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

n-Butylhalosilanes. Determination of Silane Hydrogen in Liquids[1]

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Careful treatment of *n*-butylsilane with $HgCl_2$, $HgBr_2$ or I_2 yields *n*-$C_4H_9SiH_2Cl$, *n*-$C_4H_9SiH_2Br$ or a mixture of *n*-$C_4H_9SiH_2I$ and *n*-$C_4H_9SiHI_2$, respectively. Hydrolysis of *n*-$C_4H_9SiH_2Cl$ furnishes (n-$C_4H_9SiH_2)_2O$, *n*-$C_4H_9SiH_2Br$ and $C_6H_5NH_2$ furnish *n*-$C_4H_9SiH_2NHC_6H_5$. Table I presents the properties of the six new compounds. A new, rapid modification of the analysis for silane hydrogen in liquids requires less than 30 minutes at room temperature and includes these respective steps: solution of the measured or weighed liquid organosilane in slightly acidic 95% ethanol; connection of the apparatus; tilting the apparatus to mix the ethanolic organosilane solution with KOH in methanol or aqueous NaOH; finally, measurement of the volume of hydrogen using the displacement of water. With adequate precautions the error in a single analysis is seldom more than 1–2%, as Table II demonstrates in the analysis of 11 alkylsilanes.

Introduction

Five earlier papers establish the use of halides of certain transitional elements and elements in regular groups in the replacement of hydrogen attached to tin[2] in $(C_2H_5)_3SnH$, to germanium[3] in $(C_2H_5)_3GeH$ or to silicon in $(C_2H_5)_3SiH$,[4] $(C_2H_5)_2SiH_2$,[4] *n*-$C_7H_{15}SiH_3$[5] or cyclo-$C_6H_{11}SiH_3$.[6]

Gradual addition of $HgCl_2$, $HgBr_2$, AgNCO or AgNCS to an excess of the appropriate alkylsilane or dialkylsilane allows fairly straightforward preparation of compounds such as *n*-$C_7H_{15}SiH_2Cl$,[5] $(C_2H_5)_2SiHBr$,[4] cyclo-$C_6H_{11}SiH_2NCO$[6] or cyclo-$C_6H_{11}SiH_2NCS$.[6]

This paper, in turn, reports the reactions of *n*-$C_4H_9SiH_3$,[7] b.p. approximately 56° under 760 mm., with $HgCl_2$, $HgBr_2$ and iodine, also the hydrolysis of *n*-$C_4H_9SiH_2Cl$ and the reaction of *n*-$C_4H_9SiH_2Br$ with aniline. Table I presents the properties of six new compounds with a single *n*-C_4H_9-Si linkage. Moreover, this paper reports a new, rapid, accurate analytical modification for the determination of silane hydrogen at room temperature in liquids, some containing chlorine, bromine, iodine, oxygen or an anilino group.

Experimental Results

Table I lists the boiling points, densities, refractive indices, molar refractions and analyses (analyses for silane hydrogen are in Table II) of the new compounds *n*-$C_4H_9SiH_2Cl$, *n*-$C_4H_9SiH_2Br$, *n*-$C_4H_9SiH_2I$, *n*-$C_4H_9SiHI_2$, *n*-$C_4H_9SiH_2NHC_6H_5$ and (n-$C_4H_9SiH_2)_2O$.

Table II lists the analyses for silane hydrogen in 11 liquid organosilanes. All individual determinations and all averages have an error of 2% or less, while most of the individual analyses have an error of 1% or less. One analysis requires less than 30 minutes in this modification at room temperature.

Experimental

Equipment included units with ground joints for preparations, micro-pycnometers, self-filling micropipets for the measurement of liquids and the subsequent analysis either through titration of available acidity or through liberation of hydrogen present as Si–H, transfer pipets and also special equipment for determining hydrogen present as Si–H, as described later.

