times in excess of II, 2. It appears, therefore, that when C^{14}-formate is fed to *N. rustica* the specific activity of the nicotine methyl carbon isolated is about one order of magnitude lower than that which results after feeding C^{14}-methylmethionine, under conditions maintained as nearly as possible constant.

The data presented above, in the opinion of the authors, constitute strong evidence for trans-methylation in higher plants. The lower specific activities obtained using formate serve as an indication that the methionine methyl group is not oxidized to formate and then reduced during the transfer of the methyl carbon to nicotine. It may be inferred that the function of formate in trans-methylation is, alternatively, that of a precursor in the biosynthesis of labile methyl groups, with serine acting as a possible intermediate. The final proof that the methionine methyl group is transferred as an entity to nicotine must await the completion of experiments involving double-labeling with carbon-14 and deuterium. These

experiments are now being conducted in this Laboratory, and the results will be forthcoming at a later date.

In view of our results indicating transmethylation from methionine to nicotine, and the failure of Kirkwood and Marion[7] to demonstrate any methyl transfer from choline to hordenine in barley, it appears that further comparative studies would be profitable. The possible function of choline as a methyl donor in nicotine biosynthesis is now under investigation.

[CONTRIBUTION NO. 535 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Reactions of Silane. I. The Alkylation and Alkoxylation of Silane

BY JOHN S. PEAKE, W. H. NEBERGALL AND YUN TI CHEN[1]

The apparatus and procedure for the preparation of silane by the lithium aluminum hydride reduction of tetrachlorosilane and the subsequent alkylation and alkoxylation of silane as a continuous process have been described. Tetraphenylsilane, tetraethylsilane, triethylsilane, diethylsilane, triisopropylsilane, tetra-2-naphthylsilane and tri-1-naphthylsilane were formed by the interaction of silane and the appropriate organolithium compound. Phenylsodium reacted with silane to form tetraphenylsilane and sodium hydride. Attempts to bring about reactions between silane and Grignard reagents, phenylcalcium iodide, diphenylcalcium and diethylzinc were unsuccessful. Silane has been found to react with various alcohols in the presence of alkoxide ions to produce tetraalkoxysilanes and hydrogen. Tetraethoxysilane, tetra-*n*-propoxysilane and tetra-*n*-butoxysilane were prepared by the reaction of silane with the appropriate alcohol; however, no reaction was observed when silane was passed through methanol containing lithium methoxide.

No method for the direct alkylation or alkoxylation of monosilane, SiH_4, has previously appeared in the literature. However, organolithium compounds have been used to replace hydrogen attached to silicon in such alkylsilanes as R_3SiH,[2] R_2SiH_2[3] and $RSiH_3$,[4] which reactions result in the formation of tetraalkylsilanes and lithium hydride.

As a result of the present investigation one may write a general equation to represent the replacement of hydrogen attached to silicon by the use of organolithium compounds.

$$R_ySiH_{4-y} + (4-y) R'Li \longrightarrow R_ySiR'_{4-y} + (4-y) LiH$$
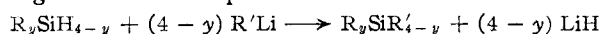
In the above equation R may be an alkyl or aryl radical and *y* may have values from zero to three.

The importance of the solvent in these substitution reactions has been noted previously[2,4] and is further verified in this report. When ethyl ether is employed as the reaction medium for the inter-

action of RLi compounds and organosilicon hydrides, tetrasubstitution is favored, but when low boiling petroleum ether is the solvent, trisubstitution appears to be the general rule. For example, ethyllithium reacts with silane to form tetraethylsilane in ethyl ether, whereas triethylsilane is the most highly substituted product formed when the reaction medium is petroleum ether.

It was observed that isopropyllithium in excess reacted with silane in petroleum ether to produce triisopropylsilane almost exclusively. Restriction to trisubstitution here does not necessarily result from the nature of the solvent in view of the fact that others have reported[5] possible steric effects of the isopropyl group in attempting to synthesize tetraisopropylsilane from tetrachlorosilane. Another case of steric hindrance was encountered in the present work in that tri-1-naphthylsilane was found to be the sole product of the reaction of an excess of 1-naphthyllithium with silane in ethyl ether. It is interesting to note, however, that tetrasubstitution was readily effected by the action of 2-naphthyllithium upon silane.

