[CONTRIBUTION FROM THE UNIVERSITY OF BUFFALO]

STUDIES IN SILICO-ORGANIC COMPOUNDS. XVIII. THE PREPARATION AND PROPERTIES OF VINYLTRIALKOXYSILANES

ROGER NAGEL, CHRIST TAMBORSKI, AND HOWARD W. POST

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INTRODUCTION

This paper reports the preparation and lists the simple physical properties of vinyltrimethoxysilane and its triethoxy, tri-*n*-propoxy, triisopropoxy, tri-*n*-butoxy, tri-sec-butoxy, triisobutoxy, and tri-*n*-amoxy homologs.

These compounds were prepared by the action of the proper anhydrous alcohol on vinyltrichlorosilane. Each product was prepared by two procedures, one with no reagents present other than alcohol and vinyltrichlorosilane and one carried out in the presence of pyridine. Physical properties will be found summarized in Table I and yields, by both processes, in Table II. Yields from the runs in which pyridine was used showed a maximum for the *n*-propyl derivative with falling yields as the radical weights varied above and below propyl. This might have been expected. Yields from the runs carried out without pyridine do not lend themselves to generalization. It is possible that free hydrogen chloride acted on the unsaturated vinyl group to produce secondary reactions or that there could have been hydrolysis with water resulting from the interaction of acid and alcohol.

EXPERIMENTAL

Vinyltrimethoxysilane. Anhydrous methyl alcohol (79 cc., 1.95 moles) was placed in a 1000 cc. three-necked round bottom flask fitted with a mercury sealed stirrer, water cooled condenser and dropping funnel. Vinyltrichlorosilane (76 cc., 0.5 mole) was added slowly with stirring. The reaction proceeded easily. After the complete addition of vinyltrichlorosilane, the reaction mixture was refluxed for 8 hours to drive off hydrogen chloride. Excess methyl alcohol was removed and the remainder of the liquid was further distilled at reduced pressures. Vinyltrimethoxysilane was isolated, b.p. 52.9° (49 mm.), 59.5° (62 mm.), n_D^{25} 1.3910, d_4^{25} 0.9669, 49 g., yield 55.2%.

Anal. Calc'd for $C_5H_{12}O_3Si$: Si, 18.93; M.R., 36.72 (1).

Found: Si, 18.88; M.R., 36.42.

1,3-Divinyltetramethoxydisiloxane was also isolated, b.p. 120.0–120.6° (46.0 mm.), n_D^{25} 1.4172, d_4^{25} 1.0627, 15.5 g., yield 20.6%.

Anal. Calc'd for $C_8H_{18}O_5Si_2$: Si, 22.42; M.R., 60.28 (1).

Found: Si, 22.52; M.R., 59.28.

Because of the low value for M.R., found, it was felt that this product was slightly contaminated with higher polymers.

For the reaction with pyridine, all of the chlorosilane (1.0 mole) and one half of the pyridine (1.75 moles) were placed in the apparatus as above. The flask was cooled in an ice bath, and the alcohol (4.6 moles) and pyridine (1.75 moles) mixture was run in over a period of 30 minutes. A white precipitate of pyridine hydrochloride was immediately formed. After complete addition, the system was refluxed for 30 minutes, filtered and the product isolated as above, giving vinyltrimethoxysilane, yield 42%.

Vinyltriethoxysilane. Vinyltrichlorosilane (0.42 mole), absolute ethyl alcohol (2.20 moles), and pyridine (1.40 moles) were used. Vinyltriethoxysilane was isolated, b.p. 62.5–63.0° (20 mm.), n_D^{25} 1.3960, d_4^{25} 0.9027, 48.0 g., yield 60.1%; without pyridine 50%.

