search, and to it we express our gratitude. We are indebted to the Texas Research Laboratories, Beacon, New York, for the gas chromatographic and ultraviolet analyses. Roy S. Anderson did the experiments responsible for the assignment of the *trans* configuration to the 2-pentenal.

The Rearrangement of α-Silyl Ketones with Alkoxides

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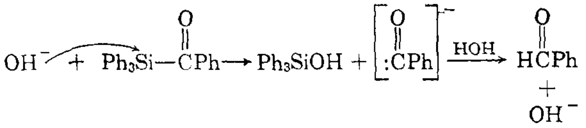
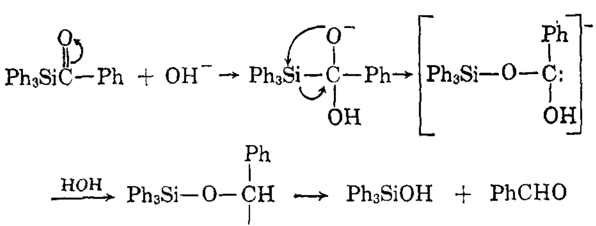
Treatment of a variety of benzoylsilanes and acetyltriphenylsilane with simple sodium alkoxides leads to two competing reactions—rearrangement of the ketone to a dialkoxysilane involving the migration of a phenyl or methyl group from silicon to carbon, and displacement of the acyl group from silicon to give an alkoxysilane and aldehyde. The polarity of the solvent appears to play an important role in determining the ratio in which these two competing reactions occur.

It has been reported that benzoyltriphenylsilane (I), a typical α-silyl ketone, is cleaved at room temperature by dilute aqueous alcoholic alkali into triphenylsilanol and benzaldehyde.[1] This reaction is readily explained, based on the great susceptibility of silicon to nucleophilic attack, as attack by hydroxide ion on silicon followed by elimination of benzoyl anion, which yields benzaldehyde on reaction with the solvent.



$$OH^- + Ph_3Si{-}\overset{O}{\overset{\|}{C}}Ph \rightarrow Ph_3SiOH + \left[:\overset{O}{\overset{\|}{C}}Ph\right]^- \xrightarrow{HOH} H\overset{O}{\overset{\|}{C}}Ph + OH^-$$

However an alternative scheme can also explain the formation of the products. Spectral data[2] have established that the carbonyl group in α-silyl ketones is highly polarized (absorption at 6.18 μ in the infrared, comparable to an enolized β-diketone) and hence the possibility of nucleophilic attack by hydroxide ion on the carbon of the carbonyl group cannot be neglected.



$$Ph_3Si\overset{O}{\overset{\|}{C}}{-}Ph + OH^- \rightarrow Ph_3Si{-}\underset{OH}{\overset{O^-}{C}}{-}Ph \rightarrow \left[Ph_3Si{-}O{-}\underset{OH}{\overset{Ph}{C}}:\right]^- \xrightarrow{HOH} Ph_3Si{-}O{-}\underset{OH}{\overset{Ph}{CH}} \rightarrow Ph_3SiOH + PhCHO$$

The product of such an attack would be an α-alkoxide. Since alkoxides from α-silylcarbinols have been shown to rearrange readily to the isomeric silyl ethers by intramolecular attack on silicon with displacement of carbon,[3-5] a similar rearrangement in this case would lead, after reaction of the carbanion with solvent, to the triphenylsilylhemiacetal of benzaldehyde, which would hydrolyze to the observed products during work-up. While the mode of attack on the ketone might be established by using ketone labelled with O^{18}, it seemed likely that the two mechanisms could be distinguished by using ethoxide ion in place of hydroxide, since in the first case triphenylethoxysilane, a known compound, would be the product, whereas in the second case the product would be expected to be the ethyltriphenylsilylacetal of benzaldehyde, which might be isolable.

