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The Preparation and Infrared Spectra of Some Dialkylsilanes

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Eight mixed disubstituted silanes have been prepared by the reaction of Grignard reagents with phenylbromosilane. The infrared absorption spectra of these compounds have been studied, and some of their physical properties have been reported.

No reference to mixed dialkylsilanes of the general class $RR'SiH_2$ has previously appeared in the literature. However, the preparation and properties of several simple dialkylsilanes, R_2SiH_2, have been reported.[1–5]

The mixed dialkylsilanes were prepared in the present investigation by the reaction of Grignard reagents with phenylbromosilane. These compounds are methyl-, ethyl-, *n*-propyl-, isopropyl-, *n*-butyl-, *n*-amyl-, *n*-hexyl- and cyclohexylphenylsilane. The phenylbromosilane was obtained by the partial bromination of phenylsilane.

Repeated attempts to prepare phenylchlorosilane by the partial reduction of phenyltrichlorosilane, using lithium aluminum hydride in ether solution, were unsuccessful. Only phenylsilane was obtained even though a large excess of phenyltrichlorosilane was employed and the reduction was carried out at low temperature.

Experimental

Phenylbromosilane.—Phenylbromosilane was prepared by brominating phenylsilane according to the procedure of McCusker and Reilly.[6] The phenylsilane was prepared by reducing phenyltrichlorosilane with lithium aluminum hydride according to the procedure of Benkeser, *et al.*[4] The phenylbromosilane was purified by fractional distillation under reduced pressure in an 18-inch column which was packed with helices and vacuum jacketed. The product distilled at 70° (17 mm.).

Alkylphenylsilanes.—Grignard reagents were prepared by adding 0.1 mole of the alkyl halide to an excess of magnesium turnings in 80 ml. of dry ether contained in a 500-ml., three-necked flask. This flask was fitted with a stirrer, a dropping funnel and a reflux condenser protected by a calcium chloride tube. After the reaction was completed, 7.7 g. (0.04 mole) of phenylbromosilane, which had been diluted with 25 ml. of dry ether, was added slowly to the Grignard reagent. The reaction mixture was allowed to cool, and then it was poured onto a mixture of cracked ice and dilute hydrochloric acid. The ether layer was separated, dried over Drierite, and the ether removed by distillation. The alkylphenylsilanes were distilled under reduced pressure and a middle fraction was collected for use in the determination of physical constants (Table I), carbon and hydrogen analyses (Table I) and infrared absorption studies (Table II).

Infrared Spectra.—The spectra of the dialkylsilanes, phenylbromosilane and phenylsilane were obtained with a Perkin–Elmer model 21 infrared spectrophotometer equipped with a sodium chloride prism. The sample cell was 0.028 mm. thick. The spectra were made from the pure liquids and from dilute solutions of the organosilanes in carbon disulfide. With the dilute solutions it was necessary to place a variable space cell capable of providing sufficiently thick layers of carbon disulfide to eliminate solvent bands in the reference beam of the spectrophotometer.

TABLE I

ALKYLPHENYLSILANES

Phenylsilane	B.p. °C.	Mm.	$n^{25}D$	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl-	53	30	1.505	57	68.79	68.91	8.28	8.31
Ethyl-	60–61	18	1.504	26	70.52	70.53	8.81	8.98
n-Propyl-	48–49	4	1.500	28	71.93	71.96	9.39	9.58
Isopropyl-	48	6	1.498	41	71.93	71.95	9.39	9.51
n-Butyl-	50	1.5	1.499	58	73.10	73.08	9.82	9.91
n-Amyl-	46	0.29	1.496	50	74.12	74.11	10.18	10.22
n-Hexyl-	56	0.29	1.486	36	74.92	75.01	10.48	10.67
Cyclohexyl-	56–58	0.29	1.509	25	76.13	76.17	9.58	9.61
Di-[a]	58	0.6	1.581	45				

[a] Ref. 2 reports the boiling point as 95–97° (13 mm.), and $n^{25}D$ as 1.580.

