Summary

Methylcyclopentane has been converted directly to benzene (and other aromatics) by simultaneous isomerization and dehydrogenation over molybdena–alumina catalyst in the presence of hydrogen. The extent of reaction is dependent on both thermodynamic conditions and length of process period.

EMERYVILLE, CALIFORNIA RECEIVED[11] MARCH 30, 1942

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[11] This manuscript was originally received on March 30, 1942, and after examination by the Editorial Board was accepted for publication in THIS JOURNAL. It was, however, referred to the National Defense Research Committee, and at their request was withheld from publication, in a confidential file, until clearance was granted on August 30, 1945.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Hydrolysis of Diphenyldichlorosilane

BY CHARLES A. BURKHARD

The hydrolysis of diphenyldichlorosilane[1] to diphenylsilanediol has been reported by several authors.[2] Depending upon the conditions under which the hydrolysis is carried out it is possible to obtain crystalline, amorphous, or oily products. The hydrolysis of diphenyldichlorosilane to polyphenylsiloxane-α,ω-diols has also been reported.[3]

The purpose of the present paper is to give a report of a study of the hydrolysis of diphenyldichlorosilane in which the direct synthesis of α,ω-diols, $HO[Si(C_6H_5)_2O]_nH$, and α,ω-dichlorides, $Cl[Si(C_6H_5)_2O]_{n-1}Si(C_6H_5)_2Cl$, in which $n \geqslant 2$, was attempted. A similar investigation has been made with dimethyldichlorosilane by Patnode,[4] in which he was able to isolate polymethyl-α,ω-dichloropolysiloxanes, $Cl[Si(CH_3)_2O]_nSi(CH_3)_2Cl$, in which $n = 1$ to 5.

Experimental

Diphenylsilanediol.[2c]—To a heterogeneous mixture of 77 ml. of toluene, 161 ml. of *t*-amyl alcohol and 666 ml. of water is added dropwise with stirring 200 g. of diphenyldichlorosilane[5] dissolved in 77 ml. of toluene. The solution is maintained at 25° with a cooling coil. About one-half hour is required for addition of the chloride, after which the solution is stirred for another ten minutes. The solution is then filtered by suction and the crystals are washed with water until free of acid and air dried. These crystals are practically free of polymeric materials. Further purification may be effected by crystallization from warm methyl ethyl ketone and chloroform; yield 156 g., 93%, m. p. 148° dec.

Anal. Calcd. for $C_{12}H_{12}SiO_2$: C, 66.62; H, 5.59; Si, 12.96; OH/molecule, 2.00. Found: C, 66.2; H, 5.34; Si, 13.1; OH/molecule, 1.95.

Hexaphenylcyclotrisiloxane.[6]—Ten grams of diphenylsilanediol is dissolved in 150 ml. of ether and 5 ml. of concd. hydrochloric acid is added. After heating under reflux for three hours, the ether is removed and the crystals are collected. Flat plates are obtained from benzene and ethanol, or glacial acetic acid; m. p. 190°, b. p. 290–300° (1 mm.).

Anal. Calcd. for $C_{36}H_{30}Si_3O_3$: C, 72.68; H, 5.09, Si, 14.16; mol. wt., 595. Found: C, 73.4; H, 5.18; Si, 14.0; mol. wt. (benzene), 567, (ethylene dibromide), 540.

Octaphenylcyclotetrasiloxane.[6]—A drop or two of aqueous caustic is added to a boiling solution of diphenylsilanediol in 95% ethanol. On cooling, the tetramer precipitates. When recrystallized from benzene and ethanol, or glacial acetic acid, needles are obtained; m. p. 201–202°, b. p. 330–340° (1 mm.).

Anal. Calcd. for $C_{48}H_{40}Si_4O_4$: C, 72.68; H, 5.09; Si, 14.16; mol. wt., 793. Found: C, 73.2; H, 5.29; Si, 14.2; mol. wt. (benzene), 810, (ethylene dibromide), 802.

Partial Hydrolysis of Diphenyldichlorosilane

Part A. Ratio of 2:1 and 1.5:1.—Four moles (1012 g.) of diphenyldichlorosilane was dissolved in 1000 ml. of ether. To this was added dropwise with vigorous stirring two moles (36 g.) of water in 400 ml. of dioxane. After complete addition of the water–dioxane solution, hydrogen chloride was blown off with dry nitrogen. The ether and dioxane were removed by distillation and the residue distilled under vacuum using dry nitrogen as an inert atmosphere. The fractions obtained in the vacuum distillation are tabulated in Table I.

