[Contribution from the Research Laboratories of Corning Glass Works and Dow Corning Corporation]

Synthesis of Methylphenyldisiloxanes

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In connection with the development of improved high-temperature silicones comprising methylphenylsiloxane polymers, a number of low-polymer members and intermediate silanes having both methyl and phenyl substituents have been synthesized and characterized. Methylphenylethoxysilanes were obtained by one-step reactions of methylethoxysilanes with magnesium and chloro- or bromobenzene; they were converted to chlorosilanes by the action of acetyl chloride. Hydrolysis afforded silanols and symmetrical disiloxanes; the latter were employed as starting materials for the preparation of unsymmetrical disiloxanes by acid- and alkali-catalyzed redistribution processes. Unsymmetrical disiloxanes were also obtained by condensation of silanols with chloro- or ethoxysilanes and by cohydrolysis of two such silanes. Controlled partial hydrolysis in ether or *t*-butanol treatment of methylphenyldichlorosilane afforded a series of ω,ω'-dichlorosiloxanes; further mild hydrolysis of the diastereomeric dichlorodisiloxane mixture afforded two (*meso* and *dl*) crystalline disiloxanediols. Thermal tests on the disiloxanes indicate high resistance to air oxidation to 250° and a stabilization of methyl by phenyl substituents. The compounds show noticeable effects due to oxidation at 300°, siloxane disproportionation above 350°, and thermal group eliminations above 400°. Other properties are tabulated.

Organosilicon compounds in which the silicon atoms are bonded to carbon of both methyl and phenyl groups are of fundamental importance because a variety of silicone fluids and resins are formulated from them. The published data for these compounds have been limited in comparison with that for compounds and polymers which are predominantly methyl-substituted. Low-polymer methylphenylsiloxanes, in particular, are of special interest because of their applications as stable heat transfer media in the 200–300° range and as actuating fluids in condensation pumps for producing high vacuum.[3]

The first methylphenylsilicon compounds to be described in the literature are methyltriphenylsilane[4] and trimethylphenylsilane.[5] The first methylphenylsiloxane was the disiloxane $(Ph_2MeSi)_2O$ (VII), which was shown to be the dehydration product of methyldiphenylsilanol.[6] The disiloxane $(PhMe_2Si)_2O$ (III)[7,13–15] and several methylphenyl-substituted trisiloxanes,[7–9] cyclosiloxanes[7,10] and polysiloxanes[11,12] have also been described.

The purpose of the present paper is to assemble a group of important low-molecular methylphenylsilicon compounds, including several unsymmetrically substituted disiloxanes which have been described briefly in patents.[13–15] The formulas and physical data for these and several related compounds are listed in Table I. In describing the new compounds, a variety of procedures by which they have been prepared and other chemical behavior are presented.

Both methylphenylchlorosilanes and methylphenylethoxysilanes were employed as intermediates for preparations of silanols and siloxanes in the present work and also in the development of methylphenyl silicone polymers. The ethoxysilanes are readily separated from each other by rectification and are conveniently prepared in the laboratory by one-step Barbier reactions. One phenylation procedure consisted of adding bromobenzene to a mixture of magnesium and the methylethoxysilane in diethyl ether, while another consisted of refluxing a solution of an excess of chlorobenzene with the required amount of ester and magnesium. The chlorosilanes $PhMe_2SiCl$ and $Ph_2MeSiCl$ were obtained in high yield from the corresponding ethoxysilanes by the action of acetyl chloride.

The hexamethyl-[16,17] and *sym*-tetramethyldiphenyldisiloxanes,[7,14a] employed as intermediates for other siloxanes in this work, were prepared by hydrolyzing trimethyl- and dimethylphenylchlorosilanes, respectively, and also by hydrolyzing the corresponding ethoxysilanes under mild acid conditions. Methyldiphenyl- and triphenylsilanols were obtained under similar mild conditions from the corresponding chloro- and ethoxysilanes, but were condensed to the symmetrical dimethyltetraphenyl-[3,6] and hexaphenyl-[18] disiloxanes under stronger acid or alkaline conditions. The unsymmetrical disiloxanes were prepared under various given sets of conditions by three general methods: (1) by cohydrolysis and condensation[13a–b,14a] of two chloro- or ethoxysilanes, (2) by equilibration of mixtures of symmetrical disiloxanes, catalyzed either by a strong acid[9,13b–c,19,20] or alkali,[7,11c,13b,15] and (3) by condensation[13a,14a,9] of silanols with chloro- or ethoxysilanes. The third method has an advantage of frequently favoring higher yields of the unsymmetrical disiloxane. A fourth method, which favors formation of unsymmetrical disiloxanes in still higher yields, consists of condensing

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(1) Dow Corning Corporation.

(2) Corning Glass Works.

(3) M. J. Hunter, U. S. Patent 2,530,356 (1950).