The infrared absorption bands common to all the alkylphenylsilanes are given in Table II.

TABLE II

INFRARED ABSORPTION BANDS COMMON TO ALL THE ALKYLPHENYLSILANES

Wave length in microns	Structural assignment	Wave length in microns	Structural assignment
3.26(M)	Ar–H[a]	6.73(M)	Ar–Si[a]
3.31(M)	Ar–H[a]	6.99(S)	Ar–Si[a]
4.70(S)	Si–H[b]	7.51(M)	C–H bending[c]
5.12(W)	C_6H_5–[d]	8.43(M)	Ar–Si[a]
5.31(W)	C_6H_5–[d]	8.96(VS)	Ar–Si[a]
5.51(W)	C_6H_5–[d]	9.76(M)	Ar–Si[a]
5.66(VW)	C_6H_5–[d]	10.02(W)	Ar–Si[a]
6.27(W)	Ar–Si[a]	14.28–14.32(VS)	C_6H_5–[c]

[a] H. Gilman, ed., "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 143–151 (by F. A. Miller). [b] Ref. 5. [c] N. B. Colthup, *J. Am. Opt. Soc.*, **40**, 297 (1950). [d] C. W. Young, R. B. DuVall and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

Discussion of the Spectra[7]

Vibrations Involving the Si–C Bonds.—Wright and Hunter[8] have attributed strong bands occurring in the region 11.6 to 14 μ or greater as being due to the stretching mode of the Si–C bond. In the region 11–15.09 μ we observed strong bands which could be due either to the benzene ring vibration or to a silicon–carbon vibration.

Vibrations Involving the $Si–CH_2R$ Group.—Kaye and Tannenbaum[9] have concluded from studies of the spectra of certain alkylsilanes that the absorption in the 7.8–8.6 μ region may be attributed to an $Si–CH_2R$ frequency, as had been pointed out earlier by Tatlock and Rochow.[10] They

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(1) A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919).

(2) F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, THIS JOURNAL, **69**, 2108 (1947).

(3) A. E. Finholt, A. C. Bond, K. E. Wilzbach and H. I. Schlesinger, *ibid.*, **69**, 2692 (1947).

(4) R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952).

(5) R. West and E. Rochow, *J. Org. Chem.*, **18**, 303 (1953).

(6) P. A. McCusker and E. L. Reilly, THIS JOURNAL, **75**, 1583 (1953).

(7) The full spectra referred to in this paper have been deposited as Document number 4242 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $8.75 for photoprints, or $3.00 for 35 mm. microfilm, payable to Chief, Photoduplication Service, Library of Congress.

(8) N. Wright and M. S. Hunter, THIS JOURNAL, **69**, 803 (1947).

(9) S. Kaye and S. Tannenbaum, *J. Org. Chem.*, **12**, 1750 (1953).

(10) W. Tatlock and E. G. Rochow, *ibid.*, **17**, 1560 (1952).

stated that when R = H the absorption band appears at 7.8 μ, when R = CH_3 it appears at 8.1–8.2 μ, while in dimethyldi-*n*-propylsilane the same band appears at 8.3 μ and in butylsilanes at 8.4–8.6 μ. The fact that the band is absent in the spectrum of vinylsilane was given as further evidence that absorption in the 7.8–8.6 μ region can be assigned to the silicon–methylene frequency.

In the present study, bands of medium intensity were found in the range 7.8–8.6 μ for methyl-, ethyl-, *n*-propyl-, *n*-butyl-, *n*-amyl- and *n*-hexylphenylsilane, all of which contain the $Si–CH_2R$ group. However, bands of medium intensity also were found in this range for cyclohexyl- and isopropylsilane, neither of which contain the silicon–methylene group. Moreover, the spectra of phenylsilane and phenylbromosilane contain weak bands at 8.66 and 8.64 μ, respectively, and this same band is much stronger in the spectrum of diphenylsilane. It would appear, then, that absorption in the region 7.8–8.6 μ is not restricted to the $Si–CH_2R$ frequency.

