[Contribution from the Department of Chemistry of the University of Buffalo]

STUDIES IN SILICO-ORGANIC COMPOUNDS. XXVI. ADDITIONAL DERIVATIVES OF VINYLTRICHLOROSILANE

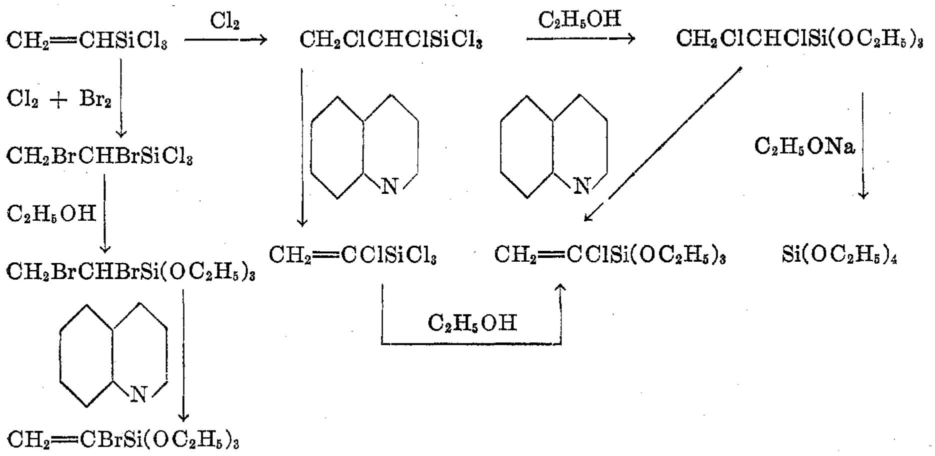
CHRIST TAMBORSKI and HOWARD W. POST[1]

Received April 18, 1952

DISCUSSION

In two previous papers of this series it has been shown that vinyltrichlorosilane reacts easily with Grignard reagents (2) and that vinyltriethylsilane adds bromine in the presence of diethylamine (1). Alcohols also react with vinyltrichlorosilane to form vinyltrialkoxysilanes (2) and these, in turn, add bromine (2).

It has now been shown that halogens add to vinyltrichlorosilane in the absence of diethylamine without loss of hydrohalogen acid and that these products react with ethyl alcohol to undergo replacement of silane chlorine by ethoxyl. Other reactions are indicated by the equations given below.



It is probable that all three dehydrohalogenation reactions resulted in retention of the *alpha*-halogen rather than the *beta*. Further study is contemplated covering the determination of the position of the halogen atom after dehydrohalogenation. However it is felt that because of the ever-present tendency toward *beta* elimination, the *beta*-halogen is lost in preference to the *alpha* one.

Vinyl chloride was a by-product of the formation of tetraethoxysilane by the action of sodium ethoxide on α,β-dichloroethyltriethoxysilane. This is analogous to other examples of *beta* elimination. Similarly, compounds with multiple halogen atoms can be titrated for "titratable halogen" which means halogen *beta* to silicon and halogen attached to silicon.

---

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

EXPERIMENTAL PART

Addition of chlorine to vinyltrichlorosilane. Vinyltrichlorosilane, (161.5 g., 1.0 mole) was placed in the usual apparatus. The flask was cooled in an ice-bath and chlorine gas was slowly bubbled into the solution until the contents had increased by 65.0 g. (0.91 mole of chlorine). The solution was fractionated yielding a fraction which was probably α,β-dichloroethyltrichlorosilane, b.p. 179° (750 mm.), yield 161.6 g., 76.2%. Silicon analyses did not check and because of the apparent ease of hydrolysis of the silane chlorines, values of refractive index and density were discounted.

Anal. Calc'd for $C_2H_3Cl_5Si$: Cl, 61.03. Found: Cl, 61.37, 60.67, 60.90.

Reaction of α,β-dichloroethyltrichlorosilane with ethyl alcohol. Under conditions similar to the above, 116 g. (0.5 mole) of α,β-dichloroethyltrichlorosilane was allowed to react with 92.0 g. (2.0 mole) of anhydrous ethyl alcohol. Refluxing for one hour completed the reaction.

