separated and dissolved in ether. The ethereal solution was extracted with 10% aqueous potassium hydroxide until a portion of the extracts gave no precipitate when acidified.[18] Treatment of the basic extract with Norite and then acidification with 10% hydrochloric acid gave a tan oil which solidified on standing. The isolated solid material was dried in a vacuum oven at 50° and then weighed 33 g. (72%) and melted at 132–155°.

Method B. A mixture of 9 g. (0.036 mole) of the tetrahydro-1,4-naphthalenediacetic acid and 52 ml. of thionyl chloride was warmed carefully until the evolution of sulfur dioxide had ceased (15 min.). After removal of the excess thionyl chloride *in vacuo,* a solution of the residual acid chloride in 100 ml. of redistilled nitrobenzene was added with stirring over a period of 2 hr. to a cold (0°) solution of 19 g. (0.145 mole) of anhydrous aluminum chloride in 300 ml. of nitrobenzene. After standing for 10–12 hr. in a refrigerator, the dark red complex was hydrolyzed with ice and 10% hydrochloric acid. The organic layer was washed with several portions of 15% hydrochloric acid and then with 5% potassium hydroxide until a portion of the aqueous extract gave no precipitate when acidified. The basic solution was worked up as described in Method A to yield 5.1 g. (61%) of the crude keto acid, m.p. 132–156°. Treatment of the solution of a portion in 10% aqueous alkali several times with Norite followed by isolation as before and recrystallization from ethanol yielded colorless crystals, m.p. 140–156°. The wide range of melting point was attributed to the presence of more than one stereoisomer.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.50. Found: C, 72.75; H, 6.58.

2a,3,4,5-Tetrahydro-5-acenaphtheneacetic acid (VIII). A modified Wolff-Kishner reduction of 7.1 g. (0.03 mole) of the keto acid with 35 ml. of 99% hydrazine hydrate, 28 ml. of ethanol, 35 ml. of diethylene glycol, and 3.3 g. of potassium hydroxide was carried out according to the procedure previously described[3] except that the crude product was not chromatographed. The oil obtained solidified on standing to yield 6 g. (90%) of material which melted at 89–96°. Recrystallization of a portion twice from petroleum ether afforded a product which melted at 99–101°[3] and apparently was predominantly the less soluble isomer. The ultraviolet and infrared absorption spectra of the recrystallized material were identical to those of a known sample.

2a,3,4,4a-Tetrahydro-1-pyracenone. Cyclization of 5.5 g. (0.025 mole) of the above tetrahydroacenaphtheneacetic acid by treatment with 50 g. of polyphosphoric acid[16] was effected as described above for the preparation of 1-keto-2a,3,4,5-tetrahydro-5-acenaphtheneacetic acid (VII). The reddish brown solution obtained was poured into cold water and the mixture stirred for 2 hr. at room temperature. The separated precipitate was dissolved in ether and the ether solution washed with 5% sodium bicarbonate, water, and saturated sodium chloride solution and then dried over magnesium sulfate. Removal of the solvent under reduced pressure left 3.9 g. (80%) of crude product. After one recrystallization from 70–90° ligroin followed by sublimation *in vacuo,* 3.0 g. (61%) of the ketone was obtained as colorless needles, m.p. 96–100°,[3] having ultraviolet and infrared absorption spectra identical to those of a known sample A small amount of starting material was recovered from the bicarbonate washes.

Pyracene (IX). The above tetrahydro-1-pyracenone was converted to 2a,3,4,4a-tetrahydropyracene as previously described.[3] A mixture of 0.24 g. (0.0013 mole) of the tetrahydropyracene, 15 ml. of anhydrous benzene, and 0.1 g. of 5% rhodium-on-alumina catalyst[19] was heated in a sealed tube at 290 ± 10° for 18 hr. in a rocker-type autoclave packed with glass wool and charged with 90 ml. of benzene. Separation of the catalyst and concentration of the filtrate yielded 0.19 g. (81%) of pyracene, m.p. 210–215°. A portion recrystallized from benzene melted at 215–216°[3] and gave no depression of melting point when mixed with a known sample.