***n*-Butylsilane.**—Although available in 53% yield from SiH_3Br and *n*-C_4H_9MgCl in (n-$C_4H_9)_2O$,[7] the actual preparation of *n*-$C_4H_9SiH_3$ is given. Gradual addition of 140 g. of *n*-$C_4H_9SiCl_3$ to 32 g. of $LiAlH_4$ dissolved in 200 ml. of di-*n*-butyl ether and then direct distillation, without hydrolysis, gave 54 g. (85% yield) of *n*-$C_4H_9SiH_3$, the center fraction of which boiled at 56.1–56.4° under 750 mm. pressure. Storage was in tubes sealed at 0°.

***n*-Butylchlorosilane.**—A reaction at 22° between 5.15 g. of *n*-$C_4H_9SiH_3$ and a total of 12.50 g. of $HgCl_2$—with addition of 2.00 g. at the start and then 6 additions of 1.75 g. every 45 minutes—stood overnight. Fractional distillation furnished 5.55 g. of *n*-$C_4H_9SiH_2Cl$ (88% yield); the center fraction had the properties listed in Table I, also a musty, irritating odor.

***n*-Butylbromosilane.**—Eight g. of $HgBr_2$ and 5.35 g. of *n*-$C_4H_9SiH_3$ stood 20 hr. at room temperature, with a tube containing soda-lime and charcoal attached. After addition of 4.3 g. of $HgBr_2$ the mixture stood 96 hr., with occasional shaking. Then careful distillation from the mixture of mercury and Hg_2Br_2 (minor explosions can occur if air mixes with warm Hg_2Br_2, mercury and admixed *n*-$C_4H_9SiH_2Br$) gave 8.30 g. (80% yield) of *n*-$C_4H_9SiH_2Br$. Table I lists the properties of center-fraction *n*-$C_4H_9SiH_2Br$, which had a musty, penetrating odor.

***n*-Butyliodosilane and *n*-Butyldiiodosilane.**—Gradual addition of 25.5 g. of iodine over 3 hr. to 11 g. of *n*-$C_4H_9SiH_3$ at 10° and then fractional distillation furnished 1.3 g. of excess *n*-$C_4H_9SiH_3$, 21.8 g. of crude *n*-$C_4H_9SiH_2I$ boiling at about 156° (82% yield) and 0.8 g. of higher-boiling liquid. Redistillation in the presence of copper wire furnished a 9.5 g. center fraction with a musty, penetrating odor and the properties listed in Table I. Similarly, 43 g. of iodine and 11 g. of *n*-$C_4H_9SiH_3$ gave 12.9 g. of *n*-$C_4H_9SiH_2I$ (yield 48%) of b.p. 155–162° and 20 g. of *n*-$C_4H_9SiHI_2$ (47% yield) of b.p. 135–141° under 65 mm. pressure. Redistillation furnished center fraction *n*-$C_4H_9SiHI_2$ as listed in Table I.

***sym*-Bis-(*n*-butyl)-disiloxane.**—Slow, careful addition of 2 g. of water to 3.55 g. of *n*-$C_4H_9SiH_2Cl$, then gentle mixing and later removal of the lower, aqueous layer, and then similar treatment with two more 2 g. portions of water, and finally removal of the last visible water by transfer pipet left 2.52 g. (92% yield) of crude (n-$C_4H_9SiH_2)_2O$. Careful fractional distillation gave a 1.5 g. center fraction with the properties listed in Table I.

***n*-Butylanilinosilane.**—A reaction of 3.8 g. of *n*-$C_4H_9SiH_2Br$ and 5.2 g., an excess, of aniline in 20 ml. of benzene gave an immediate heavy white precipitate of $C_6H_5NH_3Br$. After standing 2 hr., the process of filtration, washing and then fractional distillation furnished 1.4 g. of excess aniline, 0.5 g. of low fraction *n*-$C_4H_9SiH_2NHC_6H_5$, next 1.20 g. of center fraction *n*-$C_4H_9SiH_2NHC_6H_5$ with the properties listed in Table I and left 1.0 g. of undistilled residue. *n*-Butylanilinosilane had a slight, agreeable odor, a viscosity slightly greater than that of any other compound in Table I and also gave a yield of approximately 50% based on crude product.