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(5) A. Bygden, *Ber.*, **45**, 707 (1912); *Z. physik. Chem.*, **90**, 246 (1915).

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(16) W. H. Daudt, U. S. Patent 2,386,441 (1945).

(17) R. O. Sauer, This Journal, **66**, 1707 (1944).

(18) (a) F. S. Kipping and L. L. Lloyd, *J. Chem. Soc.*, **79**, 449 (1901); (b) F. S. Kipping and A. G. Murray, *ibid.*, **132**, 360 (1929); (c) C. A. Kraus and W. K. Nelson, This Journal, **56**, 195 (1934).

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TABLE I: PHYSICAL AND ANALYTICAL DATA OF METHYLPHENYLSILOXANES AND INTERMEDIATE SILANES

No.	Compound Formula	M.p., °C.	B.p. (°C.) at 740–760 mm.	B.p. (°C.) at low p.	mm.	η_{25} (cstks.)	SIC (1 kc.) (25°)	d^{25}_4 (vac.)	$n^{25}D$	Sp. refraction[c] Calcd.	Sp. refraction[c] Found	Si, % Calcd.	Si, % Found		Cl, OH, % Calcd.	Cl, OH, % Found	
I	$Me_3SiOSiMe_3$	−67	98.5			0.65	2.22	0.756	1.3730	0.301	0.301	34.6	34.8	34.6			
II	$PhMe_2SiOSiMe_3$	< −80	206	93	16	1.5	2.53	.891	1.4588	.306	.307	25.0	24.9	24.9			
III	$PhMe_2SiOSiPhMe_2$	< −80	292	165	17	3.4	2.75	.971	1.5149	.309	.309	19.6	19.5	19.5			
IV	$Ph_2MeSiOSiMe_3$	(pour pt.) −65	285	129	3.5	4.9	2.77	.974	1.5166	.309	.310	19.6	19.4	19.4			
V	$Ph_2MeSiOSiPhMe_2$	(pour pt.) −45	364	189	5	13.0	2.85	1.031	1.5549	.311	.311	16.1	16.1	16.2			
VI	$Ph_3SiOSiMe_3$	51	349	232	7	46[a]	[b]	1.032[a]	1.5587[a]	.311	.313[a]	16.1	16.3	15.9			
VII	$Ph_2MeSiOSiPh_2Me$	50	418	180	0.1	94[a]	3.0[b]	1.076[a]	1.5866[a]	.312	.312[a]	13.7	13.7	13.6			
VIII	$Ph_3SiOSiPhMe_2$	50	415	231	4	151[a]		1.076[a]	1.5843[a]	.312	.311[a]	13.7	13.8	13.8			
IX	$Ph_3SiOSiPh_2Me$	76	466	250	3	11,000[a]		1.112[a]	1.6124[a]	.313	.313[a]	11.9	12.0	11.9			
X	$Ph_3SiOSiPh_3$	226	494						1.59, 1.68, 1.71			10.5	10.5				
XI	$(PhCH_3)_2SiOSiMe_3$	37		224	6	24[a]	2.95[b]	1.018[a]	1.5540[a]	.313	.315[a]	14.4	14.3				
XII	$PhMe_2SiOSiMe_2OSiMe_3$	< −80	233	117	4	2.0	2.35	.911	1.4450	.293	.292	28.2	28.0	27.7			
XIII	$PhMe_2SiOSiMe_2OSiPhMe_2$	(pour pt.) −75	307	178	13	3.9	2.7	.975	1.4913	.297	.297	23.4	23.3	22.6			
XIV	$PhMeClSiOSiPhMeCl$			154	4			1.153	1.5318	.268	.269	17.2	17.0	17.0	Cl, 21.7	21.8	21.4
XV	$PhMeClSiOSiPhMeOSiPhMeCl$			188–191	1			1.153	1.5375	.272	.271	18.2	18.4	18.6	Cl, 15.3	14.7	14.8
XVI	$PhMeClSi[OSiPhMe]_2OSiPhMeCl$			231–233	1			1.155	1.5411	.275	.272	18.7	19.0	19.1	Cl, 11.8	11.2	11.8
XVII	$PhMeSi(OH)OSiPhMe(OH)$ "A"	111										19.3	19.1		OH, 11.7	11.4	11.3
XVIII	$PhMeSi(OH)OSiPhMe(OH)$ "B"	84										19.3	19.3		OH, 11.7	11.7	
XIX	$PhMe_2SiOEt$		197	87.5	17	1.3		.923[20]	1.4809[20]	.308	.308	15.6	15.6				
XX	$PhMeSi(OEt)_2$		218	112	18	1.6		.962[20]	1.4678[20]	.290	.289	13.0	13.1				
XXI	$Ph_2MeSiOEt$		291	171	16	4.9		1.018[20]	1.5440[20]	.311	.310	11.6	11.6				
XXII	Ph_3SiOEt	63		225	17							9.22	9.29				
XXIII	$PhMe_2SiCl$		191	79	15	1.35		1.032[20]	1.5082[20]	.291	.289				Cl, 20.8	20.6	
XVIV	$Ph_2MeSiCl$		295	176	25	5.2		1.110[20]	1.5740[20]	.299	.297				Cl, 15.2	14.9	15.1
XXV	$Ph_2MeSiOH$			184–187	24	198	3.81	1.084	1.5777	.307	.306	13.1	13.3		OH, 7.9	8.0	