When the reaction between sodium ethoxide and benzoyltriphenylsilane in benzene–ethanol was carried out, the yellow color of the ketone disappeared and the main product isolated was benzhydryloxyethoxydiphenylsilane (VI) together with smaller amounts of triphenylethoxysilane (III), benzaldehyde, diphenyldiethoxysilane (VII), benzhydrol, triphenylsilanol, and diphenylsilanediol.[6] The structure of the major product clearly indicated: (a) that initial attack by ethoxide ion occurred at silicon; (b) that displacement of a phenyl group from silicon to neighboring carbon occurred; (c) that additional rearrangement occurred in which a silicon-oxygen bond was formed and a silicon-carbon bond was broken. These facts together with the other products isolated are satisfactorily explained by the reaction scheme on the following page.

Thus attack by ethoxide ion must occur on the silicon atom of benzoyltriphenylsilane (I), presumably giving rise to the pentacovalent (sp^3d) intermediate II. This intermediate either eliminates benzoyl anion yielding ethoxytriphenyl-(III) and benzaldehyde (or some triphenylsilanol by hydrolysis of III during work-up) or else undergoes rearrangement. Which path predominates seems to depend in part at least on the polarity of the solvent as will be discussed later. If rearrange-

[1] A. G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957).

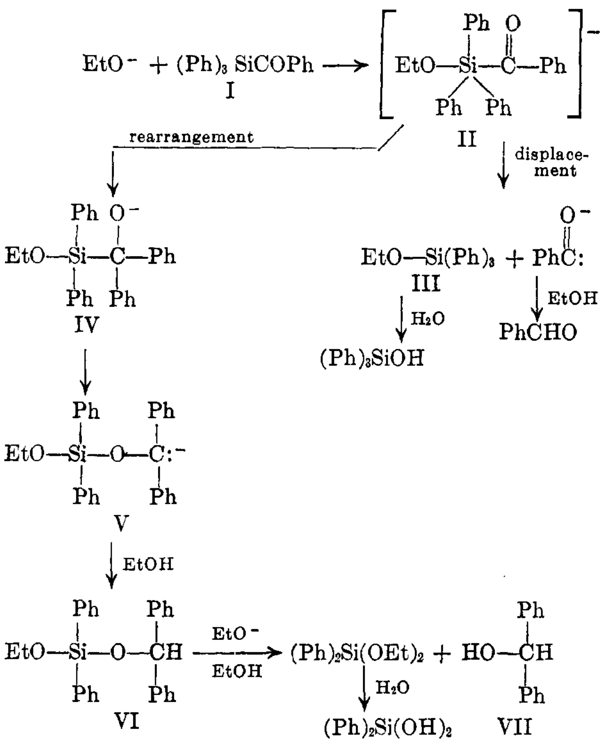
[2] A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *ibid.*, **82**, 5102 (1960).

[3] A. G. Brook, *ibid.*, **80**, 1886 (1958).

[4] A. G. Brook, C. M. Warner, and M. E. McGriskin, *ibid.*, **81**, 981 (1959).

[5] A. G. Brook and Bruno Iachia, *ibid.*, **83**, 827 (1961).

[6] A. G. Brook, *J. Org. Chem.*, **25**, 1072 (1960).



ment occurs, migration of a phenyl group from silicon to adjacent carbon gives the alkoxide ion IV which rearranges further *via* carbanion V to give the observed product benzhydryloxyethoxydiphenylsilane (VI). Quite conceivably the migration and rearrangement of the alkoxide ion could be concerted. Under some conditions VI is readily susceptible to further attack by ethoxide ion displacing benzhydrol and yielding diphenyldiethoxysilane (VII) (or some diphenylsilanediol by partial hydrolysis during work-up). Comparable reaction schemes account satisfactorily for the products obtained from five different ketones and four different alkoxides. The details of these reactions are given in Table I.

