amount to make the ionic strengths of the final solutions constant.

Comparison with Previous Results.—Both ΔH^0_A and ΔH^0_B were determined by Owen[8] by the e. m. f. method. The values obtained by him are given in Table V, together with values calculated by other workers from his data. The values of ΔH_A and ΔH_B at zero ionic strength found in this research are also given in the table for comparison. The agreement in the case of ΔH^0_A is probably within the accuracy of the e. m. f. data. The excellent agreement in the case of ΔH^0_B is, of course, fortuitous, though, as pointed out above, one would expect better agreement in this case.

TABLE V

IONIZATION HEATS OF GLYCINE AT 25°

			Calculated from Owen's e. m. f. data by		
		Owen[8]	Harned and Owen[2]	Everett and Wynne-Jones[b]	This Research
ΔH^0_A	joules per mole	4848	4915	4602	3891
	calories[a] per mole	1159	1175	1100	930
ΔH^0_B	joules per mole	11570	11570	11710	11591
	calories[a] per mole	2765	2765	2800	2771

[a] One calorie = 4.1833 international joules.

[b] Everett and Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939).

The application of the calorimeter developed by the author to these amino acid reactions has been carried out at the suggestion of Professor Edwin J. Cohn of the Harvard Medical School.

Summary

Calorimetric measurements of the heats of neutralization of glycine by hydrochloric acid and sodium hydroxide at 25° are reported. The results of these measurements are interpreted to yield values of the acidic and basic ionization heats which are in satisfactory agreement with the less accurate values deduced from electromotive force measurements.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 24, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 83]

Studies in Organo-Silicon Synthesis. III. Two-Stage Wurtz Reactions with Silicon Halides

BY WALTER C. SCHUMB AND CHARLES M. SAFFER, JR.[1]

In the first paper of this series[2] it was shown that hexaaryldisilanes are not formed from hexachlorodisilane and hexachlorodisiloxane in the Wurtz reaction with aryl halides and sodium. Instead the Si–Si or Si–O–Si bond was invariably broken, leading to the formation of the tetrasubstituted monosilanes. In an attempt to elucidate the mechanism of the general reaction, the Wurtz reactions between hexachlorodisilane and hexabromodisiloxane with chlorobenzene and sodium have been carried out in two stages. The intermediate sodium compound was first prepared from chlorobenzene and sodium. Then the silicon halide was allowed to react with it. Although some tetraphenylsilane resulted, the main products of the two reactions were hexaphenyldisilane and hexaphenyldisiloxane, respectively. These two latter compounds had been prepared previously from the same silicon halides only by a special use of the Grignard reagent.[3] These results seem to indicate that in the ordinary one-stage Wurtz reaction the energy liberated in the system by the formation of sodium phenyl is enough to rupture the Si–Si and Si–O–Si bonds. When this energy is evolved and dissipated before the silicon halide is added, no bond fission occurs. The presence of some tetraphenylsilane in both reactions is explained by the incomplete conversion of the chlorobenzene to phenylsodium.

To test the further substitution of sodium compounds for the Grignard reagent in organo-silicon synthesis, the reaction between excess silicon tetrachloride and phenylsodium was carried out. The products were the same as those obtained when phenylmagnesium bromide was used. Benzylsodium was condensed with hexachlorodisilane and the hitherto unreported hexabenzyldisilane was obtained. In order to establish its identity more completely, this compound also was prepared from benzylmagnesium chloride and Si_2Cl_6 by the Grignard reaction, since previous work[3] had proved that hexasubstituted disilanes are readily prepared by this method. The resulting

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(1) Present address: Converse Memorial Laboratory, Harvard University, Cambridge, Mass.

(2) Schumb, Ackerman and Saffer, THIS JOURNAL, **60**, 2486 (1938).

(3) Schumb and Saffer, *ibid.*, **61**, 363 (1939).

product showed physical properties identical with those exhibited by the product obtained from benzylsodium, and a mixture of the two solids showed no depression of the melting point.

A new method for the synthesis of organo-silicon compounds is thus suggested, which constitutes an extension of the work of Morton[4] and others involving the use of sodium in organic synthesis. It is, however, limited at present by the difficulty of obtaining the clearly characterized sodium compound, since the usual methods of preparation lead to mixtures.

Experimental

Reactions of Phenylsodium

I. Reaction with Si_2Cl_6.—Phenylsodium was prepared according to the directions of Morton and Massengale[5] from 35 g. of chlorobenzene and 20 g. of sodium sand in 200 cc. of petroleum ether. The chlorobenzene was added over a period of one hour to the sodium at a temperature of 20–30°. The mixture was then stirred for one hour and 9 g. of pure hexachlorodisilane[6] m. p. -1 to 0° gradually added. Stirring was continued for an hour and the petroleum ether was then distilled off. The remaining solids were heated for two hours at 160–180°. Excess sodium was eliminated by reaction with alcohol and the products were then extracted first with warm benzene and then with boiling xylene. About 5 g. of white solid crystallized from the xylene and melted at 352° on recrystallization. It was identified as hexaphenyldisilane (mixed m. p. with known sample). The benzene extract yielded 2 g. of tetraphenylsilane, m. p. 231° (identified by mixed m. p. with known sample).