[a] Values on supercooled liquids. [b] SIC increases with orientation during measurement. [c] Calculated from bond refraction data of Warrick, THIS JOURNAL, 68, 2455 (1946).

chlorosilanes with alkali metal salts of silanols[14b]; this will be described in another paper.

Inspection of Table I reveals how the physical and analytical properties of the different reported compounds vary according to the number and disposition of the methyl and phenyl substituents; data for hexamethyl- and hexaphenyldisiloxanes are included for comparison. Resistance of the individual methylphenyldisiloxanes toward air oxidation at elevated temperatures is indicated by air-blowing tests.[23] Traces of oxidation products are produced when the compounds are heated in contact with air above 250°. Consequently, their stability to oxidation is comparable to that reported recently for polymethylphenylsiloxanes[21] and considerably greater than that for polymethylsiloxanes, which show evidence of oxidation at 175–200°.[22] However, they are less stable than hexaphenyldisiloxane, which air-oxidizes slowly above 300°. These results indicate that the methyl group is more susceptible to oxidation scission than the phenyl group and that the former is stabilized by presence of the latter. This stabilizing action is also indicated in mixtures of dimethylsiloxane polymer fluids with minor proportions of dissolved methylphenylsiloxanes.[23] One benzylmethyldisiloxane (XI) was prepared and found to be highly susceptible to air oxidation of its benzyl groups above 150°.

The symmetrical dimethyltetraphenyldisiloxane (VII) and hexaphenyldisiloxane are stable to 400° in the absence of air, but above this temperature they resinify with attendant loss of benzene and hydrogen. The unsymmetrically substituted methylphenyldisiloxanes disproportionate slowly above 350° in the absence of catalyst, and at lower temperatures in contact with traces of alkali.

Controlled partial hydrolysis in ether[24] or *t*-butanol treatment of methylphenyldichlorosilane[7,11a] afforded a series of ω,ω′-dichlorosiloxanes (XIV–XVI), of which each member is probably a diastereomeric mixture. A further mild hydrolysis of the dichlorodisiloxane member (XIV) gave two (*meso* and *dl*) crystalline 1,3-dimethyl-1,3-diphenyldisiloxanediols (XVII and XVIII). One of these is found to be isomorphous with a previously reported crystalline 1,3-diethyl-1,3-diphenyldisiloxanediol.[25]

Experimental Part

Dimethylphenylethoxysilane (XIX).—A small quantity of Grignard reagent, prepared in a test-tube by heating magnesium with a few drops of bromobenzene in chlorobenzene, was added as a primer to a refluxing mixture of 225 g. (2.0 moles) of chlorobenzene, 334 g. (2.3 moles) of dimethyldiethoxysilane and 48.6 g. (2.0 moles) of magnesium turnings. The mixture was then held under reflux for seven to ten hours, when the magnesium had reacted and precipitation of the ethoxychloride was complete. The liquid product was most conveniently separated from the salt by strip-distilling to 150° (25 mm.), with reduced pressure applied after removing low-boiling compounds to 145° (atm. pressure). The salt was porous and actually promoted even boiling. Redistillation through a 2-ft. column

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[21] C. M. Murphy, C. E. Saunders and D. C. Smith, *Ind. Eng. Chem.*, **42**, 2462 (1950).

[22] D. C. Atkins, C. M. Murphy and C. E. Saunders, *ibid.*, **39**, 1395 (1947).

[23] W. H. Daudt, U. S. Patent 2,468,869 (1949).

[24] C. A. Burkhard, THIS JOURNAL, **67**, 2173 (1945).

[25] R. Robison and F. S. Kipping, *J. Chem. Soc.*, **101**, 2156 (1912).

afforded 50 g. of unreacted dimethyldiethoxysilane, 152 g. (42%) of dimethylphenylethoxysilane, b.p. 87.5° (17 mm.), and higher-boiling material from which small amounts of biphenyl, dimethyldiphenylsilane,[6] b.p. 160° (18 mm.) and *p*-terphenyl were identified. It is preferable that the reactants be mixed initially; for, in another run in which chlorobenzene was added slowly to the other reactants with stirring under reflux, the magnesium and salts became coated with an oily complex which arrested the reaction.