It seemed worthwhile to investigate the effect of alkoxide ions on silylketones having some or all of the phenyl groups attached to silicon replaced by methyl groups. On the basis of the meager evidence available, displacement of alkyl groups from silicon to carbon would not be anticipated. Thus Eaborn and Jeffrey[7] found that phenyldimethylchloromethylsilane on treatment with sodium ethoxide gave phenyldimethylethoxymethylsilane (displacement of chloride), phenyldimethylethoxysilane (displacement of chloromethyl), and other products which suggested the intermediate formation of dimethylbenzylethoxysilane, a reaction involving attack of ethoxide ion on silicon with migration of phenyl from silicon to carbon, displacing chloride. However, no evidence of methyl migration could be found in this case or in the related reaction of trimethylchloromethylsilane[8] with sodium ethoxide.

The treatment of benzoyldiphenylmethylsilane or benzoyldimethylphenylsilane with sodium ethoxide gave products comparable with those obtained from benzoyltriphenylsilane, where in each case only migration of a phenyl group was observed. However, with benzoyltrimethylsilane, where only methyl migration could occur if rearrangement was possible at all, considerable methyl migration was observed. It was found that as the number of methyl groups attached to silicon increased, the susceptibility toward further reaction with ethoxide ion of the dialkoxysilane analogous to VI increased, so that carbinols and diethoxysilanes were the main products of reaction isolated from the trimethyl- and dimethylphenylbenzoylsilanes. However, the fact that at least 65% of 1-phenylethanol was isolated in the former case plainly shows that substantial methyl migration occurred. This we believe is the first clearly authenticated case reported of alkyl group migration from silicon to carbon under conditions of nucleophilic attack although this is a well documented phenomenon with electrophilic reagents.[9] A related rearrangement involving migration of a hydride ion during attack by hydroxide ion has recently been reported.[10]

From the results with mixed phenyl-methylbenzoylsilanes there appears to be considerable preference for phenyl rather than methyl migration. This result is not surprising in view of Eaborn's work or from the known preference for aryl migration in such well studied reactions as the pinacol rearrangement,[11] which while carried out under rather different conditions nevertheless also involve migration of a group with its electrons. Further work on relative migratory aptitudes in this reaction is in progress.

Similar rearrangements to that described above also occur with acetyl- and other alkylsilylketones. Thus treatment of acetyltriphenylsilane with sodium ethoxide in ethanol–benzene gave rise to ethoxy-1-phenylethoxydiphenylsilane in 72% yield.

An interesting trend noted during these reactions was that as the polar character of the solvent decreased, the amount of rearrangement relative to simple displacement tended to increase. Thus benzoyltriphenylsilane in 8% ethanol–benzene gave 64% rearrangement and 13% displacement but in ethanol alone, only 40% of products representing rearrangement were isolated together with 23% of products representing displacement. This was even more marked with benzoyltrimethylsilane where in 3% ethanol in benzene 50% rearrange-

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[7] C. Eaborn and J. C. Jeffrey, *J. Chem. Soc.*, 135 (1957).

[8] J. L. Speier, *J. Am. Chem. Soc.*, **70**, 4142 (1948).

[9] See C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, p. 434.

[10] L. H. Sommer, W. P. Barie, and D. R. Weyerberg, *J. Am. Chem. Soc.*, **81**, 251 (1959).

[11] See E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt, New York, 1959, p. 607.