TABLE I

PHYSICAL PROPERTIES OF HALOSILANES AND DERIVATIVES

COMPOUND	B.P., °C.	MM.	n_D^{25}	d_4^{25}
$CH_2ClCHClSiCl_3$	179	750		
	177–178	745		
$CH_2ClCHClSi(OC_2H_5)_3$	120	9	1.4308	1.1130
$Si(OC_2H_5)_4$	163–165	745	1.3811	0.9256
$CH_2{=}CClSi(OC_2H_5)_3$	175–176	748	1.4122	1.0123
	175–176	750	1.4128	1.0120
$CH_2{=}CClSiCl_3$	123–124	745		
$CH_2BrCHBrSiCl_3$	209–211	745		
$CH_2BrCHBrSi(OC_2H_5)_3$	112–113	2	1.4600	1.4430
$CH_2{=}CBrSi(OC_2H_5)_3$	78.5–79.0	5.5	1.4321	1.1951

Fractionation yielded α,β-dichloroethyltriethoxysilane, b.p. 120° (9 mm.), n_D^{25} 1.4308, d_4^{25} 1.1130, yield 104.0 g., 80%.

Anal. Calc'd for $C_8H_{18}Cl_2O_3Si$: Si, 10.74; Titrable Cl, 13.37;. MR. 60.76.

Found: Si, 10.84, 11.00; Titrable Cl, 13.57, 13.62, 13.67; M.R., 60.73.

Reaction of α,β-dichloroethyltriethoxysilane with sodium ethoxide. In a flask cooled by ice, 52.2 g. (0.2 mole) of α,β-dichloroethyltriethoxysilane was treated with 9.2 g. (0.4 mole) of sodium in 178 g. of dry ethyl alcohol. After refluxing for two hours, a few grams of liquid was found in the Dry Ice-acetone trap connected to the reflux condenser. This liquid had b.p. $-10°$ (uncorr.). Vinyl chloride has b.p. $-12°$. Distillation gave tetraethoxysilane, b.p. 163–165° (745 mm.), n_D^{25} 1.3811, d_4^{25} 0.9256, yield 31.0 g.

Anal. Calc'd for $C_8H_{20}O_4Si$: Si, 13.46; M.R., 51.84 (3).

Found: Si, 13.02, 13.03; M.R., 52.27.

Interaction of α,β-dichloroethyltriethoxysilane and quinoline. Similarly, 26.1 g. (0.1 mole) of α,β-dichloroethyltriethoxysilane was allowed to react with 12.9 g. (0.1 mole) of anhydrous quinoline. After refluxing for two hours at 180–190° and filtration of quinoline hydrochloride, fractionation gave α-chlorovinyltriethoxysilane, b.p. 175–176° (748 mm.), n_D^{25} 1.4122, d_4^{25} 1.0123, yield 4.0 g., 18%.

Anal. Calc'd for $C_8H_{17}ClO_3Si$: Si, 12.48; Cl, 15.78; M.R., 55.45 (3).

Found: Si, 12.41, 12.07; Cl, 15.80, 15.55; M.R., 55.27.

Interaction of α,β-dichloroethyltrichlorosilane and quinoline. Reaction similar to the above, between 42.8 g. (0.18 mole) of α,β-dichloroethyltrichlorosilane and 23.2 g. (0.18 mole) of anhydrous quinoline resulted in the formation of α-chlorovinyltrichlorosilane, b.p. 123–124° (745 mm.), 18.0 g. As in the case of α,β-dichloroethyltrichlorosilane, analysis was limited in its scope.

Anal. Calc'd for $C_2H_2Cl_4Si$: Cl, 54.29. Found: Cl, 54.54, 54.66.

Interaction of α-chlorovinyltrichlorosilane and ethyl alcohol. α-Chlorovinyltrichlorosilane (14.0 g., 0.071 mole) reacted with 16.3 g. (0.36 mole) of anhydrous ethyl alcohol to form, after a 30-minute reflux, α-chlorovinyltriethoxysilane, b.p. 175–176° (750 mm.), n_D^{25} 1.4128, d_4^{25} 1.0120, yield 7.8 g., 49%.

Anal. Calc'd for $C_8H_{18}ClO_3Si$: Si, 12.48; M.R., 55.43 (3).

