154–157°, and 24.4 g. (119 mmoles, 87%) of iodobenzene, b.p. 75–77° at 25 mm. A sample of the toluene was oxidized by alkaline permanganate to benzoic acid, m.p. 120–121°.[21]

Similar reactions run on a smaller scale with ethylmagnesium bromide, phenylmagnesium bromide and phenyllithium[5] gave ethylbenzene, b.p. 134–137° (37%, characterized as 4-ethylbenzoylbenzoic acid, m.p. 121–122°, lit.[30] 122°), and biphenyl, m.p. 69–70°[21] (33% and 46%).

To a well-stirred suspension of 4.0 g. (108 mmoles) of lithium aluminum hydride in 100 ml. of ether there was added 18.0 g. (49.8 mmoles) of diphenyliodonium bromide portionwise (rapid exothermic reaction). After the addition the reaction mixture was removed from the ice-bath, stirred overnight and treated with 50 ml. of water. Distillation of the ether extract gave 1.59 g. (20.3 mmoles, 41%) of benzene, b.p. 79–81° (characterized as *o*-benzoylbenzoic acid, m.p. 126–127°, lit.[30] 127–128°), 0.20 g. (1.3 mmoles, 2.6%) of bromobenzene and 8.21 g. (40.2 mmoles, 81%) of iodobenzene. Investigation of the aqueous layer showed that less than 1% of the iodine was converted to iodide ion.

BROOKLYN 2, N. Y.

---

[30] H. W. Underwood, Jr., and W. L. Walsh, THIS JOURNAL, **57**, 940 (1935).

[CONTRIBUTION OF THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

The Hydrolysis of Methoxysilanes. Dimethylsilanediol

BY SIMON W. KANTOR

RECEIVED JANUARY 19, 1953

A new method has been found for the preparation of organo silanols. This involves the hydrolysis of the corresponding methoxysilane with distilled water which allows the isolation of unstable silanols. Dimethylsilanediol, a white crystalline solid melting at 101°, has been prepared for the first time by the hydrolysis of dimethyldimethoxysilane with distilled water. The properties of this diol are described. Trimethylmethoxysilane has also been hydrolyzed with distilled water to give the trimethylsilanol–hexamethyldisiloxane azeotrope. Methyltrimethoxysilane and phenyltrimethoxysilane have also been hydrolyzed by distilled water, but in these cases the monomeric silanetriols have not been obtained. Instead, water and alcohol soluble materials have been obtained which are considered to be condensation products of the monomer.

Two general methods have been used to prepare silanols. Kipping and Hackford[1] obtained silanols R_3SiOH where the R's may be the same or different by the reaction of siloxanes with the desired Grignard reagent followed by hydrolysis of the magnesium complex. The second method, which has been used more extensively, involves hydrolysis of organochlorosilanes under carefully controlled conditions. Organosilanediols, $R_2Si(OH)_2$ where R is ethyl, *n*-propyl and *n*-butyl have been obtained in pure form by this method.[2] The failure to prepare dimethylsilanediol has been attributed to the rapid condensation of this compound even at 0°.[3] In this investigation it has been found that alkoxysilanes can be hydrolyzed by using neutral water to form silanols.

When a mixture of dimethyldimethoxysilane and excess water was heated at the boiling point, the organosilane slowly dissolved and very soon a clear solution was obtained. Evaporation of this solution at room temperature left a semi-solid which after washing with hot *n*-hexane gave the crystalline dimethylsilanediol in essentially pure form; the crystals had the appearance of white, shiny plates.

$$(CH_3)_2Si(OCH_3)_2 + 2H_2O \longrightarrow (CH_3)_2Si(OH)_2 + 2CH_3OH$$

Dimethylsilanediol is a white solid melting at 101° with condensation. Each successive fusion of the same sample lowers the melting point markedly. The diol is very sensitive to traces of acid or base, both of which condense it to polysiloxanes; the major part of the condensation product consists of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane. Dimethylsilanediol has been kept for several weeks in an evacuated glass tube in liquid nitrogen. It will not keep very well in soft glass at room temperature, presumably because there is sufficient alkali from the glass to condense it. It is important that the hydrolysis of dimethyldimethoxysilane be carried out in glass which has been acid washed followed by many rinsings with distilled water, or preferably in quartz equipment. If this precaution is neglected, condensation will occur during the evaporation forming tetramethyldisiloxanediol-1,3.[4] The properties of dimethylsilanediol are very similar to those of the higher dialkylsilanediols.[2]

