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Polydimethylsilanes

BY CHARLES A. BURKHARD

Many publications dealing with the alkyl-substituted polysiloxanes have appeared in recent years,[1] but only very little interest has been shown in the alkyl-substituted polysilanes. An investigation of this latter type of compound has now been made. These new materials are the first alkyl-substituted polysilanes reported in which more than two silicon atoms are directly united. Hexamethyldisilane,[2] hexaethyldisilane,[2c,3] and hexa-*n*-propyldisilane[3e] have been prepared previously.

A similar investigation has been reported by Kipping[4] and co-workers in which the preparation and properties of aryl-substituted polysilanes are given. From diphenyldichlorosilane and molten sodium, Kipping was able to prepare several polydiphenylsilanes, which included a "*saturated*" $Si_4(C_6H_5)_8$ compound and a second $Si_4(C_6H_5)_8$ compound, which was reported to be an "*unsaturated*" compound. This apparent "*unsaturation*" was thought to be due to the presence of two tervalent silicon atoms in the $Si_4(C_6H_5)_8$ molecule. In addition to these materials, Kipping also isolated several $[Si(C_6H_5)_2]_n$ compounds in which n varied from approximately six to eight as determined from chemical evidence. The extreme insolubility of these compounds made it impossible to obtain molecular weights. The majority of the product obtained from the reaction of sodium with diphenyldichlorosilane was soluble in the inert hydrocarbon solvent, and on evaporation of the solvent was found to be a glue-like or resinous mass.

In contrast to these results, it has now been found that dimethyldichlorosilane reacts with molten sodium to give a major quantity of hydrocarbon-insoluble material together with a minor quantity of hydrocarbon-soluble material. Analysis of the hydrocarbon-insoluble product (I) shows it to be a polymer of $[(CH_3)_2Si]$. Its extreme insolubility has made it difficult to make accurate molecular weight determinations. However, a molecular weight was obtained ebulliometrically in biphenyl and the results indicate an average degree of polymerization of approximately 55. X-Ray powder data indicate that this material is somewhat crystalline. It is unstable thermally; in fact, if heated in air at 200° for sixteen hours, a gel-like material is produced.

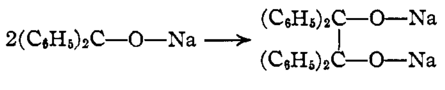
Isolation of hydrocarbon-soluble products by distillation at reduced pressure was difficult as evidenced by erratic heat-temperature readings in the column. However, it was possible to isolate a crystalline material, which when recrystallized from methanol and water, was shown by analytical and molecular weight data to be the cyclic hexamer, dodecamethylcyclohexasilane (II), $[(CH_3)_2Si]_6$.

After II was recovered, a high boiling residue (III) remained which is a grease-like solid at room temperature. Analytical data indicate that III is a copolymer of $[(CH_3)_2Si]$ and $[(CH_3)_2SiO]$ units. A small amount of chlorine is also present in this product. Analytical data indicate that on an average approximately three silicon atoms are directly united for each siloxane linkage present.

Martin[5] has reported hydrocarbon-insoluble polymers which contain both Si–Si and Si–O–Si linkages. These materials were prepared by the reaction of the methyl Grignard reagent with hexachlorodisilane followed by hydrolysis of the remaining silicon–halogen bonds. From a consideration of the method of preparation and the reported analytical data, it is seen that the polymers obtained by Martin have no more than two silicon atoms directly united and that the methyl to silicon ratio is less than two.

The blue color[4a] that develops when the arylchlorosilanes react with molten sodium is observed also when dimethyldihalogenosilanes are allowed to react with molten sodium. In both cases, the blue color is discharged by water. The development of this blue color recalls the reaction in which ketones, that are incapable of forming enols, form colored metal ketyls. For example, benzophenone reacts with sodium to form a blue derivative, which dimerizes to form a new carbon–carbon bond.[6] The blue color of the metallic ketyls is discharged by water.

$$(C_6H_5)_2CO + Na \longrightarrow (C_6H_5)_2C{-}O{-}Na \quad (1)$$



$$2(C_6H_5)_2C{-}O{-}Na \longrightarrow \begin{array}{l}(C_6H_5)_2C{-}O{-}Na\\ \quad\ \ |\\ (C_6H_5)_2C{-}O{-}Na\end{array} \quad (2)$$

From the similarity in behavior between the blue substances formed in the reaction of sodium with diorganodihalogenosilanes and the metallic

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[1] Burkhard, Rochow, Booth and Hartt, *Chem. Rev.*, **41**, 97 (1947).