Dimethylphenylethoxysilane was also prepared in 51% yield from dimethyldiethoxysilane by a Barbier reaction, in which bromobenzene was added dropwise to a stirred mixture of magnesium turnings and the diethoxysilane in an equal volume of diethyl ether. When the volume of ether was substantially less, the magnesium became coated with an oily complex.

Addition of an excess (112 g.) of acetyl chloride to 45.1 g. (0.25 mole) of dimethylphenylethoxysilane caused warming for several hours. After standing four days, the mixture was distilled, affording the excess of acetyl chloride, ethyl acetate, and 395 g. (93%) of **dimethylphenylchlorosilane**[7] **(XXIII)**, b.p. 189–191° (739 mm.). Hydrolysis of this chlorosilane, or of the ethoxysilane with a trace of hydrochloric acid, afforded **tetramethyl-1,3-diphenyldisiloxane** (III),[7,14a] b.p. 162–162.5° (13 mm.), in yields exceeding 90%. When the ethoxysilane was hydrolyzed with acid amounting to more than 10 mole per cent. that of the silane, or when the chlorosilane hydrolyzate was refluxed with 20% hydrochloric acid to complete hydroxyl group condensation, some phenyl group hydrolysis occurred, giving rise to higher-boiling compounds, from which **hexamethyl-1,5-diphenyltrisiloxane (XIII)**,[13b] b.p. 178° (13 mm.), was fractionated.

Prolonged treatment of the disiloxane at room temperature with a stream of hydrogen chloride formed dimethylphenylchlorosilane (31%), benzene (20%), products of dephenylation and aqueous hydrochloric acid; when this reaction was promoted by the presence of anhydrous zinc chloride, an increased yield (48%) of dimethylphenylchlorosilane was obtained. Refluxing of the disiloxane in air for 300 hours at 290–295°, or air-blowing treatment at 255° for 122 hours, gave faint traces of phenol and formaldehyde and left the disiloxane essentially unchanged. When the disiloxane was heated at 425° in a pressure autoclave, benzene and hydrogen were split out, with formation of compounds of higher molecular weight.

Methylphenyldiethoxysilane[26] **(XX)**, b.p. 112° (18 mm.), and **methyldiphenylethoxysilane (XXI)**, b.p. 171° (16 mm.), were prepared together in one-step reactions of methyltriethoxysilane and magnesium with either chlorobenzene or bromobenzene, by procedures analogous to those given above for dimethylphenylethoxysilane. Treatment of 118.5 g. of methyldiphenylethoxysilane with an excess (177 g.) of acetyl chloride formed 110 g. (97%) of **methyldiphenylchlorosilane (XXIV)**,[6] b.p. 175–176° (24 mm.). Hydrolysis of this chlorosilane or of the corresponding ethoxysilane with dilute acid, afforded principally **methyldiphenylsilanol (XXV)**,[6] b.p. 184–187° (24 mm.). Hydrolysis of the ethoxysilane with 10% aqueous hydrochloric acid, or heating the mild hydrolysis product with either constant-boiling hydrochloric acid or with a small amount of powdered sodium hydroxide at 100°, condensed the silanol to **1,3-dimethyltetraphenyldisiloxane** (VII),[3,6] which was conveniently recrystallized in high yield as plates from hexamethyldisiloxane.

Air-blowing treatment of the disiloxane VII at 255–260° for 123 hours produced only minute traces of formaldehyde and phenol, which were detected in an attached cold trap. The sample recrystallized on cooling; it then showed only a slightly depressed melting range (45.5–47°) and unchanged silicon content (found 13.8, 13.6% Si). However, similar treatment at 305–310° produced small amounts of benzene, phenol and formaldehyde and converted the sample into a highly viscous red oil having a 1.6% higher silicon content. In the absence of air, the disiloxane underwent negligible change below 360°, but it disproportionated into benzene, hydrogen, and a hard amber thermoplastic resin when held 90 hours at 420–450°.

Triphenylethoxysilane (XXII), b.p. 225° (17 mm.), m.p. 63°, was prepared together with phenyltriethoxysilane,[26a,27] biphenyl, diphenyldiethoxysilane,[28] *p*-terphenyl, tetraphenylsilane,[18a,29] and other high-boiling compounds by refluxing ethyl silicate with chlorobenzene and magnesium. **Triphenylsilanol**[4,18a,29] was prepared by mild hydrolysis of triphenylethoxysilane in presence of a trace of hydrochloric acid, and also from triphenylchlorosilane.[4,18a] **Hexaphenyldisiloxane**[18] **(X)**, m. p. 225–226°, obtained from the silanol by treatment with a small amount of sodium hydroxide in alcohol, is more resistant to high temperature air oxidation than any of the methylphenylsiloxanes. It was essentially unchanged with prolonged air-blowing up to 305°, where it emitted only a faint trace of phenol. Under reflux, at 475–480°, benzene and hydrogen were split out slowly, leaving a brittle thermoplastic resin after ten hours.