Trimethylmethoxysilane was also hydrolyzed with hot water, but in this case the trimethylsilanol–hexamethyldisiloxane azeotrope was obtained. It was not possible to carry this reaction out under any conditions which did not give the azeotrope. The use of quartz equipment which should contain a minimum of alkali did not help to stop the condensation of trimethylsilanol. Apparently prolonged heating at 100° will slowly condense trimethylsilanol to hexamethyldisiloxane.

When methyltrimethoxysilane was treated with hot water the hydrolysis proceeded with the formation of water soluble material along with some polymerization to a dense insoluble oil (monomethylpolysiloxane polymer, methyl-T-oil). This oil was insoluble in toluene and soluble in methanol. On heating, the methyl-T-oil condensed with loss of water to a brittle, transparent insoluble solid. The water solution obtained from the hydrolysis of methyltrimethoxysilane was unstable and slowly precipitated more T-oil on standing. Several attempts to isolate a monomeric silanetriol from the water solution have failed. Working in acid-washed glassware or even in quartz equipment has not helped in the isolation of methylsilanetriol. The water solution which is obtained from the hydrolysis of methyltrimethoxysilane probably

---

[1] F. S. Kipping and J. E. Hackford, *J. Chem. Soc.*, **99**, 138 (1911).

[2] P. D. George, L. H. Sommer and F. C. Whitmore, Paper presented before the division of Organic Chemistry, 109th Meeting, American Chemical Society, Atlantic City, April, 1946.

[3] E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 69.

[4] G. R. Lucas and R. W. Martin, THIS JOURNAL, **74**, 5225 (1952).

contains a mixture of very reactive silanols (low condensation products of the monomer) making their isolation very difficult. The evaporation of the water solution in vacuum at low temperature produced a clear gel which was partially water-soluble, toluene-insoluble and soluble in methanol.

It was anticipated that of all the silanetriols phenylsilanetriol should be the most stable. However, hydrolyses of phenyltrimethoxysilane have not produced the monomeric phenylsilanetriol. Phenyltrimethoxysilane did slowly hydrolyze with distilled water with the partial formation of a water insoluble oil. This oil was completely soluble in methanol and partially soluble in toluene. It was probably low polymers of phenylsilanetriol. On heating the oil it dehydrated very rapidly to leave a completely insoluble monophenylpolysiloxane. This insoluble polymer had the appearance of clear, shiny, brittle plates which looked like mica. The hydrolysis of phenyltrimethoxysilane in quartz equipment also failed to yield the monomeric phenylsilanetriol.

Finally, it was observed that the hydrolysis of dimethyldiethoxysilane also proceeded with the formation of dimethylsilanediol. This hydrolysis occurred more slowly than the corresponding methoxy hydrolysis and the longer heating caused condensation to polysiloxanes along with tetramethyldisiloxanediol-1,3. This result is in agreement with the observation that the hydrolysis of various silicates becomes slower the larger the alkyl group.[5]

Experimental

Organoalkoxysilanes.—They were prepared by treating the appropriate chlorosilane with the appropriate alcohol using dimethylaniline to take up the liberated hydrogen chloride. When dimethylaniline was left out, the reaction did not go to completion and the hydrogen chloride could not be completely removed from the reaction mixture by distillation. The use of dimethylaniline as hydrogen chloride acceptor was preferred to that of pyridine since in the reaction mixture dimethylaniline hydrochloride precipitated out in a lower liquid phase and was easily separated. The yields of alkoxy silanes by these methods were consistently from 50 to 80%. A typical procedure is described for the preparation of dimethyldimethoxysilane.

To a stirred solution of 645 g. (5 moles) of dimethyldichlorosilane and 606 g. (5 moles) of dimethylaniline was gradually added a solution of 641 g. (20 moles) of methyl alcohol and 631 g. (5.2 moles) of dimethylaniline. The exit end of the addition tube was below the level of the reaction mixture and the addition was maintained at a rate that caused gentle refluxing. When all the material was added (2 hours), the mixture was refluxed for 1 hour and after cooling to room temperature, the upper layer was separated and fractionated. Dimethyldimethoxysilane, b.p. 80–80.5° (reported b.p. 81.7–82.2°),[6] was isolated in pure state; yield 40–50%.