TABLE I. REARRANGEMENT PRODUCTS OF VARIOUS α-SILYL KETONES

Ketone (moles)	Alkoxide (moles)	Solvents (volumes, ml.)	Reaction[a] Time	Products	% Yields
$(C_6H_5)_3SiCOC_6H_5$	$NaOC_2H_5$				
(0.0069)	(0.0008)	C_2H_5OH–Bz (2 + 25)	11 min.	$C_2H_5OSi(C_6H_5)_2OCH(C_6H_5)_2$ C_6H_5CHO	64 13
(0.0275)	(0.01)	C_2H_5OH–Bz (50 + 100)	2 hr.	$C_2H_5OSi(C_6H_5)_2OCH(C_6H_5)_2$ $(C_6H_5)_3SiOH$ $(C_6H_5)_2Si(OC_2H_5)_2$ $(C_6H_5)_3SiOC_2H_5$	35 3 7 13.5
(0.0165)	(0.0015)	C_2H_5OH (80)	4 hr.[b]	$(C_6H_5)_2Si(OC_2H_5)_2$ $(C_6H_5)_2Si(OH)_2$ $(C_6H_5)_2CHOH$ $(C_6H_5)_3SiOC_2H_5$ $(C_6H_5)_3SiOH$ C_6H_5CHO	39 1 25 18 5 9
(0.0137)	(0.004)	C_2H_5OH-Bz (25 + 50)	6 hr.	$C_2H_5OSi(C_6H_5)_2OCH(C_6H_5)_2$ $(C_6H_5)_2Si(OC_2H_5)_2$ $(C_6H_5)_2CHOH$	61 8 8
	NaOMe				
(0.0083)	(0.002)	CH_3OH–Bz (25 + 50)	2.25 hr.	$CH_3OSi(C_6H_5)_2OCH(C_6H_5)_2$ $(C_6H_5)_2Si(OCH_3)_2$ $(C_6H_5)_2CHOH$	20 15 31
	NaO-*i*-Pr				
(0.015)	(0.004)	*i*-PrOH–Bz (5 + 50)	16 hr.[c]	*i*-$PrOSi(C_6H_5)_2OCH(C_6H_5)_2$ $(C_6H_5)_2CHOH$ $(C_6H_5)_2SiO$-*i*-Pr	24 7 15
(0.012)	(0.002)	*i*-PrOH–Bz (1 + 50)	15 min.	*i*-$PrOSi(C_6H_5)_2OCH(C_6H_5)_2$ $(C_6H_5)_3SiCOC_6H_5$ (rec)	16 35
	NaO-*t*-Bu				
(0.0137)	(0.004)	*t*-BuOH–Bz (2 + 50)	13.5 hr.	*t*-$BuOSi(C_6H_5)_2OCH(C_6H_5)_2$	42[d]
	NaOH				
(0.0055)	(0.0055)	Bz–THF–H_2O (53 + 22 + 2)	30 min.	$(C_6H_5)_3SiOH$ C_6H_5CHO[e]	83
(0.0055)	(0.00025)	Bz–Acetone–H_2O (50 + 60 + 1)	1 hr.	$(C_6H_5)_3SiOH$ C_6H_5CHO[e]	84
(0.003)	(0.00025)	THF–H_2O (25 + 2.5)	19 min.	$(C_6H_5)_3SiOH$ C_6H_5CHO[e]	81
$(C_6H_5)_2CH_3SiCOC_6H_5$	$NaOC_2H_5$				
(0.015)	(0.002)	C_2H_5OH–Bz (4 + 50)	5 min.[f]	$C_2H_5OSiC_6H_5CH_3OCH(C_6H_5)_2$ $(C_6H_5)_2CHOH$	54 11
(0.0165)	(0.005)	C_2H_5OH–Bz (4 + 50)	5 min.[f]	$C_2H_5OSiC_6H_5CH_2OCH(C_6H_5)_2$ $C_6H_5CH_3Si(OC_2H_5)_2$ $(C_6H_5)_2CHOH$	30 29 26
$C_6H_5(CH_3)_2SiCOC_6H_5$	$NaOC_2H_5$				
(0.029)	(0.003)	C_2H_5OH–Bz (5 + 50)	10 min.	$(C_6H_5)_2CHOH$ C_6H_5CHO	52 4
(0.0196)	(0.004)	C_2H_5OH–Bz (5 + 50)	12 hr.[g]	$(CH_3)_2Si(OC_2H_5)_2$ $(C_6H_5)_2CHOH$	30 27
(0.0125)	(0.0015)	C_2H_5OH–Bz (4 + 50)	12 min.	$(C_6H_5)_2CHOH$ $C_2H_5OSi(CH_3)_2OCH(C_6H_5)_2$	26 40[h]
$(CH_3)_3SiCOC_6H_5$	$NaOC_2H_5$				
(0.019)	(0.002)	C_2H_5OH–Bz (25 + 50)	9.5 hr.	C_6H_5CHO	77
(0.028)	(0.001)	C_2H_5OH (50)	11 hr.[i]	C_6H_5CHO $(CH_3)_3SiOC_2H_5$	47 70
(0.056)	(0.013)	C_2H_5OH–$(C_2H_5)_2O$ (10 + 75)	1 hr.[j]	$C_6H_5CH(OH)CH_3$ $(CH_3)_3SiOC_2H_5$ C_6H_5CHO	51 17 7.5
(0.028)	(0.001)	C_2H_5OH–Bz (1.5 + 50)	1.5 hr.	$C_6H_5CH(OH)CH_3$ $(CH_3)_3SiCOC_6H_5$ (rec)	65 18[k]
$(C_6H_5)_3SiCOCH_3$	$NaOC_2H_5$				
(0.005)	(0.0005)	C_2H_5OH–Bz (2 + 25)	10 min.	$C_2H_5OSi(C_6H_5)_2OCHCH_3C\ H_5$	72