The possibility of employing other organometallic compounds in addition to those of lithium was in-

(1) Part I from a thesis to be submitted by Yun Ti Chen to the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) R. N. Meals, THIS JOURNAL, **68**, 1880 (1946); H. Gilman and S. P. Massie, *ibid.*, **68**, 1128 (1946); H. Gilman and H. W. Melvin, Jr., *ibid.*, **71**, 4050 (1949); R. A. Benkeser and F. J. Riel, *ibid.*, **73**, 3472 (1951).

(3) Unpublished work carried out in this Laboratory.

(4) W. H. Nebergall, THIS JOURNAL, **72**, 4702 (1950).

(5) H. Gilman and R. N. Clark, *ibid.*, **69**, 1499 (1947).

vestigated. Phenylsodium was found to react with silane giving tetraphenylsilane and presumably sodium hydride.

$$SiH_4 + 4C_6H_5Na \longrightarrow (C_6H_5)_4Si + 4NaH$$
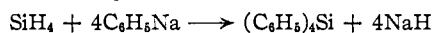
Attempts to alkylate silane using Grignard reagents, phenylcalcium iodide, diphenylcalcium and diethylzinc were unsuccessful.

Silane was found to react with certain alcohols in the presence of the corresponding alkoxide ions as catalysts to form tetraalkoxysilanes and hydrogen.

$$SiH_4 + 4ROH \xrightarrow{OR^-} Si(OR)_4 + 4H_2$$
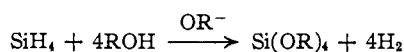
Although silane was found to interact readily with ethanol, n-propanol and n-butanol with the corresponding lithium alkoxide as a catalyst, all attempts to bring about a similar reaction between silane and methanol met with failure. In addition, silane did not react with ethanol in the presence of lithium methoxide, nor did it react with methanol in the presence of lithium ethoxide.

Experimental

Preparation of Organometallic Compounds.—The organolithium compounds (RLi) used in this investigation were prepared by treating lithium metal in the form of ribbon or shot with an organic halide (RX) corresponding to the desired compound. The apparatus and method used for this type of preparation have been described in a previous report.[6] In general petroleum ether (b.p. 20–40°) was used as the solvent in which the organic halide reacted with lithium metal. In certain experiments where it was desired to study the effect of reaction of the organolithium compound (RLi) with silane in a different solvent medium, the petroleum ether was distilled off the organolithium compound and replaced with the desired solvent. Ethyl ether was used as the solvent for the preparation of phenyllithium. Phenylsodium was prepared by the method of Morton and Massengale.[7] Diethylzinc was prepared according to the synthesis described by Noller.[8] Diethylcalcium was prepared in approximately 50% yield by the reaction of metallic calcium with diethylzinc in dry benzene solutions under dry nitrogen atmosphere according to the method of Gilman and Woods.[9] Phenyl calcium iodide was prepared by the method of Gilman, Kirby, Lichtenwalter and Young.[10]

Description of Apparatus.—The organometallic compounds prepared as described above were subjected to contact with silane by placing solutions of these compounds in the proper solvent in the reaction chambers of the apparatus shown in Fig. 1.