Anal. Calcd. for $C_4H_{12}SiO_2$: C, 39.97; H, 10.07. Found: C, 39.6; H, 10.6.

In addition, there was also obtained a methanol–dimethyldimethoxysilane azeotrope, b.p. 59.5–60.5°. This azeotrope was broken with *n*-hexane to give the methanol–*n*-hexane azeotrope, b.p. 47–48°, along with more dimethyldimethoxysilane (total yield 60–70%).

Trimethylmethoxysilane, b.p. 55° (reported b.p. 57°),[7] was prepared by treating trimethylchlorosilane and methanol in the presence of dimethylaniline. There was also obtained the methanol–trimethylmethoxysilane azeotrope, b.p. 47.5°.

Methyltrimethoxysilane, b.p. 103–103.5° (reported b.p. 102.8–103.8°)[6] was prepared by treating trimethylchlorosilane and methanol either in the presence of pyridine or dimethylaniline. In this case the methanol–methyltrimethoxysilane azeotrope, b.p. 47.5°, also was obtained.

Phenyltrimethoxysilane,[8] b.p. 130° at 45 mm., $n^{20}D$ 1.4736, was prepared from 2 moles of phenyltrichlorosilane and 6 moles of methanol in ether using pyridine as the hydrogen chloride acceptor. In this case an excess of methanol was not used, thereby avoiding the formation of any azeotrope and the solid pyridine hydrochloride precipitated. The yield of purified product was 52%.

Anal. Calcd. for $C_9H_{14}SiO_3$: C, 54.51; H, 7.12; Si, 14.17. Found: C, 54.4; H, 6.6; Si, 13.9.

Hydrolysis of Dimethyldimethoxysilane. Dimethylsilanediol.—A mixture of 10 g. of dimethyldimethoxysilane and 40 ml. of distilled water was heated at refluxing temperature in a flask and condenser that had been thoroughly washed with cleaning solution and distilled water. No boiling stone was used and the mixture was constantly shaken to prevent bumping. After 10 minutes, a clear solution was obtained which was cooled immediately to room temperature. This solution was placed in a clean crystallizing dish and allowed to evaporate at room temperature with a current of dry nitrogen passing over the surface. A semi-solid residue was obtained which was washed twice with 50-ml. portions of hot *n*-hexane leaving the insoluble dimethylsilanediol (5–6 g., 65–78%) in essentially pure form. The crystals were boiled for three minutes with 40 ml. of *n*-hexane and after filtering the hot mixture the insoluble solid was rapidly transferred to a glass tube and dried *in vacuo*. Dimethylsilanediol melted at 100–101° with previous shrinking at 96°.

Anal. Calcd. for $C_2H_8SiO_2$: C, 27.07; H, 8.75; Si, 30.45. Found: C, 26.5, 26.2; H, 8.7, 8.8; Si, 29.6, 30.3.

An active hydrogen determination by the lithium aluminum hydride method[9] gave 2.2 active H/molecule.

Dimethylsilanediol is extremely sensitive to traces of acids or alkali. For example, an aqueous solution of dimethylsilanediol precipitated polymeric oils by the addition of traces of hydrochloric acid, sodium hydroxide, sodium carbonate, sodium bicarbonate, or ammonia. Even the trace of alkali that is usually present in soft or Pyrex glass equipment, was sufficient slowly to condense dimethylsilanediol.

The infrared spectrum of dimethylsilanediol was taken in a Nujol mull with a Perkin–Elmer recording spectrophotometer. The spectrum shows absorption maxima at 3.20 μ (O–H), 7.92 and 7.97 μ (Si–CH_3), 8.53, 9.42 μ (Si–O), 10.55, 11.47 and 12.68 μ (Si–C). This spectrum is very similar to that of tetramethyldisiloxanediol-1,3. This siloxanediol shows absorption bands at 3.08 μ (O–H), 7.94 μ (Si–CH_3), 9.70 μ (Si–O), 11.12, 11.60, 12.33 μ (Si–C) and 12.73 μ. The strong bands at 3.40, 3.50, 6.83 and 7.24 μ in both of these spectra are C–H absorption obtained with the Nujol. The shift in the O–H frequency to 3.20 μ for dimethylsilanediol is indicative of the large amount of interaction and hydrogen bonding present in this compound. A trialkylsilanol such as trimethylsilanol has an O–H vibration which occurs at 3.07 μ while the tetramethyldisiloxanediol-1,3, O–H band is at 3.10 μ.