Bz = benzene, THF = tetrahydrofuran. [a] Reactions run at room temp. unless otherwise noted. [b] Refluxed 1 hr., then cooled to room temp. during 3 hr. [c] Solution turned red at once, then slowly faded. [d] Crude yield was 75%. [e] Product not isolated quantitatively. [f] Solution warm and orange after 0.5 min., pale yellow after 1 min. [g] Solution colorless after 1 min. but allowed to stand for 12 hours. [h] Material could not be completely purified for analysis. [i] Solution colorless after 1 min. but allowed to stand 11 hr. [j] Solution boiled and turned red almost immediately—external cooling required. [k] No Me_3SiOEt formed, as shown by gas chromatography.

TABLE II

NEW ORGANOSILICON COMPOUNDS

Compound	Formula	M.P.	C Calcd.	C Found	H Calcd.	H Found
$CH_3OSi(C_6H_5)_2OCH(C_6H_5)_2$	$C_{26}H_{24}O_2Si$	45–47.5	78.8	78.8	6.06	6.03
$C_2H_5OSi(C_6H_5)_2OCH(C_6H_5)_2$	$C_{27}H_{26}O_2Si$	77–78.5	79.0	78.8	6.38	6.38
i-$PrOSi(C_6H_5)_2OCH(C_6H_5)_2$	$C_{28}H_{28}O_2Si$	30–33.5	79.3	78.8	6.60	6.61
t-$BuOSi(C_6H_5)_2OCH(C_6H_5)_2$	$C_{29}H_{30}O_2Si$	60.64	79.5	80.2	6.83	6.83
$C_2H_5OSiCH_3C_6H_5OCH(C_6H_5)_2$	$C_{22}H_{24}O_2Si$	[a]	75.9	75.4	6.89	6.89[b]
$C_2H_5OSi(CH_3)_2OCH(C_6H_5)_2$	$C_{17}H_{22}O_2Si$	[c]				
$C_2H_5OSi(C_6H_5)_2OCH$-$CH_3C_6H_5$	$C_{22}H_{24}O_2Si$	[d]	75.8	75.2	6.95	6.69

[a] B.p. 164/0.2 mm, $n^{20}D$ 1.5274. [b] Si, calcd: 8.05. Found: Si 7.86. [c] B.p. 84/0.01 mm. $n^{20}D$ 1.5427. Infrared spectrum indicated slight contamination by benzhydrol which could not be removed by distillation, so no analyses are reported. [d] B.p. 129°/0.1 mm.

ment and 18% recovered ketone were obtained whereas in ethanol only displacement products (70%) were isolated.

