[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BUFFALO]

# STUDIES IN SILICO-ORGANIC COMPOUNDS. XXI. ALKYL AND PHENYL DERIVATIVES OF VINYLTRICHLOROSILANE

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## DISCUSSION

Vinyltrichlorosilane has been prepared by the abstraction of hydrogen chloride from chloroethyltrichlorosilane (1) as well as by the high temperature interaction of vinyl chloride and a silicon alloy (1–4).

In this work, vinyltrichlorosilane was allowed to react with the proper Grignard reagent to form vinyltrimethylsilane and its triethyl, tri-*n*-propyl, tri-*n*-butyl, and tri-*n*-amyl homologs. Vinyltriallylsilane, vinyltriphenylsilane, and vinyltribenzylsilane were similarly prepared.

In the presence of an equivalent amount of diethylamine, bromine was found to react with vinyltriethylsilane to form bromovinyltriethylsilane with the bromine probably attached to the *alpha* carbon. Further work on this reaction is contemplated. It is felt that, in view of the well known tendencies toward *beta* elimination, bromine attached to the *alpha* carbon would be more stable than if attached to the *beta* one.

## EXPERIMENTAL

*Vinyltrimethylsilane.* Methylmagnesium bromide (400 cc. of 3 *M* in *n*-butyl ether) was placed in a 1-l. three-necked flask fitted with a mercury-sealed stirrer. Vinyltrichlorosilane (44.5 cc., 0.35 mole) was added slowly with stirring. The reaction proceeded very rapidly. After the complete addition of the silicon compound, the reaction mixture was refluxed for six hours. Excess methylmagnesium bromide was then hydrolyzed using an ammonium chloride solution and the ether layer was separated. After drying overnight over calcium chloride, the ether layer was distilled at atmospheric pressure with isolation of vinyltrimethylsilane, b.p. 54.4° (745.4 mm.), $n_D^{25}$ 1.3880, $d_4^{25}$ 0.6865, 32 g., yield 91.4%.

*Anal.* Calc'd for $C_5H_{12}Si$: Si, 28.00; M.R., 34.44.

Found: Si, 27.80; M.R. 34.44.

*Vinyltriethylsilane.* Ethylmagnesium bromide (0.47 mole) in ethyl ether and 12.7 cc. (0.10 mole) of vinyltrichlorosilane, reacted as indicated above, afforded vinyltriethylsilane b.p. 144.0° (740.4 mm.), $n_D^{25}$ 1.4340, $d_4^{25}$ 0.7674, 7.45 g., yield 52.3%.

*Anal.* Calc'd for $C_8H_{18}Si$: Si, 19.72; M.R., 48.33.

Found: Si, 19.68; M.R., 48.29.

*Vinyltri-n-propylsilane.* Using *n*-propylmagnesium bromide (0.875 mole) in ethyl ether and 0.25 mole of vinyltrichlorosilane, and the procedures outlined above, vinyltri-*n*-propylsilane was isolated, b.p. 73.0° (4.5 mm.), $n_D^{25}$ 1.4432, $d_4^{25}$ 0.8310, 23.5 g., yield 51.0%.

*Anal.* Calc'd for $C_{11}H_{24}Si$: Si, 15.22; M.R., 62.22; Mol. wt., 184.36.

Found: Si, 15.19; M.R., 58.85; Mol. wt., 184.2 (cryoscopic from benzene).

*Vinyltri-n-butylsilane.* *n*-Butylmagnesium bromide (1.75 mole) in diethyl ether was treated with 57.0 cc. (0.45 mole) of vinyltrichlorosilane as before, with isolation of vinyltri-*n*-butylsilane, b.p. 99.0° (6.5 mm.), $n_D^{25}$ 1.4479, $d_4^{25}$ 0.8261, 63.0 g., yield 61.8%.

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[1] A portion of the thesis presented by the first author as partial requirement for the degree of Doctor of Philosophy at the University of Buffalo.

*Anal.* Calc'd for $C_{14}H_{30}Si$: Si, 12.39; M.R., 76.11; Mol. wt., 226.4.
Found: Si, 12.20; M.R., 73.17; Mol. wt., 226.6 (cryoscopic from benzene).

*Vinyltri-n-amylsilane.* *n*-Amylmagnesium bromide (1.80 mole) in diethyl ether was similarly treated with 0.45 mole of vinyltrichlorosilane. Vinyltri-*n*-amylsilane was isolated, b.p. 145.3° (7.5 mm.), $n_D^{25}$ 1.4480, $d_4^{25}$ 0.8078, 55 g., yield 45.6%.

*Anal.* Calc'd for $C_{17}H_{36}Si$: Si, 10.45; M.R., 90.00; Mol. wt., 268.5.
Found: Si, 10.49; M.R., 88.98; Mol. wt., 269.5 (cryoscopic from benzene).

*Vinyltriallylsilane.* Allylmagnesium bromide (0.784 mole) was treated in the same manner with 0.20 mole of vinyltrichlorosilane with the isolation of vinyltriallylsilane, b.p. 69.7° (6.0 mm.), $n_D^{25}$ 1.4790, $d_4^{25}$ 0.8315, 18.0 g., yield 51.8%.

*Anal.* Calc'd for $C_{11}H_{18}Si$: Si, 15.74; M.R., 60.81.
Found: Si, 15.67; M.R., 60.81.

*Vinyltriphenylsilane.* Phenylmagnesium bromide (0.99 mole) was treated with 0.3 mole of vinyltrichlorosilane as described above; then the product was frozen out of solution and purified by recrystallization from ether, m.p. 58–59°, 29.2 g., yield 34.0%.