II. Reaction with Si_2OBr_6.—Phenylsodium was prepared as described above from 55 g. of chlorobenzene and 35 g. of sodium sand. To it was added gradually with stirring 33 g. of pure hexabromodisiloxane, b. p. 81° at 1.5 mm. After stirring for an hour, the petroleum ether was distilled off and the remaining solids heated at 160–180° for two hours. Alcohol was added to eliminate excess sodium and after an extraction with hot water, a hot benzene extraction was made. Hexaphenyldisiloxane (10 g.), m. p. 220°, crystallized from the solution and was identified by a mixed m. p. with a known sample; 1 g. of tetraphenylsilane, m. p. 230°, was also obtained.

III. Reaction with $SiCl_4$.—Phenylsodium from 45 g. of chlorobenzene and 30 g. of sodium sand was prepared in the usual manner in a three-necked flask. One neck of the flask was connected to a tube leading to another three-necked flask, outfitted with stirrer and condenser, containing 45 g. of silicon tetrachloride in 250 cc. of anhydrous ether. When the phenylsodium had been prepared, it was forced by nitrogen pressure through the tube into the silicon tetrachloride. Although the flask was cooled to 0° a vigorous reaction ensued. When the phenylsodium had been completely added, the resulting mixture was stirred for one hour. The solution was then filtered and the ether, silicon tetrachloride and petroleum ether distilled off on the steam-bath. The remaining liquid, about 50 cc., was vacuum distilled. The largest fraction, 20 cc., distilled at 110° (50 mm.) and on redistillation a sample distilled at 195–200° at atmospheric pressure, the reported boiling point for phenylsilicon trichloride.[7] A chloride analysis further characterized this compound. Sample 0.2010 g. gave 0.4155 g. of silver chloride, equivalent to 51.1% Cl. Calculated for $C_6H_5SiCl_3$: Cl, 50.3.

Preparation of Hexabenzyldisilane.—Benzylsodium was prepared according to the directions of Morton and Massengale[5] by an exchange reaction of toluene with phenylsodium; 68 g. of chlorobenzene was added over a period of two hours to 37 g. of sodium sand in 200 cc. of petroleum ether at about 30°. The mixture was stirred for an hour and 135 g. of toluene was added slowly. Enough petroleum ether was distilled off so that the reflux temperature became 83°. The mixture was refluxed at this temperature for two hours, after which time 11 g. of hexachlorodisilane was added. A vigorous reaction ensued. Stirring and refluxing were continued for an hour. Most of the remaining toluene was then distilled off and the resulting semi-solid mass heated at 110–125° for an hour. After cooling, the excess sodium was removed with alcohol (in the presence of nitrogen) and the mixture extracted with water. A benzene extraction of the remaining solids yielded a white, crystalline material, which proved to be hexabenzyldisilane. It was readily soluble in benzene, toluene and chloroform, and appreciably soluble in warm alcohol and ether. It was recrystallized from benzene to give a product, m. p. 194°.

In the preparation of the compound by the Grignard method, 100 g. benzyl chloride and 12 g. of Si_2Cl_6 in 250 cc. of ether was allowed to drop with stirring upon 15 g. of magnesium activated by an iodine crystal. After completion of the vigorous reaction, the ether was distilled and the remaining material heated at 140–150° for three hours. The excess Grignard reagent was then decomposed with dilute hydrochloric acid, the products extracted with ether, and recrystallized from benzene, m. p. 194°.

The analysis for silica was carried out by repeated digestion of the compound with hot, concentrated sulfuric-nitric acid mixture in a platinum crucible. The resulting silica was ignited and weighed. Calcd. for $C_{42}H_{42}Si_2$: C, 83.6; H, 7.02; Si, 9.3. Found: C, 82.1[8]; H, 7.0; Si, 9.1.

The authors wish to express their thanks to Mr. D. F. Holloway of this Laboratory for the preparation of hexabenzyldisilane by the Grignard method, and to acknowledge the helpful advice of Professor A. A. Morton.

Summary

1. Although the preparation by the usual Wurtz synthesis of compounds of the type R_3–

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(4) Morton and co-workers, THIS JOURNAL, 1931–1940.

(5) Morton and Massengale, *ibid.*, **62**, 120 (1940).

(6) For the preparation of Si_2Cl_6 see "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 42.