TABLE I

Cut	Press., mm.	*T*, °C.	Wt., g.	% Cl	Remarks
1	44–45	175–210	285	22.9	Fluid
2	1	120–190	18	19.4	Fluid
3	1	220–256	202	13.3	Fluid
4	1	256–290	70	8.2	Crystallized
5	1	280–305	63	6.3	Crystallized
6	1	300–340	66	6.8	Viscous liquid
Residue	...	.....	...	5.8	Glassy

Cuts 1 and 2 were impure diphenyldichlorosilane. Cut 3 was combined with cuts of the same boiling range from other hydrolyses and redistilled. The majority boiled at 238–241° (1 mm.). The tetraphenyl-1,3-dichlorodisiloxane which was thus isolated was purified by crystallization from hexane to give waxy hexagonal rods; m. p. 38°, b. p. 238–241° (1 mm.).

Anal. Calcd. for $C_{24}H_{20}Si_2OCl_2$: Cl, 15.72. Found: Cl, 15.3.

Hexaphenyl-1,5-dichlorotrisiloxane was isolated from cut 5 boiling at 290–303° (1 mm.). Considerable hexaphenylcyclotrisiloxane was also found in this boiling range but, by extracting with *n*-heptane, separation of the dichloride from the cyclic polymer was effected. Attempts

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[1] A discussion of the nomenclature used in this paper is given by Sauer (*J. Chem. Ed.*, **21**, 303 (1944)).

[2] (a) Dilthey and Eduardoff, *Ber.*, **37**, 1139 (1904); (b) Martin, *ibid.*, **45**, 403 (1912); (c) Kipping, *J. Chem. Soc.*, **101**, 2108 (1912); (d) Kipping and Robinson, *ibid.*, **105**, 487 (1914); (e) Hyde and DeLong, THIS JOURNAL, **63**, 1194 (1941).

[3] (a) Kipping, *J. Chem. Soc.*, **101**, 2125 (1912); (b) Kipping and Robinson, *ibid.*, **105**, 484 (1914).

[4] Patnode, THIS JOURNAL, unpublished.

[5] The diphenyldichlorosilane (27.68% Cl) was furnished by Dr. Gilliam [THIS JOURNAL, **67**, 1772 (1945)].

[6] The identities of the cyclic diphenylsilanediol condensation products, which have beeen described by Kipping,[3a] have been questioned in a recent publication.[2e] A discussion of this point is given in a later paper [Burkhard, Decker and Harker, THIS JOURNAL, **67**, 2174 (1945)].

to crystallize this compound were without success. Cut 4 also contained hexaphenylcyclotrisiloxane. The residue was subjected to a molecular distillation and was collected in four fractions of increasing viscosity. The chlorine content of these cuts was 5.4, 4.3, 4.1, and 5.2%, respectively.

When 1.5 moles of diphenyldichlorosilane per mole of water was used, the yield of tetraphenyl-1,3-dichlorodisiloxane decreased while larger yields of hexaphenyl-1,5-dichlorotrisiloxane and hexaphenylcyclotrisiloxane were obtained.

Part B. Ratio of 1:1 and 0.67:1.—The method of hydrolysis was similar to that described in Part A, except that ratios of chlorosilane to water used were 1:1 and 0.67:1. In both cases almost the theoretical quantities of hexaphenylcyclotrisiloxane were obtained. No α,ω-diols were isolated.

The occurrence of hexaphenylcyclotrisiloxane in the partial hydrolysis products would indicate that diphenylsilanediol was formed and subsequently dehydrated and polymerized through the action of hydrochloric acid. It is also conceivable that due to the steric effect of the *gem* diphenyl group the —O—Si—O— angle is reduced to a point where the formation of the cyclic trimer from the open chain intermediates (dichloro-, dihydroxy- or chlorohydroxypolysiloxanes) is facilitated.

Tetraphenyldisiloxane-1,3-diol.[3]—When tetraphenyl-1,3-dichlorodisiloxane was hydrolyzed in the same manner as was diphenyldichlorosilane, it gave the corresponding diol. The rate of hydrolysis was approximately one-eighth that observed for diphenyldichlorosilane. The reaction may be accelerated somewhat if the aqueous layer is changed several times during the hydrolysis. The diol was recrystallized from benzene and *n*-heptane; yield (from 20 g. of dichloride), 17 g., 92%, m. p. 113–114°.