Analysis of Silane Hydrogen.—Previous analyses for silane hydrogen[5,6] used a procedure somewhat different from the methods in Table II herein—and less satisfactory. There was emphasis both on the solvent and on mechanical features in the modification presented below. Note that previous experience with titrations of acidity using micropipets and NaOH in 95% ethanol established[8] the excep-

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[1] Presented at Southwestern Regional A.C.S. Meeting, Baton Rouge, La., December, 1959.

[2] H. H. Anderson, THIS JOURNAL, **79**, 4913 (1957).

[3] H. H. Anderson, *ibid.*, **79**, 326 (1957).

[4] H. H. Anderson, *ibid.*, **80**, 5083 (1958).

[5] H. H. Anderson and A. Hendifar, *ibid.*, **81**, 1027 (1959).

[6] H. H. Anderson, *ibid.*, **81**, 4785 (1959).

[7] H. E. Opitz, J. S. Peake and W. H. Nebergall, *ibid.*, **78**, 293 (1956).

[8] H. H. Anderson, *ibid.*, **71**, 1801 (1949); *Anal. Chem.*, **24**, 579 (1952).

TABLE I

PROPERTIES OF NEW *n*-BUTYLSILANE DERIVATIVES

Compound	B.p., °C.	d^{20}_4	n^{20}[c]	Mol. refr. Calcd.	Mol. refr. Found	Silicon[a] Calcd.	Silicon[a] Found	Halide[b] Calcd.	Halide[b] Found	Distilled at °C.	Distilled at Mm.
n-$C_4H_9SiH_2Cl$	102.8	0.888	1.4192	34.94	34.89	22.9	22.6	28.9	29.0[e]	103.1–103.4	771
n-$C_4H_9SiH_2Br$	124.6	1.183	1.4514	37.91	38.02	16.8	16.7	47.8	47.7	124.5–124.8	755
n-$C_4H_9SiH_2I$	155.4	1.454	1.5028	43.65	43.52	13.12	13.3	59.3	59.2	155.8–156.4	765
(*n*-$C_4H_9SiH_2)_2O$	182.4	0.811	1.4181	59.26	59.18	29.5	29.6	..	..[e]	97–98	41
n-$C_4H_9SiH_2NHC_6H_5$	229[d]	0.932	1.5219	58.83[f]	58.68	15.66	15.7	51.4	50.9[e]	118–121	1
n-$C_4H_9SiHI_2$	219	2.007	1.5791	56.30	56.32	8.26	8.30	74.6	74.7	106.6–107.4	15

[a] Analyses for silicon involve careful treatment of compound with fuming nitric acid and fuming sulfuric acid and weighing as SiO_2; the anilino and disiloxane derivatives involve no nitric acid. Also, weighing of NHC_6H_5 as $C_6H_5NH_3Cl$ in a single analysis. [b] Average of two closely agreeing determinations. [c] In white light. [d] Slow decomposition occurs. [e] Table II contains analyses for silane hydrogen. [f] Approximate value, from Vogel, *J. Chem. Soc.*, 654 (1948).

TABLE II

ANALYSES FOR SILANE HYDROGEN (H AS Si–H) IN LIQUIDS[a]