These observations can be explained as follows. Assuming that a pentacovalent intermediate is the precursor of both displacement and rearrangement, rearrangement of the negatively charged pentacovalent intermediate will involve considerably more charge dispersal, involving both the silicon atom and carbonyl group, than would simple displacement. Charge dispersal is generally found to be retarded by strongly solvating solvents such as ethanol,[12] so that the charge dispersal involved in rearrangement should be favored by less polar solvent media such as ethanol–benzene. Conversely, less charge dispersal would be involved in the simple displacement of the benzoyl group and this process might be expected to be facilitated by the more polar, better solvating solvent ethanol.

It has also been noted that in many cases addition of a solution of sodium alkoxide to the yellow ketone solution results in a short-lived but almost immediate intensification of the color, prior to fading to colorless. This observation has been confirmed colorimetrically, and leads to the speculation as to whether this phenomenon is a manifestation of the formation of the pentacovalent intermediate. This charged species might well be expected to absorb somewhat more intensively, and perhaps at a higher wave length than the ketone alone. It is hoped that further work will confirm this speculation.

In the light of the rearrangements just described the question arises as to whether, under suitable conditions, treatment of benzoyltriphenylsilane, or other ketones, with aqueous alkali will not similarly give rise to rearrangement, rather than to the displacement yielding silanol and aldehyde previously reported. A number of attempts were made in homogeneous benzene–acetone–water or benzene–tetrahydrofuran–water systems involving a minimum of water, alkali, and water-miscible solvents to observe rearrangement. However, in no case was rearrangement detected and in each case triphenylsilanol in excess of 80% yield was isolated. Presumably sufficiently nonpolar solvent systems have not yet been found for rearrangement to be favored.

Experimental[13]

The details of the experiments carried out are summarized in Table I. A few typical experiments, together with structure proving reactions are outlined below. The infrared spectra of all compounds were consistent with the assigned structure: in particular, the presence of bands at approximately 6.9 μ ($C—C_6H_5$), 7.0 μ ($Si—C_6H_5$), 8.0 μ ($Si—CH_3$), 9.0 μ ($Si—C_6H_5$), 9.2–9.5 μ (Si—O, usually two bands with dialkoxysilanes) was confirmed in appropriate cases. Details of the new products formed are given in Table II.

Benzoyltriphenylsilane with Sodium Ethoxide in Benzene.—To a solution of 2.5 g. (0.0069 mole) of benzoyltriphenylsilane in 25 ml. of sodium-dried benzene was added 2 ml. of a solution containing 0.0008 mole of sodium ethoxide in ethanol. The mixture became slightly more intensely yellow and became warm after 2 min.; after 11 min. the bright yellow color had faded almost completely. The solution was washed with 100 ml. of dilute hydrochloric acid, the aqueous layer was extracted once with ether, and the combined benzene and ether layers were dried over magnesium sulfate and concentrated under reduced pressure. The oily residue was dissolved in about 15 ml. of hot ethanol and on cooling 2.1 g. (74%) of crude benzhydryloxyethoxydiphenylsilane, m.p. 67–75°, was deposited. Recrystallization from ethanol gave 1.8 g. (64%) of product, m.p. 77–78.5°.

Anal. Calcd. for $C_{27}H_{26}O_2Si$: C, 79.0; H, 6.38. Found: C, 78.8; H, 6.38.

The mother liquor from the crude product was concentrated and treated with 2,4-dinitrophenylhydrazine reagent. The crude precipitate was recrystallized to give 0.25 g. (13%) of benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 243–244°, which did not depress the mixed melting point with an authentic sample.

Hydrolysis and Ethanolysis of Benzhydryloxyethoxydiphenylsilane.—A mixture of 0.50 g. (0.0012 mole) of benzhydryloxyethoxydiphenylsilane in 5 ml. of ethanol and 3 ml. of 10% potassium hydroxide was refluxed for 1 hr. and then, on cooling, was drowned in dilute acid and extracted with ether. After drying the ether extracts they were concentrated under reduced pressure and the residue treated with 2–3 ml. of petroleum ether (b.p. 60–70°). Crude, insoluble diphenylsilanediol was filtered off which after recrystallization from toluene weighed 0.20 g. (75%), m.p. 160–166°. The petroleum ether solution after concentration and cooling gave 0.16 g. (71%) of benzhydrol, m.p. after recrystallization, 66–68°. The identity of the

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(12) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935).

