Found (dried room temperature *in vacuo*): C, 61.6; H, 7.5; dried at 80° *in vacuo:* C, 63.6; H, 7.4; OCH_3, 32.0, 32.1.

The free base regenerated from the hydrochloride crystallized with difficulty from methylene chloride–hexane only after most of the solvent had evaporated, m.p. 122°, $[\alpha]_D$ 120° (chloroform)[5], $\lambda_{max}^{C_2H_5OH}$ 218 (37,800), 280–282 (15,100), and 302 (14,400).

Anal. Calcd. for $C_{21}H_{25}O_4N$: C, 71.0; H, 7.1. Found: C, 70.6; H, 7.3.

Acknowledgment. We are grateful to Dr. E. Schlittler for his continued interest and encouragement and to Mr. E. Solook, Developmental Research, for carrying out the extraction for us. We are indebted to Hofmann La Roche Inc. for the gift of the papaverine used in this work.

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Some Properties and Reactions of Phenylacetoxysilanes

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Although a number of papers,[2–9] have appeared on organoacetoxysilanes, few have dealt with phenylacetoxysilanes.

In the present paper, the authors wish to report on some properties and reactions of both diphenyldiacetoxysilane and phenyltriacetoxysilane.

Each acetoxysilane was obtained as an acicular crystal at room temperature; concentrated solutions of these acetoxysilanes were found to have a marked tendency of supercooling.

The x-ray powder pattern data and the infrared spectra data for the purified sample are also given.

Diphenyldiacetoxysilane undergoes reactions with diphenyldichlorosilane and with dipotassiumdiphenylsilanolate producing diphenylpolysiloxane.

TABLE I

X-RAY POWDER PATTERN DATA[a] AND INFRARED SPECTRA DATA OF ACETOXYSILANES IN CARBON TETRACHLORIDE

d, kx	I/I_0	Positions of Band, Cm.$^{-1}$	Int.	Assignment[10,11]
		$(C_6H_5)_2Si(OCOCH_3)_2$		
7.38	1.00	1750	S	C═O
5.99	0.09	1730	M	
5.19	0.50	1600	W	
4.90	0.05	1540	W	
4.62	0.31	1440	M	Si-Phenyl
4.44	0.03	1380	M	CH_3—C
4.23	0.25	1300	W	
3.92	0.25	1250	S	C—O—
3.68	0.03	1220	S	C—O—
3.47	0.03	1190	W	
3.28	0.15	1135	M	Si-Phenyl
3.12	0.02	1125	M	Si-Phenyl
2.99	0.03	1050	W	
2.88	0.06	1020	M	Si—O—C
2.68	0.05	995	W	
2.51	0.03	940	M	Monosubstituted benzene
2.44	0.03	695	M	
2.38	0.05			
2.25	0.03			
2.11	0.06			
2.73	0.09			
		$C_6H_5Si(OCOCH_3)_3$		
5.95	0.11	1750	S	C═O
5.57	0.11	1720	M	
5.19	0.11	1590	W	
4.40	0.10	1540	W	
4.19	0.20	1440	M	Si-Phenyl
4.11	0.10	1375	M	CH_3—C
3.85	0.30	1295	W	
3.68	0.10	1260	M	C—O—
3.55	0.20	1210	S	
3.44	1.00	1135	M	Si-Phenyl
3.34	0.21	1110	W	
2.90	0.26	1045	W	
2.76	0.25	1015	M	Si—O—C
2.72	0.10	995	W	
		940	M	
		690	W	Monosubstituted benzene

[a] Cu Kα radiation filtered by Ni was used to obtain the powder diffraction data; d = interplanar spacing; I/I_0 = relative intensity.

Stoichiometry supports the following equations;

$$(C_6H_5)_2Si(OCOCH_3)_2 + (C_6H_5)_2SiCl_2 \longrightarrow {}^2/_3[(C_6H_5)_2SiO]_3 + 2CH_3COCl \text{ and}$$

$$(C_6H_5)_2Si(OCOCH_3)_2 + (C_6H_5)_2Si(OK)_2 \longrightarrow {}^2/_3[(C_6H_5)_2SiO]_3 + 2CH_3COOK$$

The reaction with gaseous ammonia was also investigated and corresponding silanols were obtained in each case.

EXPERIMENTAL

Preparation and some properties of diphenyldiacetoxysilane and Phenyltriacetoxysilane. Diphenyldiacetoxysilane was prepared by the method of Schuyten, by the reaction of

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anhydrous sodium acetate with diphenyldichlorosilane in diethyl ether with a yield of 68.4% (mean).

A concentrated solution of freshly prepared diphenyldiacetoxysilane was easily supercooled to 0°, and vigorous stirring or shaking with or without seeding resulted in an exothermic crystallization, producing an acicular crystal. Further purification was effected by recrystallization from diethyl ether, and a large prismatic crystal was obtained thereby.