Compound	Base	Hydrogen (as Si–H) Calcd.	Hydrogen (as Si–H) Found
n-$C_4H_9SiH_3$[b]	KOH[c]	3.427	3.44, 3.40, 3.42 (3.42 ± 0.01)
n-$C_4H_9SiH_2Cl$[d]	NaOH	1.643	1.64, 1.66, 1.64 (1.65 ± 0.01)
n-$C_4H_9SiH_2NHC_6H_5$[f]	KOH[c]	1.124	1.15, 1.15, 1.13 (1.14 ± 0.01)
(*n*-$C_4H_9SiH_2)_2O$[g]	NaOH[e]	2.117	2.11, 2.10, 2.11 (2.11 ± 0.01)
$(C_2H_5)_2SiHBr$[4,f]	NaOH[e]	0.603	0.603, 0.605, 0.606, 0.599 (0.603 ± 0.002)
$(C_2H_5)_2SiHI$[4,f]	NaOH[e]	0.471	0.477, 0.471, 0.471 (0.473 ± 0.002)
$[(C_2H_5)_2SiH]_2O$[4,f]	NaOH[e]	1.059	1.06, 1.05, 1.05, 1.05 (1.05 ± 0.01)
$C_6H_5SiH_3$[g,h]	NaOH[e]	2.795	2.796, 2.796, 2.804, 2.797 (2.798 ± 0.003)
cyclo-$C_6H_{11}SiH_3$[6,g]	NaOH[e]	2.647	2.66, 2.66, 2.65 (2.66 ± 0.01)
n-$C_7H_{15}SiH_2Cl$[5,f]	NaOH[e]	1.223	1.21, 1.22, 1.20, 1.20 (1.21 ± 0.01)
n-$C_7H_{15}SiH_3$[5,g]	NaOH, KOH	2.321	2.30, 2.29, 2.28[e]; 2.26, 2.29, 2.28, 2.28[c] (2.28 ± 0.01)

[a] In all cases 95% ethanol is the main solvent; the usual volume is 3–4 ml. [b] Volume of sample is 27.17 microliters. [c] Base is 0.2–0.4 ml. of 8.3 *M* KOH in methanol. Gas volume is 9–34 ml. [d] Volume of sample is 8.05 microliters. Runs involve tiny equipment, 0.6 ml. of ethanol, 0.15 ml. of base and 2.9 ml. of gas. [e] Base is 0.2–0.4 ml. of saturated aqueous NaOH. Gas volume is 9–34 ml. [f] Fifty microliters of sample. [g] Weight of compound is in range of 40–50 mg. [h] Pure compound made from $C_6H_5SiCl_3$ and $LiAlH_4$ in ether.

tional usefulness of measuring the liquid compound in a self-filling micropipet and then titrating the acidity.

The following is a description of the main borosilicate (Pyrex) glass equipment for the analysis of silane hydrogen in liquids. Unit ABCD, 10 cm. long with 1 ml. internal volume, has a 1 mm. stopcock at B and a male 10/30 standard taper ground joint at CD, all connected by 1 mm. i.d. heavy wall capillary tubing. Unit CDEFGHI, with an internal volume of 12.5 ml., is made up of: a 10/30 female ground joint at CD; a length of 8.5 cm. at CDE; a 10-ml. bulb at E; the sidearm FGHI 6 mm. i.d. with FG, approximately 5 cm. long, tilting 10° *below horizontal,* thus when *exactly vertical* along ACE capable of holding 0.4–0.7 ml. of base at G; a 7 cm. length GHI with a male standard taper 10/30 ground joint at HI. Unit HIJKL, with 0.6 ml. volume in the capillary part, has a female 10/30 ground joint at HI, a length IJK almost completely of 2 mm. i.d. capillary, two 180° bends at J and K, a 23 cm. length JK, also 18 cm. length KL chiefly of capillary averaging 0.3 mm. in i.d. and 2.5 mm. in o.d. At L escaping gas bubbles displace water from a 20, 30 or 40 ml. gas buret.

In the typical procedure place 3 to 4 ml. of 95% ethanol of *p*H 6.8, a yellow color of cresol red indicator, in bulb E and use a separate transfer pipet to place the NaOH or KOH solution (the latter seems preferable) at G. Then weigh the compound in a tiny transfer pipet or preferably measure the (substituted) alkylsilane in a self-filling micropipet and transfer[8] into the ethanol solution, with 4 later rinsings using ethanol taken from a microbeaker. Next connect the units ABCD, CDEFGHI and HIJKL, immersing below FG in water in a 2 liter beaker to regulate the temperature to ± 1°; agitate gently for 2 minutes, close the stopcock at B and then place the gas buret over capillary KL. Upon careful tilting *make G higher than F;* the alkaline solution flows into the ethanolic solution, making the resultant mixture alkaline and dark red. *Now hydrogen evolves completely* within 10 minutes if aided by occasional gentle agitation, displacing water from the gas buret. Measure the volume of the hydrogen liberated (one mole of H_2 per mole of Si–H) and calculate the percentage of silane hydrogen.