TABLE I

PHYSICAL CONSTANTS OF VINYLTRIALKYLSILANES

| COMPOUND | B.P., °C. | MM. | $n_D^{25}$ | $d_4^{25}$ | M.P., °C. |
|---|---|---|---|---|---|
| $CH_2{=}CHSi(CH_3)_3$ | 54.4 | 745.4 | 1.3880 | 0.6865 | |
| $CH_2{=}CHSi(C_2H_5)_3$ | 144.0 | 740.4 | 1.4340 | .7674 | |
| $CH_2{=}CHSi(C_3H_7\text{-}n)_3$ | 73.0 | 4.5 | 1.4432 | .8310 | |
| $CH_2{=}CHSi(C_4H_9\text{-}n)_3$ | 99.0 | 6.5 | 1.4479 | .8261 | |
| $CH_2{=}CHSi(C_5H_{11}\text{-}n)_3$ | 145.3 | 7.5 | 1.4480 | .8078 | |
| $CH_2{=}CHSi(CH_2CH{=}CH_2)_3$ | 69.7 | 6.0 | 1.4790 | .8313 | |
| $CH_2{=}CHSi(C_6H_5)_3$ | | | | | 58–59 |
| $CH_2{=}CHSi(CH_2C_6H_5)_3$ | | | | | 76.5–77.5 |
| $(C_2H_2Br)Si(C_2H_5)_3$ | 66.8–67.0 | 4.5 | 1.4770 | 1.1200 | |

*Anal.* Calc'd for $C_{20}H_{18}Si$: Si, 9.80. Found: Si, 9.75.

*Vinyltribenzylsilane.* Benzylmagnesium chloride (0.87 mole) in diethyl ether was treated with 0.25 mole of vinyltrichlorosilane, with isolation, by freezing, of vinyltribenzylsilane, m.p. 76.5–77.5°, 31.0 g., yield 37.8%.

*Anal.* Calc'd for $C_{23}H_{24}Si$: Si, 8.54. Found: Si, 8.46.

*Bromovinyltriethylsilane.* Vinyltriethylsilane (32.0 g., 0.365 mole) was placed in the usual apparatus. Bromine (18.7 cc., 0.36 mole) was added slowly with stirring. After the complete addition of the bromine, the reaction mixture was heated gently with stirring for one hour. Diethylamine (42.5 cc., 0.41 mole) was then added slowly with cooling in ice-water. A dense white precipitate formed immediately. The mixture was refluxed for five hours with stirring, followed by separation of diethylammonium chloride by filtration. Excess diethylamine was removed at atmospheric pressure and the remainder of the liquid was distilled at reduced pressure with the isolation of bromovinyltriethylsilane, b.p. 66.8–67.0° (4.5 mm.), $n_D^{25}$ 1.4770, $d_4^{25}$ 1.1200, 25.2 g., 31.2% yield.

*Anal.* Calc'd for $C_8H_{17}BrSi$: Si, 12.69; Br, 36.13; M.R., 56.01.
Found: Si, 12.88; Br, 36.02; M.R., 55.81.

*Materials.* *Vinyltrichlorosilane* was obtained through the courtesy of the Linde Air Products Co. Other reagents were either prepared as needed or were purchased from other reputable sources. Physical constants were satisfactory.

## ANALYSIS

*Silicon* was determined by three different gravimetric procedures. For compounds involving four Si-C bonds a sample was weighed in a platinum crucible which had been placed in an ice-water or a Dry Ice-acetone bath depending upon its volatility. To this was added six drops of chlorobenzene, two cc. of concentrated sulfuric acid, and six drops of 40% perchloric acid. The crucible was then placed on a hot plate and taken to fumes of sulfur trioxide. Next it was ignited over a Fisher burner and then carefully treated with five to six drops of fuming nitric acid. This treatment, ignition and addition of nitric acid, was repeated until the residue had achieved a white color and a constant weight. An alternative procedure for compounds containing Si-O bonds was also applied. In this case the weighed sample was treated with approximately 20 drops of fuming sulfuric acid. The crucible was placed on a hot plate and taken to fumes of sulfur trioxide. Then it was ignited on a Fisher burner and treated with fuming nitric acid with ignition as in the first method. A modification of these methods was carried out successfully for compounds involving three Si-O bonds and one Si-C bond. The weighed sample was treated immediately with fuming nitric acid and taken to dryness on a hot plate. Then it was ignited over a Fisher burner and treated with more nitric acid until the residue had achieved a white color and a constant weight.

*Chlorine* and *bromine* were determined by volumetric procedures after sodium treatment.

*Grignard reagents* were standardized by titration. A 2-cc. sample of the reagent was pipetted slowly into approximately 50 cc. of ice-water. Excess standard hydrochloric acid was added and the excess acid was titrated with standard sodium hydroxide. The indicator employed was phenolphthalein.

## SUMMARY

1. Vinyltrichlorosilane reacts with the proper Grignard reagent to form vinyltrimethyl-, vinyltriethyl-, vinyltri-*n*-propyl-, vinyltri-*n*-butyl-, vinyltri-*n*-amyl-, vinyltriallyl-, vinyltriphenyl-, and vinyltribenzyl-silane.

2. Bromine reacts with vinyltriethylsilane and stoichiometric amounts of diethylamine to form bromovinyltriethylsilane with the bromine probably attached to the *alpha* carbon.

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