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[18] A small amount of yellow, base insoluble material from the ether solution was isolated. It gave a positive reaction with 2,4-dinitrophenylhydrazine but could not be identified as the diketone resulting from cyclization of both carboxyl side chains.

[19] Baker and Company, Inc., Newark 5, N. J.

[CONTRIBUTION FROM THE RAHWAY RESEARCH LABORATORY OF THE METAL & THERMIT CORP.]

Preparation of Some Vinylsilanes with Vinylmagnesium Chloride[1]

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Received May 31, 1957

Tetravinylsilane, trivinylmethylsilane, trivinylphenylsilane, trivinylsilane, dibutyldivinylsilane, dimethyldivinylsilane, diphenyldivinylsilane, trimethylvinylsilane, and triphenylvinylsilane have been prepared by the reaction of vinylmagnesium chloride with appropriate silicon chlorides.

The development of the new intermediate, vinylmagnesium chloride, in this laboratory[2] has made possible the direct synthesis of organosilanes containing more than one vinyl group. In order to ascertain the utility of vinylmagnesium chloride, a group of nine organosilanes was prepared.

The development of the synthesis of tetravinylsilane involved the preparation of this compound in several solvent systems. The basic reaction of vinylmagnesium chloride in tetrahydrofuran with silicon tetrachloride in a solvent was used in all preparations. The solvents used were tetrahydrofuran, heptane, and benzene. The yields of tetravinylsilane ranged from 40% to 60%. Finally, as more was learned about the physical properties of tetravinylsilane, pentane was used as it was

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[1] This paper was presented before the 130th meeting of the AMERICAN CHEMICAL SOCIETY at Atlantic City, N. J., Sept. 1956.

[2] H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint, and R. Cserr, unpublished results. S. D. Rosenberg, A. J. Gibbons, Jr., and H. E. Ramsden, *J. Am. Chem. Soc.,* **79,** 2137 (1957).

TABLE I

PHYSICAL PROPERTIES OF SOME VINYLSILANES

Compound	B.P. or M.P.	n_D^{25}	d_4^{25}	Yield,[a] %	Analyses, % Si Calcd.	Analyses, % Si Found
$(CH_3)_4Si$[4]	26.5°	1.3591[b]	0.6480[c]			
$(CH_3)_3SiCH{=}CH_2$	55°	1.3898	0.6917	64.0	28.00	27.50
$(CH_3)_2Si(CH{=}CH_2)_2$	80°	1.4182	0.7408	67.1	25.01	24.86
$CH_3Si(CH{=}CH_2)_3$	107.6°	1.4411	0.7692	72.0	22.59	22.29
$(CH_2{=}CH)_4Si$	130.6°	1.4611	0.7926	87.5	20.60	20.42
$C_6H_5Si(CH{=}CH_2)_3$	39–41° 0.05 mm.	1.4932	0.9159	81.4	15.06	14.76
$(C_6H_5)_2Si(CH{=}CH_2)_2$	130–131° 0.05 mm.	1.5350	1.0092	80.0	11.87	12.01
$(C_6H_5)_3SiCH{=}CH_2$	m. 57.5–59.5°			86.1	9.80	9.63
$(C_6H_5)_4Si$[5]	m. 228°					
$(CH_2{=}CH)_3SiH$	92.5°	1.4498	0.7725	54.7	25.46	25.21
$(n\text{-}C_4H_9)_2Si(CH{=}CH_2)_2$	59–61° 2.0 mm.	1.4528	0.7916	81.0	14.29	14.41

[a] Based on the mole of silicon chloride used. [b] n_D^{20}. [c] d_4^{20}.

thought that this low-boiling solvent would exert a moderating influence upon the reaction. This solvent proved to be beneficial: an 87% yield of tetravinylsilane was obtained.

$$CH_2{=}CHMgCl + SiCl_4 \xrightarrow[\text{at reflux}]{\text{Pentane}} (CH_2{=}CH)_4Si$$

Similarly, it was possible to prepare trivinylmethylsilane, trivinylsilane, dimethyldivinylsilane, and trimethylvinylsilane from vinylmagnesium chloride in tetrahydrofuran and the appropriate organochlorosilane in pentane.