In another hydrolysis, the aqueous solution obtained after hydrolyzing dimethyldimethoxysilane was distilled *in vacuo* removing the water at room temperature. When about two-thirds of the water had been taken off, an oily layer separated. The distillation was continued until most of the water had been removed. The residue was dissolved in 125 ml. of *n*-hexane and the resulting solution was distilled to remove all the water as the hexane–water azeotrope keeping the volume constant by adding more hexane. When the distillate became clear, the residue was cooled in an ice-bath precipitating long needles of tetramethyldisiloxanediol-1,3, m.p. and mixed m.p. 65.5 to 66°,[4] after one recrystallization from *n*-hexane. The melting point of a sample of tetramethyldisiloxane-diol-1,3 was depressed to 44–49° upon admixture with an authentic sample of dimethylsilanediol.

---

(5) L. Galimberti, *Ann. chim. applicata*, **38**, 55 (1948).

(6) W. Simpson, Brit. Patent 635,726 (April 12, 1950).

(7) R. O. Sauer, THIS JOURNAL, **66**, 1709 (1944).

(8) J. R. Ladd and C. Kamienski of this Laboratory carried out this experiment.

(9) F. A. Hochstein, THIS JOURNAL, **71**, 305 (1949).

Hydrolysis of Trimethylmethoxysilane. Trimethylsilanol.—A mixture of 10 g. of trimethylmethoxysilane and 40 ml. of water was refluxed for two hours using acid-washed equipment as indicated above. After cooling, the organic layer was extracted with 50 ml. of ether and the resulting ether solution was dried over sodium sulfate and distilled. There was obtained the trimethylsilanol–hexamethyldisiloxane azeotrope as the sole product, b.p. 89–90°, $n^{20}\text{D}$ 1.3790 (reported b.p. 90°, $n^{20}\text{D}$ 1.3800).[7] This azeotrope contains 33 to 35% silanol. Several hydrolyses of trimethylmethoxysilane were carried out with water in quartz equipment, but in each case the same azeotrope was obtained. The use of a solvent such as dioxane or methanol to dissolve the methoxysilane prior to hydrolysis did not stop the condensation to hexamethyldisiloxane.

Hydrolysis of Methyltrimethoxysilane.—A mixture of 10 g. of methyltrimethoxysilane and 40 ml. of distilled water was refluxed using acid-washed equipment. The upper layer of alkoxysilane slowly went into solution. After 15 minutes of refluxing, the aqueous solution became cloudy and slowly an oil precipitated. A total of 20 minutes was needed to dissolve the upper organic layer but during the last 5 minutes approximately 1 cc. of heavy oil had settled to the bottom of the flask. The mixture was cooled and filtered to remove most of the oil. Although the filtrate was kept cold to minimize condensation, nevertheless, more oil slowly precipitated. The water-insoluble oil was soluble in methanol and insoluble in toluene. On heating the oil lost water to give a clear hard and brittle solid which was extremely thermally stable. The aqueous solution precipitated a gel either upon acidification with hydrochloric acid or basification with sodium hydroxide. The aqueous solution was evaporated *in vacuo* to leave a clear gel which was partially water soluble and completely methanol soluble. The evaporation of several drops of the methanol solution on a glass plate in an oven at 150° gave a brittle, crazed, clear residue. No crystalline solid was isolated from the water solution of the hydrolysis products which possibly included the monomeric trimethylsilanetriol but certainly included lower polymers therefrom. Several hydrolyses of methyltrimethoxysilane using quartz equipment failed to yield the monomeric trimethylsilanetriol.