Found: Si, 12.42, 12.51; M.R., 55.36.

Interaction of chlorine, bromine, and vinyltrichlorosilane. Vinyltrichlorosilane (97.0 g., 0.6 mole) was treated with 40.0 g. (0.5 mole) of bromine dropwise while, at the same time, chlorine gas was bubbled through at such a rate as to keep the bromine solution a light yellow color. The addition required one hour. The reaction was exothermic and external cooling of the flask with ice-water was necessary. Fractionation yielded 21.0 g. of unreacted vinyltrichlorosilane, 36.2 g. of α,β-dichloroethyltrichlorosilane, and 60.8 g. of α,β-dibromoethyltrichlorosilane, b.p. 209–211° (745 mm.). The compound was analyzed only for titratable halogen.

Anal. Calc'd for $C_2H_3Cl_3Br_2Si$: Titratable Cl, 33.11; Titratable Br, 24.87.

Found: Titratable Cl, 33.05, 33.84; Titratable Br, 24.85, 25.48.

The action of ethyl alcohol on α,β-dibromoethyltrichlorosilane. α,β-Dibromoethyltrichlorosilane (58.0 g., 0.18 mole) reacted, as above, with 34.5 g. (0.75 mole) of anhydrous ethyl alcohol forming, after a one hour reflux, α,β-dibromoethyltriethoxysilane, b.p. 112–113° (2 mm.), n_D^{25} 1.4600, d^{25} 1.4430, yield 29.0 g., 46%.

Anal. Calc'd for $C_8H_{18}Br_2O_3Si$: Si, 8.01; Titratable Br, 22.82; M.R., 66.44 (3).

Found: Si, 7.92, 8.35; Titratable Br, 22.98, 22.60; M.R., 66.46.

Interaction of α,β-dibromoethyltriethoxysilane and quinoline. α,β-Dibromoethyltriethoxysilane (29.0 g., 0.083 mole) reacted with 10.32 g. (0.080 mole) of dry quinoline to form, after a one hour reflux, bromovinyltriethoxysilane (probably *alpha*-bromo), b.p. 78.5–79.0° (5.5 mm.), n_D^{25} 1.4321, d_4^{25} 1.1951, yield 5.0 g., 22%.

Anal. Calc'd for $C_8H_{17}BrO_3Si$: Si, 10.42; M.R., 58.29 (3).

Found: Si, 10.61, 10.76; M.R., 58.45.

Supplies of *vinyltrichlorosilane* were made available through the courtesy of the Linde Air Products Co.

Titrable halogens were calculated on the assumption that all halogen atoms connected to silicon and one of the two found in the ethyl group (probably the β) would be capable of hydrolysis in alkali.

SUMMARY

1. Chlorine adds to vinyltrichlorosilane to form α,β-dichloroethyltrichlorosilane. α,β-Dibromoethyltrichlorosilane results from the action of a mixture of chlorine and bromine, always with a small amount of the pentachloro compound.

2. Anhydrous ethyl alcohol reacts with α,β-dichloroethyltrichlorosilane and with α,β-dibromoethyltrichlorosilane to form the corresponding triethoxysilanes. Chlorovinyltrichlorosilane (probably *alpha*-chloro) reacts to form chlorovinyltriethoxysilane. When sodium ethoxide reacts with α,β-dichloroethyltriethoxysilane, tetraethoxysilane and vinyl chloride are formed.

3. Three dehydrohalogenations are reported, through the action of quinoline — α,β-dichloroethyltriethoxysilane to chlorovinyltriethoxysilane, α,β-dichloroethyltrichlorosilane to chlorovinyltrichlorosilane, and α,β-dibromoethyltriethoxysilane to bromovinyltriethoxysilane. The halogens in these products were probably attached to the *alpha*-carbon, although definite proof is not yet available.

BUFFALO, NEW YORK

BIBLIOGRAPHY

(1) NAGEL AND POST, *J. Org. Chem.*, **17**, this issue, paper XXI (1952).

(2) NAGEL AND POST, *J. Org. Chem.*, **17**, this issue, paper XXII (1952).

(3) WARRICK, *J. Am. Chem. Soc.*, **68**, 2455 (1946).