[2] (a) Bygden, *Ber.*, **45**, 707 (1912); (b) Blitz and Lemke, *Z. anorg. allgem. Chem.*, **186**, 387 (1930); (c) Dolgov and Volnov, *Zhur. Obshchei Khim. Ser.*, **1**, 91 (1931); (d) Brockway and Davidson, THIS JOURNAL, **63**, 3287 (1941).

[3] (a) Friedel and Ladenburg, *Compt. rend.*, **68**, 923 (1869); (b) *Ann.*, **203**, 241 (1880); (c) *Ann. chim. phys.*, **289**, 390 (1880); (d) Kraus and Nelson, THIS JOURNAL, **56**, 195 (1934); (e) Schumb and Saffer, *ibid.*, **61**, 363 (1939).

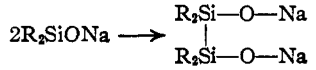
[4] (a) Kipping and Sands, *J. Chem. Soc.*, **119**, 830 (1921); (b) Kipping, *ibid.*, **123**, 2590 (1923); (c) **123**, 2598 (1923); (d) **125**, 2291 (1924); (e) 2719 (1927); (f) Kipping, *ibid.*, 2728 (1927); (g) Steele and Kipping, *ibid.*, 1431 (1928); (h) Kipping and Murray, *ibid.*, 360 (1929); (i) Kipping, Murray and Maltby, *ibid.*, 1180 (1929); (j) Kipping and Short, *ibid.*, 1029 (1930); (k) Kipping, Blackburn and Short, *ibid.*, 1290 (1931).

[5] (a) Martin, *Ber.*, **46**, 2442 (1913); (b) **46**, 3289 (1913).

[6] Bachman, THIS JOURNAL, **55**, 1179 (1933).

ketyls, it is reasonable to believe that a radical of the type $R_2Si–O–Na$ is formed which would be capable of forming Si–Si bonds by subsequent dimerization. The presence of oxygen can be explained by contact with air during the reaction or from the oxide film on the surface of the sodium.

$$R_2SiCl_2 \xrightarrow{Na + O_2} R_2Si—O—Na \qquad (3)$$



$$2R_2SiONa \longrightarrow \begin{array}{l} R_2Si—O—Na \\ \quad | \\ R_2Si—O—Na \end{array} \qquad (4)$$

Further evidence in support of the structure for this intermediate radical is given by the fact that dimethyldibromo- and dimethyldichlorosilane both react with molten sodium to give this blue color. If sodium is to be expected to form a radical with the dimethylsiloxane unit which is similar to the radical that was formed with benzophenone, it is required that the "*enol*" form of the siloxane be incapable of existence.

The formation of the "*enol*" form of the siloxane requires the simultaneous formation of a carbon–silicon double bond; however, attempts to synthesize carbon–silicon double bonds have met with failure in spite of many diligent trials.[7] Thus it is reasonable to assume that the dimethylsiloxane unit differs from its carbon analog, acetone, in that it is incapable of existing in an enolic form. Therefore, the formation of the radical $R_2Si–O–Na$ in which R is methyl or phenyl is not considered unreasonable.

Kipping[8] experienced considerable difficulty in hydrolyzing the Si–Si bonds in the polydiphenylsilanes with aqueous and alcoholic alkali. Kipping found, however, that moist piperidine would hydrolyze these materials quantitatively. In contrast I is not hydrolyzed by aqueous caustic or by moist piperidine. In order to hydrolyze this compound, it was found necessary to heat it with alkali in hexanol.