This apparatus consisted essentially of a silane generator, reaction chambers and suitable traps connected as shown. Air must be excluded from the apparatus to prevent explosion of the silane. This was accomplished by first evacuating the apparatus and then filling it with nitrogen. By having originally a large excess of lithium aluminum hydride in the flask (A) of the silane generator, successive amounts of silane could be generated by placing in the dropping funnel (B) the required amount of silicon tetrachloride dissolved in the desired solvent. A manually operated stirrer (C) was fitted into a metal stuffing box (best made of stainless steel) so that the lithium aluminum hydride could be agitated occasionally to provide access of the solution to the solid material. The silane delivery tube (D) was jacketed with a tube (E) filled with crushed ice in order to condense as much as possible of the solvent carried over by the silane, thus preventing excessive accumulation of frozen solvent in the cold-trap. The trap (F) was provided to catch any liquid entrained by the silane. The line from the generator to the cold-trap was connected to a 30-inch
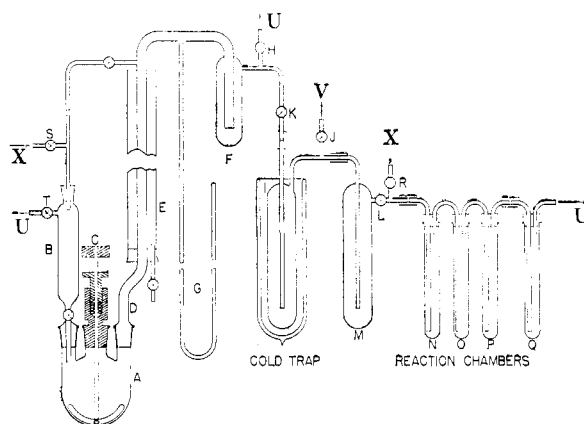
(6) W. H. Nebergall, THIS JOURNAL, **72**, 4702 (1950).

(7) A. A. Morton and J. T. Massengale, *ibid.*, **62**, 120 (1940).

(8) C. R. Noller, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., N. Y., 1943, p. 184.

(9) H. Gilman and L. A. Woods, THIS JOURNAL, **67**, 520 (1945).

(10) H. Gilman, *et al.*, *Rec. trav. chim.*, **55**, 79 (1936).

Fig. 1.—Silane generator: U, to fume hood; V, to vac-pump; X, N₂.

manometer (G) provided to permit the reading of the pressure within the generator at all times. In the event of the plugging of the cold-trap the excessive pressure in the generator could be relieved by opening the stopcock (H). The cold-trap (I) was cooled by means of a solution of Dry Ice in alcohol. The system could be evacuated through stopcock (J) to remove air. Nitrogen to replace the air could be admitted either through stopcock (R) or stopcock (S). It was possible to evacuate only the cold-trap and trap (M) by leaving stopcocks (K) and (L) closed. This permitted the generator to be left filled with silane between experiments without the need of repeated purging of air from it, yet permitting the cold-trap to be emptied and replaced between experiments. In order to increase the efficiency of absorption without danger of plugging porous media with reaction products, the organometallic solutions were divided into three parts and placed in successive reaction chambers (N, O, P). Access of air to the reaction chambers was excluded by the use of a mercury air seal in trap (Q). The reaction chambers and air seal could be purged of air by admitting nitrogen through stopcock (R). After adding fresh silicon tetrachloride solution to the dropping funnel (B), the air could be displaced by adding nitrogen through stopcock (S) and exhausting it through stopcock (T).

Generation of Silane.—The quantity of silane to be generated was determined by the amount of organometallic compound to be treated. It was calculated in terms of the amount of silicon tetrachloride added to the lithium aluminum hydride in the generator. The yield of silane from the reaction of these two compounds has been found to be 99% by Finholt, Bond, Wilzbach and Schlesinger.[11] This yield was confirmed in this present investigation. The yield of substituted silanes obtained by the reaction of silane with the organometallic compounds in the reaction chambers is limited in part by the time of contact between the gas and the solutions.

The reaction of silicon tetrachloride with lithium aluminum hydride goes much more smoothly in the presence of a mutual solvent for the two substances. For this purpose ethyl ether or 1,4-dioxane served well. By the use of dioxane the carry-over of solvent by the silane is reduced and the generation of silane goes more smoothly. The yield of silane is, however, lower than when ether is used. Adding the solvent to the silicon tetrachloride made it possible to evacuate the system after each new charge of dry lithium aluminum hydride was added to the silane generator. It also permitted better control of the rate of generation of silane.

Reaction of Silane with Organometallic Compounds.—For reaction of silane with the organometallic compounds a period of contact by bubbling it through the solutions in the reaction chambers amounting to one to two hours was employed.