The problem of separation of the product from tetrahydrofuran becomes more difficult with each succeeding silane because of the proximity of boiling points (Table I). The problem is further complicated by the fact that these silanes, particularly trivinylsilane, polymerize when held at their boiling points for prolonged periods. This problem was partially solved by using columns with sufficient efficiency and throughput to achieve the separation of the tetrahydrofuran from the product with a minimum of reflux return. Once the tetrahydrofuran was separated, the columns were by-passed and the product distilled rapidly through a simple still-head. In the case of trimethylvinylsilane,[3] the product distills first and careful fractionation on a 75-theoretical plate column was used.

The preparation of the last four compounds of the series was straight forward. Triphenylvinylsilane is a low-melting solid which was crystallized from ethanol-benzene.

Diphenyldivinylsilane, trivinylphenylsilane, and dibutyldivinylsilane are liquids which were purified by distillation under reduced pressure. Because of the danger of heat-induced polymerization, very low pressures should be maintained when distilling these materials.

Although pentane was used as the solvent in the work reported, exploratory work showed that heptane was a satisfactory solvent in the preparation of diphenyldivinylsilane and trivinylphenylsilane. These results indicate that heptane should be useful in the preparation of these high boiling silanes, eliminating the hazards of pentane.

In the reactions reported here tetrahydrofuran as delivered by the Du Pont Co., purified new tetrahydrofuran and purified recovered tetrahydrofuran were used as solvents in the preparation of vinylmagnesium chloride. No difference was noted in the behavior of the reactions in comparative duplicate runs provided the solvents were maintained anhydrous. In our hands tetrahydrofuran exhibited no unusual behavior or hazard provided standard safety precautions were observed.

EXPERIMENTAL

Vinylmagnesium chloride. In a 12.0-l. flask equipped with a stainless steel anchor stirrer, a dropping funnel, and a Dry Ice–acetone cold condenser, was placed 414 g. (17.0 g.-atom) of magnesium turnings. To this was added 100 ml. of a solution of 1274 g. (20.4 mole) of vinyl chloride in 3680 g. (51.0 mole) of tetrahydrofuran. The temperature of the mix was raised to 40° by warming with an electric mantle and 5.0 ml. of ethyl bromide was added to initiate the reaction. When the temperature of the mix reached 50°, the mantle was removed and the remainder of the solution was added at a rate to maintain a reaction temperature of 45–55°. The addition time was 6.0 hr. The reaction mix was then stirred for 3.0 hr. while the reaction temperature was gradually raised to 60° using the heating mantle. The vinylmagnesium chloride was now ready for use. The yield, as ascertained by back-titration with standard acid and base, was 15.6 mole (91.8%).

Tetravinylsilane. In a 22.0-l. flask equipped with a stainless steel anchor stirrer, a dropping funnel, and a water condenser, was placed 15.6 mole of vinylmagnesium chloride in 3680 g. of tetrahydrofuran. To this was added, at a rate to maintain reflux, 595 g. (3.5 mole) of silicon tetrachloride in 8.0 l. of pentane. The addition took 3.0 hr. On

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(3) L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. S. Evans and F. C. Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954).

(4) H. H. Anderson, *J. Am. Chem. Soc.*, **69**, 3049 (1947).

(5) A. Polis, *Ber.*, **18**, 1542 (1885).

completion of the addition, the mix was refluxed for 5.0 hr. The mix was then partially hydrolyzed by the cautious addition of 2.3 l. of 5% aqueous hydrochloric acid. At this point $MgCl_2 \cdot 6H_2O$ dropped out of suspension and the clear organic layer was separated. The salt was then dissolved by the addition of 2.0 l. of water. The very small organic layer that resulted was separated and combined with the major fraction.

The solution was fractionally distilled through a column of 8 theoretical plates to yield (*1*) 6800 ml. (85%) of pentane, b.p. 35–40° and (*2*) 3128 g. (85%) of tetrahydrofuran, b.p. 63–68°.