Discussion

Slowly and at 22° or less, gradual addition of the corresponding mercuric halide or iodine to excess *n*-$C_4H_9SiH_3$, b.p. 56°, yields *n*-$C_4H_9SiH_2Cl$, *n*-$C_4H_9SiH_2Br$ or a mixture of *n*-$C_4H_9SiH_2I$ and *n*-$C_4H_9SiHI_2$ satisfactorily.

Five pairs of isomeric substituted alkylsilanes allow comparisons of the normal boiling points, which are: *n*-$C_4H_9SiH_2Cl$, 102.8° and $(C_2H_5)_2SiHCl$, 99.2° [9] or 99.7° [10]; *n*-$C_4H_9SiH_2Br$, 124.6° and $(C_2H_5)_2SiHBr$, 121.3° [4]; *n*-$C_4H_9SiH_2I$, 155.4° and $(C_2H_5)_2SiHI$, 149.6° [4]; [*n*-$C_4H_9SiH]_2O$, 182.4° and $[(C_2H_5)_2SiH]_2O$, 170.6° [4]; last, with little difference, *n*-$C_4H_9SiHI_2$, 219° and $(C_2H_5)_2SiI_2$, 220–221° [11] or 221°.[12] In the first four pairs of isomers the higher boiling point clearly belongs to the isomer with the longer straight chain, namely, the substituted *n*-butylsilane. This conclusion is in general agreement with information on the isomeric forms of $C_4H_{12}Si$, in which the isomers with the longest straight chains have the highest b.p. and the comparatively symmetrical $(CH_3)_4Si$ has the lowest b.p.[13]

Normal boiling points of 129.0° for *n*-$C_4H_9SiHCl_2$[10] and of 129° for $(C_2H_5)_2SiCl_2$ are identical. Table II of the present paper shows a very useful

(9) H. J. Emeleus and S. R. Robinson, *J. Chem. Soc.*, 1592 (1947).

(10) C. A. MacKenzie and others, THIS JOURNAL, **72**, 2032 (1950).

(11) C. Eaborn, *J. Chem. Soc.*, 2761 (1949).

(12) H. H. Anderson and others, THIS JOURNAL, **73**, 2144 (1951).

(13) S. N. Borisov, M. G. Voronkov and B. N. Dolgov, *Doklady Akad. Nauk* (*U.S.S.R.*), **114**, 93 (1957).

new rapid modification for the analysis of silane hydrogen *in liquids*, applicable even to n-C_4H_9-SiH_3, b.p. 56°, if one delivers the contents of the micropipet into bulb E from a nearly horizontal position. Little true comparison with results of other investigators[13] appears possible at present; uncertainties in the work of numerous others may involve the purity of the compound, the analytical method or both.

PHILADELPHIA 4, PA.

[CONTRIBUTION FROM THE ETHYL CORPORATION]

Reductive Carbonylation Synthesis of Metal Carbonyls. II. Synthesis of Manganese Carbonyl and Group VI-B Metal Carbonyls by the Alkylaluminum Method[1]

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Manganese and Group VI-B metal carbonyls may be prepared by reductive carbonylation of an appropriate salt of the metal employing an alkylaluminum compound, generally triethylaluminum, as the reducing agent. Manganese carbonyl thus can be prepared conveniently in 55–60% yield by employing a 4:1 mole ratio of triethylaluminum to manganese acetate in isopropyl ether at 80–100°, 3000 p.s.i.g. carbon monoxide pressure. Similarly, chromium, molybdenum and tungsten carbonyl can be prepared readily in high yield (90%) from the corresponding metal chlorides. The effect of various reaction variables on the yield is discussed, and the results are compared with those of the Grignard method. The differences can be explained in terms of the lower reactivity and hence the greater selectivity of an alkylaluminum compound compared to a Grignard reagent in its reaction with a transition metal salt. A mechanism is proposed for the formation of metal carbonyls by the alkylaluminum method which involves essentially the formation of an alkyl transition metal intermediate in a rate-determining step and then its facile reaction with carbon monoxide.