After treatment with silane the solutions in the reaction chambers were combined for the operation of product recovery. The excess organometallic compound was decomposed by means of cracked ice and dilute sulfuric acid. The two layers were allowed to separate and the aqueous

(11) A. E. Finholt, *et al.*, THIS JOURNAL, **69**, 2692 (1947).

TABLE I

THE REACTIONS OF SILANE WITH ORGANOMETALLIC COMPOUNDS

Reactant with silane	Mol. ratio of reactant to silane	Reaction medium	Product	B.p. or m.p.,[a] °C.	Mm.	$n^{20}D$	Yield, %	Analyses Silicon, % Calcd.	Found
C$_6$H$_5$Li	4.6	Et$_2$O	(C$_6$H$_5$)$_4$Si[b]	M 234–235			40.5		
C$_2$H$_5$Li	8.6	Et$_2$O	(C$_2$H$_5$)$_4$Si[c]	B 149–150	737	1.4232	63.0		
C$_2$H$_5$Li	4.8	Pet. ether (20–40°)	(C$_2$H$_5$)$_3$SiH[d]	B 105–106	739	1.4112	36.0		
			(C$_2$H$_5$)$_2$SiH$_2$[e]	B 53–56	739	1.3915	27.0		
i-C$_3$H$_7$Li	8.5	Pet. ether (20–40°)	(i-C$_3$H$_7$)$_3$SiH[f]	B 60	10	1.4365	37.5		
1-C$_{10}$H$_7$Li	14.5	Et$_2$O	(1-C$_{10}$H$_7$)$_3$SiH	M 236–237			39.0	6.81	6.64, 6.71
2-C$_{10}$H$_7$Li	2.7	Et$_2$O	(2-C$_{10}$H$_7$)$_4$Si[g]	M 216–217			50.0[k]		
C$_6$H$_5$Na	6.9	Et$_2$O	(C$_6$H$_5$)$_4$Si	M 234–235			21.0	8.33	8.24, 8.21
C$_2$H$_5$OH and C$_2$H$_5$OLi	37.0	C$_2$H$_5$OH	(C$_2$H$_5$O)$_4$Si[h]	B 167–168	740	1.3830	67.0		
n-C$_3$H$_7$OH and n-C$_3$H$_7$OLi	28.0	n-C$_3$H$_7$OH	(n-C$_3$H$_7$O)$_4$Si[i]	B 73.5	3	1.4020	77.5	10.62	10.60, 10.55
n-C$_4$H$_9$OH and n-C$_4$H$_9$OLi	26.0	n-C$_4$H$_9$OH	(n-C$_4$H$_9$O)$_4$Si[j]	B 138–140	11	1.4134	41.0	8.85	8.71, 8.71

[a] All melting points and boiling points are corrected. [b] S. Sugden and H. Wilkins, *J. Chem. Soc.*, 126 (1931), report the melting point as 234°. [c] M. Manulkin, *J. Gen. Chem., U. S. S. R.*, 16, 235 (1936), reports the boiling point as 150–151° (760 mm.) and $n^{20}D$ as 1.4234. [d] F. C. Whitmore, *et al.*, THIS JOURNAL, 69, 2108 (1947), report the boiling point as 107° (733 mm.) and $n^{20}D$ as 1.4117. [e] A. E. Finholt, *et al., ibid.*, 69, 2692 (1947), report the boiling point as 53–57° (760 mm.) and $n^{20}D$ as 1.3918. [f] H. Gilman and R. N. Clark, *ibid.*, 69, 1499 (1947), report the boiling point as 60–61° (3.5 mm.) and $n^{20}D$ as 1.4358. [g] H. Gilman, *et al., ibid.*, 72, 4280 (1950), report the melting point as 216–217°. [h] H. D. Cogan, *et al., Ind. Eng. Chem.*, 39, 1364 (1947); L. Holzapfel, *et al., Z. Elektrochem.*, 47, 327 (1941), report the boiling point as 168.1° (760 mm.) and $n^{20}D$ as 1.3832. [i] G. Abati, *Z. phys. Chem.*, 25, 353 (1898), reports the boiling point as 225–227° (760 mm.). [j] D. Peppard, *et al.*, THIS JOURNAL, 68, 77 (1946), report the boiling point as 140–142° (32 mm.) and $n^{20}D$ as 1.4131. [k] This yield is based upon the quantity of 2-C$_{16}$H$_7$Li used.