(13) Most of the reactions of the ketones with nucleophilic reagents were carried out under a dry nitrogen atmosphere, although no differences were observed in air. Anhydrous solvents were employed. Melting points were corrected against reliable standards.

products were confirmed by mixed melting points and infrared spectra.

Benzhydryloxyethoxydiphenylsilane, 0.44 g. (0.0011 mole), was dissolved with warming in 25 ml. of ethanol in which 0.05 g. (0.0002 g.-atom) of sodium had been dissolved. After standing for 22 hr., the reaction mixture was drowned in dilute acid and ether extracted. Removal of the ether from the dried extracts under reduced pressure left a gummy solid which was washed with cold petroleum ether to give, after recrystallization 0.04 g. (17%) of diphenylsilanediol, m.p. 163–167°. Concentration of the washings gave 0.18 g. of crude benzhydrol which after recrystallization gave 0.12 g. (62%) benzhydrol, m.p. 67–68°. The mother liquor from the benzhydrol was distilled to give 0.09 g. (31%) of diphenyldiethoxysilane, b.p. 131°/2 mm., n^{20}D 1.5281. The identity of solids was established by mixed melting points and all products had infrared spectra identical with authentic samples.

Benzoyltriphenylsilane with Sodium Ethoxide in Ethanol.—To 6.0 g. (0.0165 mole) of benzoyltriphenylsilane in 75 ml. of boiling ethanol was added 0.0015 mole of sodium ethoxide in 4 ml. of ethanol. The solution turned deeper yellow almost immediately. After refluxing gently for 1 hr., during which time the color faded to pale yellow, the solution was allowed to cool over 3 hr. and then was poured into 200 ml. of dilute hydrochloric acid. After three extractions with ether, the ether layers were dried over magnesium sulfate and concentrated under reduced pressure. The residue was dissolved in petroleum ether (b.p. 60–70°) and 0.05 g. (1%) of insoluble diphenylsilanediol, m.p. 158–164°, was filtered off. The material was identified by mixed melting point and infrared spectrum. The petroleum ether solution deposited 0.9 g. of a solid, m.p. 65–67°, whose melting point was unchanged by several recrystallizations from petroleum ether. Chromatography of 0.5 g. of this solid on silica gel and elution with benzene yielded 0.2 g. (40%) of benzhydrol, m.p. 65–67°, identified by mixed melting point and infrared spectrum, and elution with 20% methanol in benzene gave 0.1 g. (20%) of triphenylsilanol, m.p. 148–150°, identified by mixed melting point. Analysis of the substance indicated that it was a molecular complex of 73.4% benzhydrol and 26.6% triphenylsilanol.

Anal. Calcd. for 73.4% $C_{13}H_{12}O$, 26.6% $C_{18}H_{16}OSi$: C, 83.05; H, 6.33. Found: C, 83.00, 83.17; H, 6.40, 6.50.

The infrared spectrum and melting point of the substance was identical with that of a mixture of 73% benzhydrol and 27% triphenylsilanol which had been crystallized from petroleum ether (b.p. 60–70°) and the mixed melting point with the synthetic mixture was not depressed. Thus the 0.9 g. of substance isolated of m.p. 65–67° contained 0.65 g. (22%) of benzhydrol and 0.25 g. (5%) triphenylsilanol.

Concentration of the mother liquor from which the above material crystallized yielded an additional 0.1 g. (3%) benzhydrol, m.p. 65–68°, identified by mixed melting point. The mother liquor was distilled under reduced pressure to give 0.15 g. (9%) of benzaldehyde, b.p. 60°/12 mm. identified as the 2,4-dinitrophenylhydrazone, 1.75 g. (39%) of diethoxydiphenylsilane, b.p. 108°/0.35 mm., n^{20}D 1.5285, infrared spectrum identical with an authentic sample synthesized from diphenyldichlorosilane and ethanol in pyridine in 54% yield, b.p. 136°/2.3 mm., n^{20}D 1.5268, and finally 0.9 g. (18%) of triphenylethoxysilane, b.p. 152°/0.2 mm. This material after recrystallization from ethanol melted at 63–65° and did not depress the mixed melting point with an authentic sample.