Vibrations Involving the Si–H Bond.—West and Rochow[5] have assigned bands appearing in the 4.77–4.80 μ region to the Si–H bond of dialkylsilanes, and those in the 4.72–4.77 μ region to the Si–H bond of diarylsilanes. The absorption band characteristic of the Si–H bond in all the compounds reported in this paper was found to appear at 4.70 μ, except in phenylbromosilane, where it appeared at 4.61 μ. This shift to a shorter wave length for the absorption by the Si–H bond is due to the inductive effect caused by the substitution of the bromine atom for the alkyl groups of the alkylphenylsilanes.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Potassium Hydroxide as a Metalating Agent. Fluorene[1]

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Fluorene is metalated easily by potassium hydroxide in ether solution at room temperature in spite of the fact that the acidity (*pK* value) of fluorene is lower by 11 than water. Metallic sodium can be used to good advantage as a dehydrating agent.

This study originated from the observation that benzene–azodiphenylamine gave the color indicative of an acid in contact with solid potassium hydroxide and other reagents.[2] One explanation might be that the hydroxide had metalated the amine with formation of a colored anion. Accordingly tests have been made of the metalating activity of potassium hydroxide upon fluorene which has an acidity 11 lower in *pK* value[3] than water. Normally little or no metalation would be expected unless the reaction is carried out at elevated temperature so that water is removed and indeed such is the condition employed when fluorene[4] is treated with this reagent in recovery and purification processes. However, despite the difference in acidity a yield of 28% and even as high as 48% (no. 7 and 11 in Table I) has been obtained at moderate temperature and every test but one (no. 1), in ether as a medium, showed some formation of fluorenylpotassium.

TABLE I

METALATION OF FLUORENE BY POTASSIUM HYDROXIDE IN THE HIGH-SPEED STIRRING APPARATUS

No.	Fluorene, moles × 10^2	KOH, moles	Solv.	Time, hr.	Yield, % Without Na	With Na
1	2.5	3	E	3	0, 2	
2	5.0	0				0
3	5.0	0.5	E	3	11	
4	5.0	1.0	E	1	12	
5	5.0	1.0	E	3	26	
6	5.0	2.0	E	1	27	
7	5.0	2.0	E	3	27, 28	45, 51
8	5.0	2.0	E	6	23	
9	5.0	2.0	B	3	0	
10	5.0	2.0	P	3	6	
11	5.0	3.0	E	3	48	27, 32, 47[a]
12	5.0	3.0	P	3	15	
13	10.0	2.0	E	3		56[b]
14	15.0	2.0	E	3		62
15	20.0	0.5	E	3		41
16	20.0	1.0	E	3		34
17	20.0	2.0	E	3	12, 13	62, 66
18	20.0	2.0	E	3		63[c]
19	25.0	2.0	E	3		63

[a] This mixture was extremely thick and the reproducibility was difficult. [b] In two experiments, where a little water was added to the reaction mixture, this yield rose to 59 and 65%. [c] Twice the usual amount of sodium metal was used in this experiment.

An explanation for the great ease of metalation in the face of this large difference in acidity lies in the fact that potassium hydroxide removes water from the equilibrium mixture in the equation below by formation of a hydrate. The existence of

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[1] This work was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] A. A. Morton and F. H. Bolton, THIS JOURNAL, **75**, 1146 (1953).

[3] J. B. Conant and G. W. Wheland, *ibid.*, **54**, 1212 (1932); W. K. McEwen, *ibid.*, **58**, 1124 (1936).

[4] R. Weissberger, *Ber.*, **34**, 1659 (1901); M. Weger and K. Doring, *ibid.*, **36**, 878 (1903); S. M. Grigorev, L. D. Gluzman, V. A. Ivanushkina and D. T. Braslavskaya, *Chemie et industrie*, **44**, 43 (1940).