Anal. Calcd. for $C_{24}H_{22}Si_2O_3$: C, 69.52; H, 5.35; Si, 13.55; OH/molecule, 2.00. Found: C, 69.9; H, 5.36; Si, 13.5; OH/molecule, 1.90.

Hexaphenyltrisiloxane-1,5-diol.[3]—Hexaphenyl-1,5-dichlorotrisiloxane was hydrolyzed to hexaphenyltrisiloxane-1,5-diol in 64% yield. The two-phase hydrolysis system was used for this hydrolysis also. The hydrolysis took two days to complete. The diol was purified by crystallizing from boiling *n*-heptane, m. p. 111°.

Anal. Calcd. for $C_{36}H_{32}Si_3O_4$: C, 70.54; H, 5.27; Si, 13.74; OH/molecule, 2.00. Found: C, 71.1; H, 5.52; Si, 13.9; OH/molecule, 2.05.

Hydrolysis of Molecular Distillation Cuts.—The two most viscous cuts of the molecular distillation were hydrolyzed in the two phase system giving non-crystalline taffy-like products.

Thermal Dehydration of Diphenylsilanediol.—Twenty grams of diphenylsilanediol was heated in a small distillation flask so that the volatile and low-molecular weight reaction products could be removed by distillation. Water was obtained as the first product and when no more could be recovered by elevating the distillation temperature, vacuum was applied and 6.3 g. of impure hexaphenylcyclotrisiloxane was obtained at 298–310° (1 mm.). At 315–330° (1 mm.) 1.3 g. of very impure hexaphenylcyclotrisiloxane was obtained. A high boiling residue weighing 7.5 g., which probably contains higher molecular weight cyclopolyphenylsiloxanes, remained.

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Summary

1. The hydrolysis of diphenyldichlorosilane in a homogeneous medium with less than one mole of water per mole of chlorosilane has been shown to yield polyphenyl-α,ω-dichloropolysiloxanes and hexaphenylcyclotrisiloxane.

2. Tetraphenyl-1,3-dichlorodisiloxane and hexaphenyl-1,5-dichlorotrisiloxane were isolated and hydrolyzed to the corresponding α,ω-diols.

3. Acids favor the formation of hexaphenylcyclotrisiloxane, while alkalies favor the formation of octaphenylcyclotetrasiloxane in the dehydration-polymerization of diphenylsilanediol.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Octaphenylcyclotetrasiloxane

BY CHARLES A. BURKHARD, BEULAH F. DECKER AND DAVID HARKER

The adequate characterization of octaphenylcyclotetrasiloxane[1] by Kipping[2] has been questioned in a recent publication.[3] As this compound has been encountered a number of times in experimental procedures, it became necessary to identify and definitely characterize it. Kipping isolated octaphenylcyclotetrasiloxane in two forms, depending on the crystallization temperature. From warm ethyl acetate or acetone he isolated long, slender, very imperfect prisms, while at ordinary temperatures either well-defined, almost rectangular, plates or long, well-defined prisms were obtained, m. p. 200–201°. The crystals obtained from cold ethyl acetate became opaque on being warmed to temperatures less than 100°. Using the well-defined, almost rectangular plates Kipping[2b] found that the crystals belong to the triclinic (anorthic) system; subclass, holohedral; $a:b:c::0.5614:1:0.5770$; $\alpha = 83°56'$, $\beta = 103°52'$, $\gamma = 96°44'$.

Hyde and DeLong report, on the other hand, that the compound which Kipping reported as the tetramer, octaphenylcyclotetrasiloxane, is in reality the trimer, hexaphenylcyclotrisiloxane. In both cases cryoscopic data are used, together with other data, to identify the polymer. Kipping found molecular weights of 685, 674, and 669 in

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[1] A discussion of the nomenclature used in this paper has been given by Sauer [*J. Chem. Ed.*, **21**, 303 (1944)].

[2] (a) Kipping, *J. Chem. Soc.*, **101**, 2138 (1912); (b) Kipping, *ibid.*, **105**, 499 (1914).

[3] Hyde and DeLong, THIS JOURNAL, **63**, 1194 (1941).