Hydrolysis of Phenyltrimethoxysilane.—A mixture of 5 g. of phenyltrimethoxysilane and 50 ml. of distilled water was refluxed for about 0.5 hour in a quartz r.b. flask using a quartz water-cooled condenser. Most of the alkoxysilane dissolved and a milky solution was obtained. The solution was cooled immediately and filtered, but the filtrate, which at first was clear, slowly precipitated a viscous oil. This oil was both benzene and alcohol soluble. A benzene solution of the oil continually precipitated some solid indicating that further condensation was taking place. The benzene solution was evaporated to dryness to leave a sticky solid which was soluble in benzene and methanol. On heating this solid lost more water and gave a shiny, white, brittle, mica-like solid (a monophenylpolysiloxane, phenyl-T-polymer). On standing in air, the oil slowly dehydrated and became less soluble. On heating the oil, water was driven out and the same phenyl-T-polymer was obtained. This solid was insoluble in water, methanol or benzene, and was extremely thermally stable.

The aqueous solution obtained from the hydrolysis of phenyltrimethoxysilane was rapidly evaporated to dryness under vacuum. In this case a solid residue was obtained which was insoluble in water indicating that condensation occurred during the evaporation. However, this residue was soluble in benzene and in methanol. On heating the solid turned to a liquid with considerable loss in water and finally the brittle phenyl-T-polymer was obtained.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

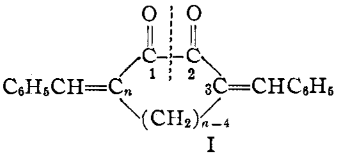
The Ultraviolet Absorption Spectra of Dibenzylidene-1,2-cycloalkanediones

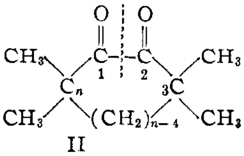
BY NELSON J. LEONARD AND GENE C. ROBINSON[1]

RECEIVED DECEMBER 15, 1952

A number of 3,*n*-dibenzylidene-1,2-cycloalkanediones (*n* = ring size = 7, 9, 10, 11) have been made and their ultraviolet absorption spectra have been determined, along with that of the open-chain analog, cinnamil. Although the cyclic system with varying ring size permits variation in the angle between the planes of the carbonyl groups, the absorption spectra of the cyclic molecules studied were found to be strikingly similar.

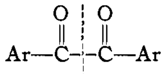
The present investigation represents a continuation of studies in this Laboratory[2–4] on the 1,2-dicarbonyl chromophore and constitutes the spectral examination of a series of 3,*n*-dibenzylidene-1,2-cycloalkanediones (I, *n* = size of ring). This particular system I was selected for synthesis and absorption spectrum determination because it provided the possibility of varying the angle between the planes of the carbonyl groups by varying the ring size, and thus of following the effect of such variation on the ultraviolet absorbing unit which consists effectively of coupled cinnamoyl groups.

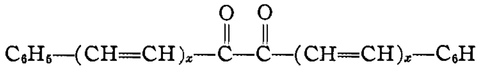

I


II

(a, *n* = 6; b, *n* = 7; c, *n* = 8; d, *n* = 9; e, *n* = 10; f, *n* = 11)

It has been shown previously, in a study of the 3,3,*n*,*n*-tetramethyl-1,2-cycloalkanediones II,[4] that the wave length of the dicarbonyl ultraviolet absorption maximum varies in a regular way with the angle between the planes of the carbonyl groups: the band moves toward shorter wave lengths as the intercarbonyl angle increases from 0° (*cis* coplanarity) to about 90° (insulation) and shifts back again toward longer wave lengths as the angle increases beyond 90°. It has also been shown, in studies of substituted benzils III, that the main contribution to the ultraviolet absorption results from the benzoyl groupings which constitute the halves of the molecule, wherein the phenyl and carbonyl groups are coplanar.[2] With increasing hindrance


III



$$C_6H_5\text{—}(CH{=}CH)_x\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{O}{\|}}{C}\text{—}(CH{=}CH)_x\text{—}C_6H_5$$

IV

(a, *x* = 1; b, *x* = 2; c, *x* = 3; d, *x* = 4)

---

[1] Monsanto Chemical Company Fellow, 1951–1952.

[2] N. J. Leonard, R. T. Rapala, H. L. Herzog and E. R. Blout, THIS JOURNAL, **71**, 2997 (1949).

[3] N. J. Leonard and E. R. Blout, *ibid.*, **72**, 484 (1950).

[4] N. J. Leonard and P. M. Mader, *ibid.*, **72**, 5388 (1950).