1,1,3-Trimethyltriphenyldisiloxane (V).[14a]—A mixture of 62.4 g. (0.26 mole) of methyldiphenylethoxysilane and 195 g. (1.08 moles) of dimethylphenylethoxysilane was hydrolyzed by addition of 24 ml. of 20% hydrochloric acid in an equal volume of ethanol. The washed product (analysis found 2.1% OH and 1.0% OEt) was distilled from 0.2 g. of sodium hydroxide to complete condensation (found 0.2% OH). Fractional distillation afforded 110 g. of **tetramethyl-1,3-diphenyldisiloxane** (III),[7,14a] b.p. 129–130° (3.0 mm.) and 140° (5 mm.); 60 g. (67% yield) of the trimethyltriphenyldisiloxane (V), b.p. 188.5–189.5° (5 mm.); and a small quantity of 1,3-dimethyltetraphenyldisiloxane (VII),[3,6] which crystallized from the residue.

Air-blowing treatment of the disiloxane V above 250° caused slight discoloration and gave vapors of formaldehyde, phenol and benzene. The viscosity of the compound increased from 12 cstks. to only 13 cstks./25° after 120 hours of air-blowing treatment at 255–260°. After an additional sixty hours at 300–305°, the viscosity rose to 53 cstks. and the silicon content showed a 0.5% Si increase (found 16.60, 16.54% Si). When heated under nitrogen for 168 hours under reflux at 364–368°, there was partial disproportionation into the symmetrical disiloxanes; traces of hydrogen and benzene were identified in a connected Dry Ice trap.

Pentamethylphenyldisiloxane (II).[13b–c,14a]—To 143.2 g. (0.5 mole) of a technical grade of tetramethyl-1,3-diphenylsiloxane (III), containing about 10% of hexamethyl-1,5-diphenyltrisiloxane[13b] (XIII) and 81.2 g. (0.5 mole) of hexamethyldisiloxane was added 1.35 g. of powdered 83% potassium hydroxide. The mixture was heated under reflux for 90 hours, during which time most of the caustic was in solution and the boiling temperature increased from 122 to 146°. It was then washed neutral with dilute hydrochloric acid, ammonia and water. Distillation afforded, in addition to some of the starting siloxanes, 2.0 g. of octamethyltrisiloxane, b.p. 50–52° (17–20 mm.); 64.1 g. (0.37 mole) of pentamethylphenyldisiloxane (II), b.p. 87.5–90.5° (14.15 mm.); and 4.2 g. (0.04 mole) of **heptamethyl-1-phenyltrisiloxane** (XII),[13b] b.p. 117–118° (14 mm.).

Pentamethylphenyldisiloxane was also prepared readily by equilibration at room temperature of the disiloxane mixture (1) upon standing 16 hours with alcoholic potassium hydroxide,[13b,15] (2) upon treatment with hydrochloric acid in ether solution,[13b–c,20] and (3) by stirring with 1% of concentrated sulfuric acid[9,13b–c,19] in the absence of solvent. It was also obtained by a dilute hydrochloric acid-catalyzed cohydrolysis of trimethylethoxysilane[17,30] and dimethylphenylethoxysilane.

This compound showed no change in viscosity or composition upon long standing, or upon blowing with a constant stream of air for 1000 hours while under reflux. However, it disproportionated to hexamethyldisiloxane (I) and tetramethyl-1,3-diphenyldisiloxane (III) on long refluxing in the presence of a trace of a sodium hydroxide or upon standing with alcoholic potassium hydroxide, or in hydrogen chloride-saturated ether solution.

Tetramethyl-1,1-diphenyldisiloxane (IV)[15a] was prepared from 75 g. (2.83 moles) of 1,3-dimethyltetraphenyldisiloxane (VII) and an excess (175 g.) of hexamethyldisiloxane.

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(26) (a) R. F. Fleming, U. S. Patent 2,386,452 (1945); (b) R. O. Sauer and E. M. Hadsell, THIS JOURNAL, **70**, 3590 (1948).

(27) E. Khotinsky and B. Seregenkoff, *Ber.*, **41**, 2946 (1908); M. N. Kalinin, *Compt. rend. acad. sci. U. R. S. S.*, **26**, (No. 4), 368 (1940).

(28) F. S. Kipping and A. G. Murray, *J. Chem. Soc.*, **130**, 2734 (1927).

(29) A. Polis, *Ber.*, **18**, 1540 (1885); F. S. Kipping and J. F. Short, *J. Chem. Soc.*, 1029 (1930).

(30) W. H. Daudt, U. S. Patent 2,390,518 (1945).