Introduction

It was reported recently by Closson, Buzbee and Ecke[2] of our Laboratories that the relatively inaccessible manganese carbonyl can be prepared in 32% yield by treating manganese chloride with two equivalents of the sodium ketyl of benzophenone in tetrahydrofuran (THF), with subsequent carbonylation and hydrolysis to produce manganese carbonyl. This represented the first satisfactory method developed for the preparation of manganese carbonyl in appreciable quantity.[3]

In the course of investigating other new methods for preparing manganese carbonyl a novel and superior method was discovered which involved the use of triethylaluminum (TEA) as a "selective reducing agent." This method then was extended to the synthesis of the carbonyls of chromium, molybdenum, tungsten and iron. The generality of this method, which we have referred to as involving a reductive carbonylation reaction, and its differences from the Grignard method were described briefly in a communication[1] from this Laboratory. Shortly before this communication appeared, L. I. Zakharkin, *et al.*,[4] reported the use of TEA and diisobutylaluminum hydride as reducing agents for the preparation of chromium, molybdenum and tungsten carbonyl. Inadvertently, we failed to acknowledge this paper in our previous communication.[5]

There are now available several adequate laboratory methods for preparing the Group VI-B metal carbonyls and in particular chromium carbonyl. The Grignard method is perhaps the best known and most common method for preparing chromium carbonyl.[6–10] This method, however, is not well adapted for the preparation of manganese[3] or molybdenum and tungsten carbonyls.[7,8] In contrast to the Grignard method for manganese[11] and the Group VI-B metal carbonyls, the metal carbonyl was found to be produced directly as such in the alkylaluminum method without requiring hydrolysis to liberate it and little or no free metal was produced as a side product. Consequently, it was concluded that TEA behaves as a more selective reducing agent than does the Grignard reagent for the preparation of metal carbonyls. It also appeared likely that since the product is formed directly without requiring hydrolysis, there might not be a theoretical limitation on the yield (below 100%) due to disproportionation,[8,10] such as imposed by the Grignard method.

Results

Effect of Manner of Contact on Yield.—Typical results are summarized in Table I. It was found that in those cases where the metal salt reacted with TEA at room temperature in the particular solvent employed, the subsequent yield of metal carbonyl was greatly reduced. This was evident in the case of manganese acetate in benzene and for molybdenum pentachloride and tungsten hexachloride in ethers and benzene. To minimize this difficulty for the purpose of the reaction variable study, the metal salt was enclosed in a glass am-

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[1] H. E. Podall, THIS JOURNAL, **80**, 5573 (1958).

[2] R. D. Closson, L. R. Buzbee and G. C. Ecke, *ibid.*, **80**, 6167 (1958).

[3] Manganese carbonyl, $Mn_2(CO)_{10}$, was first predicted by Hieber, *et al.*, *Ber.*, **65**, 1090 (1932), and its formation by the Grignard method was indicated by D. T. Hurd, G. W. Sentell, Jr., and F. J. Norton, THIS JOURNAL, **71**, 1899 (1949). Its preparation in sufficient quantity (in about 1% yield) for characterization was first reported by E. O. Brimm, M. A. Lynch, Jr., and W. J. Sesny, *ibid.*, **76**, 3831 (1954).

[4] L. I. Zakharkin, V. V. Gavrilenko and O. Yu. Okhlobystin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 100 (1958).

[5] It is of interest to note that no mention was made by these workers of the applicability of this method to the preparation of manganese carbonyl—the compound, curiously enough, for which our independent discovery of the alkylaluminum method was first made.

[6] A. Job and A. Cassal, *Compt. rend.*, **183**, 392–4 (1926).

[7] A. Job and J. Rouvillois, *Bull. soc. chim.*, **41**, 1041 (1927).

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[10] W. M. Cumming, J. A. Horn, and P. D. Ritchie, *J. Appl. Chem.*, **2**, 624 (1952).

[11] V. Hnizda (to Ethyl Corporation) U. S. Patent 2,822,247 (1958).