(7) F. S. Kipping, *Trans. Chem. Soc.*, **101**, 2106 (1912).

(8) The consistently low carbon values may be explained by retention of carbon by silica during combustion, a difficulty repeatedly encountered in the analysis of this type of compound.

$Si–Si–R_3$ or $R_3Si–O–SiR_3$, from the corresponding silicon halides, leads to complete fission of the Si–Si or Si–O–Si bonds (resulting in the formation of tetrasubstituted monosilanes), it has been found that by interrupting the synthesis so as to execute it in two stages, this fission may be largely eliminated.

2. In this way $(C_6H_5)_6Si_2$, $(C_6H_5)_6Si_2O$ and $C_6H_5SiCl_3$, hitherto obtainable from Si_2Cl_6, Si_2OBr_6 and $SiCl_4$, respectively, only by means of the Grignard reaction, have been prepared.

3. Hexabenzyldisilane, m. p. 194°, has been synthesized from Si_2Cl_6 and benzylsodium, as well as by the Grignard reaction between Si_2Cl_6 and benzylmagnesium chloride.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, STATE COLLEGE OF WASHINGTON]

Compressed Films at Solid–Liquid Interfaces[1]

BY J. L. CULBERTSON AND L. L. WINTER

Recent studies of the densities of silica gel and active ash-free charcoal as measured by means of various liquids acting as buoying fluids clearly supported the concept that when a solid is wetted by a liquid a definite compression of the liquid occurs in the interfacial layer.[1a] If such be the case, it is obvious that the compressed layer must suffer changes in its properties commensurate with the degree of compression, and such changes have been observed in connection with many other studies. For example, the freezing point,[2] vapor pressure[3] and dielectric constant[4] of adsorbed liquids have been investigated with indications of decided property changes. While the effect has been described as a compression, it is extremely unlikely that the molecular attraction which is the causal factor may be considered as strictly analogous to a physical pressure. This must be true in all cases in which the liquid molecules possess any degree of dissymmetry, for in such cases tendencies toward molecular orientation would be a natural consequence.

Numerous studies,[5] both with organic and inorganic material, have been made of the extent of liquid binding at solid–liquid interfaces. Considering only those in which aqueous systems have been investigated, most have been concerned with a determination of "bound" water, and the methods used may be classified as calorimetric, cryoscopic, and dilatometric. No critical comparison of these methods will be attempted in this paper, but it is pointed out that in view of the fact that the properties of the "bound" liquid are undoubtedly quite different from the normal ones, it is obviously impossible for any such method to yield absolute values of the quantities of the affected substance, if, in the application of the method, calculations are made that are based on the normal physical constants of the liquid. In view of this fact no emphasis is laid in this paper on the absolute quantities of water affected by the forces at the solid surface, but the writers consider that the comparisons made of the same interface under different conditions and of the different interfaces are valid and significant.

Since previous studies of the heat of wetting[6] indicated marked variations in the intensity of binding of liquid at various solid surfaces, it was decided to make a comparison of the silica–water and the carbon–water systems by this method.

Materials, Apparatus, and Method.—The silica gel and active ash-free carbon were identical with those previously used and their preparation has been described.[1a] The experimental method consisted in determining the amount of water which, at equilibrium, remained unfrozen in a sample of a known weight of the solid in the presence of an excess of water. These determinations were made at various temperatures below the normal freezing point of the water. The apparatus consisted of a freezing-bath for freezing the sample and a calorimeter in which the ice was melted. The freezing-bath was made from a low 1.2-gal. Dewar vessel which was closed with a two-inch Celotex cover. In the cover were mounted, (a) a cali-

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(1) Original manuscript received November 20, 1939.

(1a) Culbertson and Dunbar, THIS JOURNAL, **59**, 306 (1937); Culbertson and Weber, *ibid.*, **60**, 2695 (1938). *Cf.* also Harkins and Ewing, *ibid.*, **43**, 1787 (1921); Lamb and Coolidge, *ibid.*, **42**, 1146 (1920); Marinesco, *Compt. rend. soc. biol.*, **103**, 872 (1930); Ewing and Spurway, THIS JOURNAL, **52**, 4635 (1930); Stamm and Hanson, *J. Phys. Chem.*, **41**, 1007 (1937).

(2) St. John, THIS JOURNAL, **53**, 4014 (1931).

(3) Lambert and Foster, *Proc. Roy. Soc.* (London), **A134**, 246 (1931).

(4) Marinesco, *Compt. rend. soc. biol.*, **103**, 872 (1930); *J. chim. phys.*, **28**, 51 (1931).

(5) Jones and Gortner, *J. Phys. Chem.*, **36**, 387 (1932); Foote and Saxton, THIS JOURNAL, **39**, 627 and 1103 (1917).

(6) Culbertson and Winter, *ibid.*, **59**, 308 (1937).