There was little reaction when the mixture was first stirred 120 hours at 50° with 0.6 g. of sodium hydroxide in 10 g. of ethanol, as most of the disiloxane crystallized on cooling. However, the siloxane interchange was effected when 7.8 g. of sodium hydroxide in 77 g. of 96% ethanol was employed as catalyst and the mixture was held under reflux for one week. Water was next added dropwise until the mixture became cloudy and two additional hours of refluxing served to hydrolyze and to condense the alkali salts in solution. Distillation of 204 g. of the water-washed reaction product afforded 127 g. of hexamethyldisiloxane (I), b.p. 98–98.5°; 71 g. (83%) of tetramethyl-1,1-diphenyldisiloxane (IV), b.p. 124.5–125° (2.5 mm.); and 6 g. of residue from which 1.1 g. of the starting dimethyltetraphenyldisiloxane crystallized. Equilibration in this experiment was probably nearly complete in less than two days, for then the solid disiloxane no longer crystallized on cooling from solution.

The disiloxane IV showed no change when refluxed over a flame and under nitrogen for 300 hours at 285–290°. A similar treatment in contact with air caused a slow evolution of formaldehyde and phenol, an amber discoloration, and a viscosity increase from 4.5 to 5.5 cstks. at 25°. The disiloxane was not attacked until heated above 250°. A sample which was held 120 hours at 255 to 260° while a constant stream of air was passing through it was found to emit traces of formaldehyde and benzene, which were identified in the attached Dry Ice trap. This sample showed a viscosity increase of only 1.1 cstks. at 25° and an unchanged silicon content. That no siloxane disproportionation occurred in any of the above experiments was indicated by the absence of hexamethyldisiloxane in the attached cold traps, and by no significant (less than 0.3%) change in silicon content. However, heating at 250–300° in the presence of a trace of powdered sodium hydroxide effected rapid disproportionation into the symmetrical disiloxanes (I and VII).

1,1,1-Trimethyltriphenyldisiloxane (VI).[13a,14a]—To a large excess (400 g.) of trimethylethoxysilane[17,30] was added 5 ml. of 36% aqueous hydrochloric acid, followed by 28.1 g. (0.10 mole) of triphenylsilanol, m.p. 150–151°. The mixture was warmed until the silanol crystals had dissolved and was allowed to stand 16 hours. Water was next added to hydrolyze the ethoxysilane. Distillation of the washed product afforded 228 g. of hexamethyldisiloxane, b.p. 98–99°, followed by 34.1 g. (96.5%) of liquid 1,1,1-trimethyltriphenyldisiloxane, b.p. 232° (27 mm.), which crystallized on standing, m.p. 49.5–51°. Recrystallization from ethanol gave elongated prisms, m.p. 50.5–51.5°. A 0.56-g. pot residue also crystallized on cooling and was recrystallized from benzene as stout prisms of **hexaphenyldisiloxane (X)**,[18] m.p. 224–225°, showing no melting depression with a sample obtained from condensation of triphenylsilanol.

When 1,1,1-trimethyltriphenyldisiloxane was heated under nitrogen and under reflux (at 350–370°), it was found to disproportionate to the hexamethyl- and hexaphenyldisiloxanes. When submitted to air-blowing treatment at 250–300°, it exhibited a behavior similar to that of its isomer (V). The melting point was depressed only 3° after 120 hours air-blowing treatment at 255–260°. However, after 60 hours air-blowing at 300–305°, the disiloxane no longer crystallized and the product was a liquid η_{25} 50 cstks.

1,1-Dimethyltetraphenyldisiloxane (VIII).[13a]—To 180.3 g. (1.0 mole) of dimethylphenylethoxysilane was added 1.0 g. of 50% aqueous sodium hydroxide, which disperses as a soluble salt and serves as a condensation catalyst. The resulting solution was heated to 110° and to it was then added 55.2 g. (0.20 mole) of triphenylsilanol in 0.3 to 0.5 g. portions in two hours, during which time some ethanol was distilled. After heating the mixture for an additional one-half hour at 110–115°, 8.0 g. of water was introduced; ethanol then distilled rapidly as the excess ethoxysilane was hydrolyzed. The mixture was heated overnight at 90–115°, taken into ether and neutralized with dilute acetic acid. The solid product was filtered, rinsed with petroleum ether and methanol, and identified as **hexaphenyldisiloxane (X)**,[18] m.p. 223–224°; yield 17.7 g. (33%). Recrystallization from chlorobenzene afforded 17.1 g. of prisms, m.p. 225–226°.

The washed, dried and concentrated filtrate (145 g.) afforded 95 g. of **tetramethyl-1,3-diphenyldisiloxane (III)**, b.p. 290–295° (737 mm.), and 37.7 g. (46%) of **1,1-dimethyltetraphenyldisiloxane**, b.p. 230–232° (4 mm.). The latter crystallized on standing and was recrystallized from ethanol–ethyl acetate as tabular, hexagonal prisms, m.p. 49–49.5°.