Experimental

Reaction of Dimethyldihalogenosilanes with Sodium.—As no reaction is obtained until the sodium is molten, it is necessary to use either a halogenosilane whose boiling point is greater than 98° or carry out the reaction in a sealed autoclave under elevated temperature and pressure. The products in either case appear to be the same. Dimethyldibromosilane, b. p. 112°, can be used when the reaction vessel is at atmospheric pressure; however, it was more advantageous to use dimethyldichlorosilane in a sealed autoclave.

Two preparations were made using the following charge of 1 lb. of sodium metal, from which most of the oxide film had been removed, 700 g. dimethyldichlorosilane (54.9% Cl_2) and 1 l. of dry benzene in each run. These materials were sealed in a 3 l. steel autoclave. The autoclave was heated and shaken. An exothermic reaction developed after the temperature had exceeded that of the melting point of the sodium. The pressure rose rapidly to 220 p. s. i. and the temperature to 200°. After cooling, the reaction vessel was again heated at 115° for approximately ten hours with continuous shaking. The extent of reaction as measured by titration of hydrolyzable halogen in the benzene solution was shown to vary between 95 and 99.6%.

The products were removed from the autoclave and filtered. A blue-colored residue and excess sodium were retained by the filter. The blue residue and excess sodium was added to a mixture (*ca.* 50–50) of glacial acetic acid and 95% ethanol to decompose the excess sodium. When the decomposition of the sodium had been completed, the entire mixture was added to water. By this time, the blue color had been discharged completely. The white powder, I, that formed was washed with water until free of acid and chloride ion. The resulting product was then dried at 75° *in vacuo.*

The benzene was removed from the combined filtrates leaving a solid product which yielded II on distillation. No definite boiling point of the fraction could be obtained as crystals of II formed, and the temperature was erratic. When the head temperature reached 170° at 2 mm., the distillation was stopped. A residue, III, remained which is grease-like. Products I and II are shown to be $[(CH_3)_2Si]_x$ polymers, and molecular weight determinations indicate that *x* is approximately 55 for I and 6 for II. Compound II was recrystallized from methanol and water. Using a melting point block fitted with Nicol prisms, it was observed that II shows a change of its crystal form at 74°. This change is reversible if II is not heated to a temperature which is much greater than 74°, and at 100° II appears to sublime.

Anal. Calcd. for I, C_2H_6Si: C, 41.32; H, 10.41; Si, 48.72. Found: C, 40.1, 40.4; H, 10.1, 10.2; Si, 48.0; mol. wt.,[9] *ca.* 3200.

Anal. Calcd. for II, $C_{12}H_{36}Si_6$: C, 41.32; H, 10.41; Si, 48.72; mol. wt., 348. Found: C, 40.9, 41.2, 40.7; H, 10.6, 10.4, 10.2; Si, 47.2; mol. wt.,[10] 318.

Anal. Found for III: C, 38.6, 38.1; H, 9.4, 9.2; Si, 42.8, 42.2; Cl, 2.9, 2.8; mol. wt.,[11] 1700.

The yield of I from the two runs is 412 g. The yield of II and III is 237 g.

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Summary

1. The reaction of molten sodium with dimethyldichlorosilane has been shown to give polydimethylsilanes as the major product.

2. Dodecamethylcyclohexasilane has been isolated and characterized.

3. A colored radical of the type $R_2Si–O–Na$, which appears to be similar to the metallic ketyls, is postulated as a by-product of the reaction of diorganodihalogenosilanes and sodium.

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[7] (a) Schlenk and Renning, *Ann.*, **394**, 221 (1912); (b) Kipping and Sands, *J. Chem. Soc.*, **119**, 831 (1921); (c) Kipping, *ibid.*, 104 (1927).

[8] Kipping and Sands, *ibid.*, **119**, 848 (1921). Schumb and Saffer also report that hexa-*p*-tolyldisilane and hexa-*n*-propyldisilane are stable toward hydrolysis with dilute aqueous alkali; see ref. 3e.

[9] Molecular weight determined ebulliscopically with diphenyl.

[10] Cyclohexane used in cryoscopic determination. Value obtained by extrapolation to zero concentration in four separate determinations.

[11] Molecular weight determined using cyclohexane.