The product melted at 66.8–67.0° (uncorrected), and contained 37.8% acetoxy groups (calcd. acetoxy groups: 39.3%), and its density determined indirectly by suspending a clean crystal specimen in aqueous calcium of matched density was 1.2740 (at 13°).

Phenyltriacetoxysilane melting at 29°[12] (uncorrected) and containing 61.2% acetoxy groups was obtained similarly.

The x-ray powder pattern data and the infrared absorption spectra data for these acetoxysilanes were recorded satisfactorily. They are listed in Table I.

These acetoxysilanes dissolved readily and endothermically in a variety of organic solvents but not in aliphatic hydrocarbons such as *n*-hexane, heptane, octane, and ligroin.

Some reactions of diphenyldiacetoxysilane. I. Hydrolysis. Neutralization of an ethanolic solution containing 30 g. (0.1 mole) of diphenyldiacetoxysilane, with 0.1N aqueous sodium hydroxide gave a white precipitate from which 20 g. (92%) of pure diphenylsilanediol was obtained by recrystallization from methyl acetate.

Another hydrolysis made at refluxing temperature without adding the alkali solution gave a crude mixture of diphenylsilanediol and hexaphenylcyclotrisiloxane as product.

II. *Reaction with diphenyldichlorosilane.* Addition of 25 g. (0.1 mole) of diphenyldichlorosilane to a refluxing solution containing 30 g. (0.1 mole) of diphenyldiacetoxysilane and 200 ml. of methyl acetate as diluent, gave crude crystalline material after 90 hr. of heating. Recrystallization of the above product yielded 24 g. (44%) of hexaphenylcyclotrisiloxane melting at 187–188°.

III. *Reaction with dipotassium diphenylsilanolate.* Addition of 30 g. (0.1 mole) of dipotassium diphenylsilanolate dissolved in 150 ml. of ethanol to a stirred solution containing 30 g. (0.1 mole) of diphenyldiacetoxysilane and 300 ml. of methyl acetate gave potassium acetate as a white precipitate. After 10 min. of refluxing the precipitate was removed by filtration. Usual treatment of the filtrate gave 33 g. of mixture of hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane.

IV. *Reaction with gaseous ammonia.* When gaseous ammonia, produced from concentrated aqueous ammonia upon heating, was bubbled into a flask in which 40 g. (0.14 mole) of phenyltriacetoxysilane and 400 ml. of diethyl ether had been placed, a white precipitate was formed gradually and after the formation of precipitate was complete, the resultant mixture was filtered by suction. After the filtrate was concentrated to about 100 ml. under reduced pressure, 500 ml. of purified *n*-hexane was added.

On evaporating the mixture under vacuum in a clean quartz crystallizing dish, there appeared characteristic shiny platelets mixed with a slightly colored oily product. The oily product was removed by filtration from the mixture and the platelets were washed with *n*-hexane and then with cold water. The x-ray powder pattern[13] and infrared spectra[14] for the product were identical with those of phenylsilanetriol.

Anal. Calcd. for $C_6H_8SiO_3$: C, 46.13; H, 5.10; Si, 17.98; OH/molecule, 3.00. Found: C, 45.7; H, 5.0; Si, 18.6; OH/molecule, 2.9.

The powdered sample melted at 127–129°. Recrystallization from methyl acetate-hexane always led to the loss of most of the sample unless the temperature was kept below 10°.

Many runs under modified conditions were always accompanied by formation of oily condensation products together with phenylsilanetriol, the yield of which did not exceed 15%. A similar procedure with diphenyldiacetoxysilane as sample gave diphenylsilanediol almost quantitatively.

With phenylsilanetriol, another attempt which involved direct hydrolysis of phenyltriacetoxysilane in a buffer solution also failed to obtain phenylsilanetriol because of its extreme instability.

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Derivatives of 2-Amino-1,3-propanediol

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Some time ago Pfeiffer and co-workers[2] demonstrated the central nervous system stimulating effect of 2-dimethylaminoethanol—a compound believed to be a precursor of acetylcholine.

As part of an investigation dealing with central nervous system active materials it seemed of interest to prepare ethanolamines—preferably substituted by hydrophilic as well as aromatic moieties—which might act as acetylcholine precursors or, alternately, as antagonists.

Our major effort was directed toward the synthesis of derivatives of 2-amino-1,3-propanediol. The following reaction sequence was explored and carried to completion in the case of the diethylaminoethyl derivative (IV. $R'' = R''' = C_2H_5$).

Condensation of tris(hydroxymethyl)nitromethane with a number of aldehydes and ketones led to the hydroxymethylnitrodioxane (I).[3] The ketals derived from acetone and cyclohexane proved to be most suitable for subsequent reactions. The *n*-butyraldehyde condensation product could be separated into its two isomers melting at 32–33° and 100–101°, respectively.[4]

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