Methylpentaphenyldisiloxane (IX).[13a]—A mixture of 6.9 g. (0.025 mole) of triphenylsilanol and 23.3 g. (0.100 mole) of methyldiphenylchlorosilane in an equal volume of diethyl ether was allowed to condense by standing ten days at room temperature. The excess chlorosilane was hydrolyzed largely to methyldiphenylsilanol by washing with water; the concentrated product (found 4.0% OH) was soluble in methanol and deposited on chilling a trace of triphenylsilanol. The mixture was then heated overnight at 80–90° with 0.10 g. of sodium hydroxide to give a completely condensed product. (*Anal.* Found: 0.0% OH). Crystallization from petroleum ether afforded 0.53 g. of hexaphenyldisiloxane (X). Distillation of the filtrate at 3 mm. afforded 15 g. of a mixture, b.p. 190–210°, from which 1,3-dimethyltetraphenyldisiloxane crystallized; and 8.7 g. of another mixture, b.p. 220–255°, from which 3.2 g. (27%) of the desired methylpentaphenylsiloxane crystallized as prisms. Two recrystallizations from methanol–petroleum ether gave prisms melting sharply at 75–76°.

Methylpentaphenyldisiloxane was also prepared by a sodium hydroxide-catalyzed cohydrolysis of triphenylethoxysilane and methyldiphenylethoxysilane.[13a]

1,1,1-Tribenzyltrimethyldisiloxane (XI).[14a]—A 2.30-g. sample of tribenzylchlorosilane, m.p. 140–142°, was cohydrolyzed with a large excess (34 g.) of trimethylethoxysilane by the addition of 36% aqueous hydrochloric acid in small portions, followed by an excess of water. A small amount of **hexabenzyldisiloxane**[31] was filtered and recrystallized from benzene–ethanol as needles, m.p. 201.5–202.5°. Hexamethyldisiloxane was next distilled at 98–100°; the rest of the product distilled at 213–214° (25 mm.) and crystallized on chilling, m.p. 33.7–35.5°. Recrystallization from methanol–petroleum ether affords long prismatic needles, m.p. 36.8–37.2°, of the tribenzyltrimethyldisiloxane. Both the latter compound and hexabenzyldisiloxane suffer ready oxidation of benzyl groups forming benzaldehyde and benzoic acid, when heated in air above 150°.

1,3-Dimethyl-1,3-diphenyldichlorodisiloxane (XIV), 1,3,5-Trimethyl-1,3,5-triphenyldichlorotrisiloxane (XV) and 1,3,5,7-Tetramethyl-1,3,5,7-tetraphenyldichlorotetrasiloxane (XVI).—To 386 g. (2.02 moles) of methylphenyldichlorosilane[7,11a] in an equal weight of diethyl ether, 18.44 g. (1.02 mole) of water was added dropwise during four hours with stirring. Fractional distillation afforded 21% (81 g.) of the starting silane, 32% of the disiloxane XIV, 1.7% of 2,4,6-trimethyltriphenylcyclotrisiloxane,[7,10] 25% of the linear trisiloxane (XV), 2% of 2,4,6,8-tetramethyltetraphenylcyclotetrasiloxane,[7,10] 7% of the linear tetrasiloxane (XVI), 4% of crude 1,3,5,7,9-pentamethyl-1,3,5,7,9-pentaphenyldichloropentasiloxane (with b.p. about 247° (1 mm.)), 4% of a crude 1,3,5,7,9,11-hexamethyl-1,3,5,7,9,11-hexaphenyldichlorohexasiloxane (with b.p. about 272° (1 mm.)) and 4% of a 365 cstk./25° liquid residue of higher ω,ω'-dichlorosiloxanes (found: Cl, 7.0; Si, 20.1).

Preparation of the above-described lower dichlorosiloxanes requires homogeneous reaction conditions, which are afforded by the ether or some other mutual solvent. In a similar run without solvent, there was obtained a higher recovery (45%) of the silane, only 8% of distillable chlorosiloxanes (including a 2% yield of the disiloxane XIV, isolated), and 47% of a liquid residue, viscosity 485 cstks./25°, comprising a mixture of higher chlorosiloxanes (*Anal.* Found: Cl, 5.75; Si, 20.6). Thus, under heterogeneous conditions, there appears to be an effective excess of water in the reaction zone and any lower dichlorosiloxanes initially formed are favorably situated for further hydrolysis.