Benzoyltrimethylsilane with Sodium Ethoxide in Ether.—To a solution of 0.013 mole of sodium ethoxide in 85 ml. of 12% (v./v.) ethanol in diethyl ether was added 10.0 g. (0.056 mole) of yellow benzoyltrimethylsilane.[2] The mixture immediately turned deep red and the ether began to boil so that cooling was required. After the reaction subsided the mixture was allowed to stand at room temperature for 1 hr., but was still red. After hydrolysis in in dilute hydrochloric acid, which caused the color to change to pale yellow, the ether layer was separated and the aqueous layer was twice extracted with ether. The combined ether layers were dried over magnesium sulfate and then fractionally distilled through a column packed with glass helices. After removal of the ether there was obtained 1.1 g. (17%) of trimethylethoxysilane, b.p. 75°, n^{20}D 1.3709, (reported[14] b.p. 75°, n^{20}D 1.3741) whose infrared spectrum was identical with an authentic sample.

The remaining material was distilled under reduced pressure to give 0.5 g. of benzaldehyde b.p. 66°/10 mm. which gave 1.2 g. (7.5%) of benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 242–244° after recrystallization, which did not depress the mixed melting point with an authentic sample. The second fraction, 5.5 g., b.p. 90–96°/10 mm. separated into two layers and redistillation caused the same phenomenon. Chromatography on silica gel and elution with benzene gave two fractions: first 0.5 g. (11%) of liquid, b.p. 140–150°/40 mm. n^{20}D 1.4178, presumed to be methylsilicone polymer on the basis of the infrared spectra which had strong Si—Me absorption at 8.0 μ and strong Si—O absorption at 9.2–9.8 μ. This material presumably arose from hydrolysis of dimethyldiethoxysilane during work-up of the reaction. The second fraction, eluted from the silica gel was 3.5 g. (51%) of 1-phenylethanol, b.p. 96°/12 mm., n^{20}D 1.5252 (reported,[15] b.p. 94°/12 mm. n^{25}D 1.5244) identified by infrared spectrum and by its conversion with phenyl isocyanate to the phenylurethane of 1-phenylethanol, m.p. 88–90°, identified by mixed melting point with an authentic specimen.

Benzoyltriphenylsilane with Sodium *t*-Butoxide in Benzene.—To 2 ml. of freshly distilled *t*-butyl alcohol was added 0.1 g. (0.004 g.-atom) of sodium. A solution of 5.0 g. (0.0137 mole) of benzoyltriphenylsilane in 50 ml. of benzene was added to the above solution and the mixture was gently refluxed for 13.5 hr. during which period the color faded to a pale yellow. After hydrolysis with acid, and drying of the organic ether extracts over magnesium sulfate, removal of the solvents under reduced pressure gave a viscous oil. Chromatography on silica gel with elution by benzene gave 4.5 g. (75%) of a viscous oil which solidified on standing to melt from about 50–60°. Several tedious recrystallizations from hexane finally gave 2.5 g. (42%) of *t*-butoxyethoxydiphenylsilane, m.p. 60–64°. This material was identified by its infrared spectrum, by analysis, and by the hydrolysis of 0.7 g. with aqueous ethanolic sodium hydroxide to give 0.1 g. (29%) of diphenylsilanediol, m.p. 147–151°, and 0.1 g. (34%) of benzhydrol, m.p. 65–66°, both compounds identified by mixed melting points with authentic samples.

Anal. Calcd. for $C_{29}H_{30}O_2Si$. C, 79.5; H, 6.83. Found: C, 80.2; H, 6.83.

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