When the temperature of the distillate at the head of the column reached 129°, the column was by-passed and the product was distilled through a simple distillation head to yield (*3*) 417.5 g. (87.5%) of tetravinylsilane, b.p. 129–132°.

Dimethyldivinylsilane. In a 22.0-l. flask was placed 13.5 mole of vinylmagnesium chloride in 3100 g. of tetrahydrofuran. To this was added 725 g. (6.0 mole) of dimethyldichlorosilane in 8.0 l. of pentane; addition time 5.0 hr., reflux time 5.0 hr. The reaction mixture was then hydrolyzed and the organic layer separated.

The solution was fractionally distilled through a column of 8 theoretical plates to remove 7.0 l. (87.5%) of pentane, b.p. 36–40°. The residue was then fractionally distilled through a column of 75 theoretical plates to remove 2985 g. (96.4%) of tetrahydrofuran, b.p. 60–68°. When the temperature of the distillate at the head of the column reached 79°, the column was by-passed and the product was distilled through a simple distillation head to yield 396.7 g. (66.1%) of dimethyldivinylsilane, b.p. 79–82°.

Diphenyldivinylsilane. In a 22.0-l. flask was placed 9.2 mole of vinylmagnesium chloride in 2160 g. of tetrahydrofuran. To this was added 1042 g. (4.12 mole) of diphenyldichlorosilane in 8.0 l. of pentane at a rate to maintain reflux; addition time 3.0 hr., reflux time 8.0 hr. The reaction mixture was then hydrolyzed and the organic layer separated.

The solvents were then stripped using steam as the heat source and the residue was distilled under reduced pressure to yield 778.9 g. (80%) of diphenyldivinylsilane distilling at 130–131°/0.05 mm.

Triphenylvinylsilane. In a 22.0-l. flask was placed 10.8 mole of vinylmagnesium chloride in 2600 g. of tetrahydrofuran. To this was added 2659 g. (9.0 mole) of triphenylchlorosilane in 5.0 l. of tetrahydrofuran plus 3.0 l. of pentane; addition time 1.5 hr., reflux time 8.0 hr. The reaction mixture was then hydrolyzed and the organic layer separated. The solvents were then removed by distillation with the last traces distilling under reduced pressure (25 mm.). The residual oil was transferred to a crock and was solidified by cooling the crock in an ice bath. The solid was ground up, transferred to a 12.0 l. flask, and crystallized by dissolving in 3.0 l. of 90% ethanol plus 1.0 l. of benzene at reflux and cooling slowly to 15° with stirring. The solid was filtered by suction and thoroughly air-dried to give 1900 g. (73.5%) of triphenylvinylsilane melting at 57.5–59.5°. Concentration of the mother liquid led to the isolation of 350 g. (13.6%) of triphenylvinylsilane melting at 53–58°.

Acknowledgment: The authors would like to thank Dr. Marie Farnsworth and her coworkers in the Physical and Analytical Section of this laboratory for their assistance throughout this work.

RAHWAY, N. J.

[CONTRIBUTION FROM THE RAHWAY RESEARCH LABORATORY OF THE METAL & THERMIT CORP.]

Arylmagnesium Chlorides. Preparations and Characterizations[1]

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Received May 10, 1957

Substitution of tetrahydrofuran for ethyl ether allows conversion of aryl chlorides to arylmagnesium chlorides.

Although phenylmagnesium chloride has been known for a number of years, no general procedure has been forthcoming for the preparation of other arylmagnesium chlorides. The preparations of phenylmagnesium chloride in chlorobenzene in the absence of solvent under pressure,[2] using freshly prepared magnesium,[3] catalytic quantities of metal salts,[4] a special magnesium-copper alloy and ethyl ether and allowing an initiating period of 4–11 days[5] or using the diethyl ether of ethylene glycol[6] do not seem to be general enough for preparing other arylmagnesium chlorides. Usually for these compounds it is necessary to use molar quantities of ethyl bromide as an entrainment carrier for the aryl chloride.[7] Compounds made in this way include phenylmagnesium chloride and *p*-chlorophenylmagnesium chloride. Pentamethylphenyl-

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(1) Parts of this paper were presented at the 130th National Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, Sept., 1956.

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