest λ_{max} obtained probably corresponds

---

[1] M. S. Kharasch and E. Sternfeld, THIS JOURNAL, **61**, 2318 (1939); M. S. Kharasch, W. Nudenberg and E. K. Fields, *ibid.*, **66**, 1276 (1944); D. R. Howton, *J. Org. Chem.*, **14**, 1 (1949).

[2] G. F. Woods and L. H. Schwartzman, THIS JOURNAL, **70**, 3394 (1948); D. R. Howton, ref. 1.

[3] G. F. Woods and L. H. Schwartzman, *ibid.*, **71**, 1396 (1949).

[4] Empirical equations for this curve will be discussed in a subsequent communication.

[5] K. W. Hausser, R. Kuhn and A. Smakula, *Z. physik. Chem.*, **29B**, 384 (1935). In this series the first peak is just reaching equality with the second by $n = 7$, the highest member studied. (The $n = 8$, $n = 11$ and $n = 15$ members of the series have been reported by Kuhn and his co-workers, but their absorption curves have apparently not been published.)

[6] Since the solutions measured had been in transit at ordinary temperatures for about 24 hours, it is probable that some polymer was present at the time the spectrum was taken.