The lower ω,ω'-dichlorosiloxanes were also prepared by adding *t*-butanol dropwise to methylphenyldichlorosilane. In this reaction both *t*-butyl chloride and hydrogen chloride are principal by-products; small amounts of polyisobutylenes and benzene also form.

meso- **and** *dl*-**1,3-Dimethyl-1,3-diphenyldisiloxanediols (XVII and XVIII)**.—Mild hydrolysis of 40 g. of the dichlorodisiloxane XIV in 200 ml. of ether was effected by shaking

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[31] G. Martin and F. S. Kipping, *J. Chem. Soc.*, **95**, 302 (1909); A. R. Steele and F. S. Kipping, *ibid.*, **131**, 1431 (1928).

with chilled 10% aqueous ammonia, and followed by immediate washing and distillation of solvent; yield 33.4 g. of a greasy solid, m.p. 70–75° with previous softening (*Anal.* Found: OH, 9.16). Recrystallization from 35–60° petroleum ether afforded 21.9 g. of a dry crystalline mixture, m.p. 79–84° (found: OH, 10.94), which was fractionally crystallized with the use of petroleum ether and of hexamethyldisiloxane containing small amounts of acetone or ethanol. There was obtained 7.8 g. of the first compound "A," as long needles with m.p. 110–111°; and 3 g. of poorly defined crystals of an isomeric compound "B," m.p. 82–84°. X-Ray powder diffraction patterns show a dissimilarity of structure between these two materials. However, compound "A" is isomorphous with and apparently structurally similar to a crystalline 1,3-diethyl-1,3-diphenyldisiloxanediol, m.p. 86–86.5°,[25] prepared in a similar manner.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OSAKA UNIVERSITY]

Dichroisms of Benzene Rings. I. The Dichroisms of Hexamethylbenzene and Hexabromomethylbenzene

BY KAZUO NAKAMOTO

The dichroisms of hexamethylbenzene and hexabromomethylbenzene, the crystal structures of which had been perfectly determined by X-ray analysis, were measured by the microscopic method. In both the cases, remarkable dichroisms were observed; the absorption for the polarized light whose electric vector vibrates parallel to the benzene ring was always more bathochromic and hyperchromic than the absorption for the light polarized perpendicularly to the benzene plane.

Introduction

A number of studies have been carried out regarding the absorption spectra of organic compounds in solutions, and their results are applied widely to various regions of organic chemistry. But absorption spectra in crystalline states have scarcely been observed, notwithstanding their theoretical and experimental importances.

This fact is due to technical difficulties. In order to measure the absorption of the crystal, it is necessary to get a large single crystal and polish its planes optically parallel, with thickness of $10^{-2} \sim 10^{-3}$ cm., which allows us to measure the absorption. Moreover, if the measurement of the pleochroism is required, we must polish the crystal taking its axial relations in consideration.

By this method, Krishnan and his co-workers[1,2] and Scheibe[3] have measured the dichroisms of aromatic crystals of the condensed ring system. But its application is possible only when large single crystals are obtainable.

In order to measure the absorption of ordinary compounds whose crystals are obtainable only in microcrystalline states, some special device is required. Scheibe and his collaborators[4] have measured the dichroisms of benzene and hexamethylbenzene crystals, by making use of the assemblage of its microcrystals which orientate practically parallel to each other. But to get the correct results, it is desirable to measure the pleochroism with only one single crystal. Fortunately, Tsuchida[5] has invented a new method, which enables us to make measurements of pleochroism in the visible and ultraviolet region with a single microscopic crystal easily obtainable in ordinary procedures of preparation. Many studies[6] on absorption spectra of crystals using this method have been carried out.

The present paper deals with the measurement of the dichroism in the π-electron band of the benzene ring. To make the discussions clearer and simpler, two aromatic compounds whose crystal structures had been perfectly determined by X-ray analysis were selected and their dichroisms in the ultraviolet region were quantitatively measured.

Experimental

Materials.—Hexamethylbenzene $C_6(CH_3)_6$ was recrystallized from the alcoholic solution, m.p. 164°, colorless planar crystal, triclinic system (α = 44°27′), oblique extinction, extinction angle being 44°. Hexabromomethylbenzene $C_6(CH_2Br)_6$ was prepared by the method of Beintema, Terpstra and von Weerden.[7] They were recrystallized from the ethylene bromide solution, m.p. 297°, colorless hexagonal prism, rhobohedral system, straight extinction.

Measurements.—The method of measuring the dichroism of the microcrystals has already been stated in the former reports.[5] In each case, the finest single crystal was selected under the microscope, by which the image of the crystal was enlarged and projected on the slit of a spectrograph in the eventual dichroism measurements. The extinction coefficient per mm., α, is given by the following expression

$$\alpha = \frac{0.9}{d}\log\frac{a_0}{a}$$

where d is thickness in mm. of the crystal, and a_0 and a are angles of the rotating sector for light through the crystal and the light for comparison.

Results and Discussion

(1) **Hexamethylbenzene.**—In 1934, Orelkin and Lonsdale[8] studied the crystal structure of hexamethylbenzene. In 1939, Brockway and Robertson[4] carried out its Fourier analysis again. According to their results, all the benzene rings in this crystal are parallel to the (001) plane and along this plane occurs the perfect cleavage. Microcrystals obtained from the alcoholic solution

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