layer was extracted with a suitable solvent. The solvent was distilled from the organic layer and from the extract. Where solid products were obtained they were recrystallized and identified by their melting points and in certain cases by analysis. Liquid products were identified by means of boiling points and refractive indices as well as by analysis of certain samples. The results of these experiments are summarized in Table I.

Reaction of Silane with Alcohols.—For reaction of silane with alcohols it was found necessary to have present some alkoxide ions as catalysts. These were provided by adding one-half gram of metallic lithium to 100 ml. of alcohol.

With the lower aliphatic alcohols lithium reacted very vigorously and gave clear solutions. With the higher alcohols the reaction with lithium was much less vigorous and required gentle heating to complete the reaction.

Following treatment of the alcohol containing alkoxide ions with silane for the proper length of time, the excess alcohol was removed by distillation (under vacuum in the case of the higher alcohols) and the products of the reaction were further purified by vacuum distillation. The results of these experiments are also included in Table I.

BLOOMINGTON, INDIANA   RECEIVED OCTOBER 15, 1951

The Synthesis of Esters of Substituted Amino Phosphonic Acids[1a]

BY ELLIS K. FIELDS[1b]
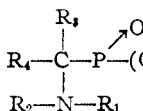
It has been found that compounds of structure

$$R_4—\underset{\underset{R_2—N—R_1}{|}}{\overset{\overset{R_3}{|}}{C}}—P\overset{\nearrow O}{—}(OR)_2$$

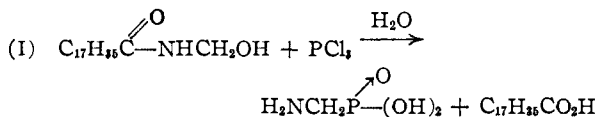may be synthesized by treating a phosphorus acid diester with (1) an aldehyde or ketone and an amine, (2) an α-alkylol amine, (3) an alkylidene diamine, (4) an N-disubstituted amino methyl ether, (5) an aldimine or ketimine derived from a primary amine. The various methods of preparation and some unusual properties of the new amino phosphonic esters are described.

This paper is concerned with the synthesis of esters of N-substituted aminomethylphosphonic acids. These compounds have the structure

$$R_4—\underset{\underset{R_2}{\underset{|}{N—R_1}}}{\overset{\overset{R_3}{|}}{C}}—P\overset{\nearrow O}{—}(OR)_2$$
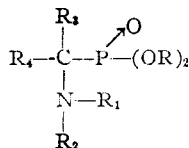
where any of the R's may be hydrogen with the exception that R$_1$ and R$_2$ may not both be hydrogen.

The only method of synthesis of such compounds known heretofore consists of treating a methylol amide with phosphorus trichloride in the presence of acetic acid and hydrolyzing the product.[2]

$$(I)\quad C_{17}H_{35}\overset{\nearrow O}{C}—NHCH_2OH + PCl_3 \xrightarrow{H_2O}$$

$$H_2NCH_2P\overset{\nearrow O}{—}(OH)_2 + C_{17}H_{35}CO_2H$$

This method has the following disadvantages: (1) it involves prolonged reaction times: from 12 hours to 7 days are necessary to complete the re-

(1) (a) Presented at the XIIth International Congress of Pure and Applied Chemistry, New York, September, 1951; (b) present address: Standard Oil Company (Indiana), Whiting, Indiana.

(2) M. Engelmann and J. Pikl, U. S. Patent 2,304,156, December 8, 1942; U. S. Patent 2,304,157, December 8, 1942; Pikl, U. S. Patent 2,328,358, August 31, 1943.