TABLE I

PHYSICAL PROPERTIES

COMPOUND	B.P., °C	MM.	n_D^{25}	d_4^{25}
CH_2=CHSi$(OCH_3)_3$	53.9	49	1.3910	0.9669
	59.9	62		
	123	760		
CH_2=CHSi$(OC_2H_5)_3$	62.5– 63.0	20	1.3960	0.9027
CH_2=CHSi$(OC_3H_7$-$n)_3$	103.0–103.5	20	1.4088	0.8903
CH_2=CHSi$(OC_3H_7$-iso$)_3$	59.7	4	1.3961	0.8627
	77.5	20		
CH_2=CHSi$(OC_4H_9$-$n)_3$	120.5	8	1.4181	0.8820
	141.5	20		
CH_2=CHSi$(OC_4H_9$-iso$)_3$	111.0	6.5	1.4130	0.8718
CH_2=CHSi$(OC_4H_9$-sec$)_3$	100.5	8	1.4155	0.8767
CH_2=CHSi$(OC_5H_{11}$-$n)_3$	147–148	7	1.4265	0.8797
	159.0	9		

TABLE II

YIELDS, %

COMPOUND	WITH C_5H_5N	WITHOUT C_5H_5N
CH_2=CHSi$(OCH_3)_3$	42	55
CH_2=CHSi$(OC_2H_5)_3$	60.1	50.4
CH_2=CHSi$(OC_3H_7$-$n)_3$	77.5	73
CH_2=CHSi$(OC_3H_7$-iso$)_3$	73.1	63
CH_2=CHSi$(OC_4H_9$-$n)_3$	64.4	64.2
CH_2=CHSi$(OC_4H_9$-iso$)_3$	63.5	61.6
CH_2=CHSi$(OC_4H_9$-sec$)_3$	53.5	71.7
CH_2=CHSi$(OC_5H_{11}$-$n)_3$	44.7	64.5

TABLE III

PHYSICAL PROPERTIES, DISILOXANES

COMPOUND	B.P., °C	MM.	n_D^{25}	d_4^{25}
$[CH_2$=CHSi$(OCH_3)_2]_2O$	120.0–120.6	46	1.4172	1.0627
$[CH_2$=CHSi$(OC_2H_5)_2]_2O$	119	19	1.4100	0.9618
$[CH_2$=CHSi$(OC_5H_{11}$-$n]_2)_2O$	199	7	1.4308	0.9150

Anal. Calc'd for $C_8H_{14}O_3Si$: Si, 14.73; M.R., 50.61.
Found: Si, 14.14, 14.43; M.R., 50.65.

1,3-Divinyltetraethoxydisiloxane. This compound was isolated from the reaction by which vinyltriethoxysilane was prepared without pyridine, b.p. 119° (19 mm.), n_D^{25} 1.4100, d_4^{25} 0.9618, yield 20%.

Anal. Calc'd for $C_{12}H_{29}O_5Si_2$: Si, 18.31; M.R., 78.80.
Found: Si, 18.35; M.R., 78.95.

This synthesis was checked by refluxing 0.36 mole of vinyltriethoxysilane with 0.18 mole of water for 2 hours at 85–90°. Fractionation yielded 1,3-divinyltetraethoxydisiloxane, b.p. 117–119° (19 mm.), n_D^{25} 1.4100, 12.7 g., yield 23.2%.

Vinyltri-n-propoxysilane. Similarly, 0.30 mole of vinyltrichlorosilane, 1.40 moles of dry *n*-propyl alcohol and 1.00 mole of pyridine reacted to form vinyltri-*n*-propoxysilane, b.p. 103–103.5° (20 mm.), n_D^{25} 1.4088, d_4^{25} 0.8903, 54.0 g., yield 77.5%; without pyridine 73%.

Anal. Calc'd for $C_{11}H_{24}O_3Si$: Si, 12.06; M.R., 64.50.
Found: Si, 12.38; M.R., 64.50.

Vinyltriisopropoxysilane. In the same manner, 1.40 moles of anhydrous isopropyl alcohol was refluxed with 0.30 mole of vinyltrichlorosilane and 1.00 mole of pyridine, then distilled, yielding vinyltriisopropoxysilane, b.p. 77.5° (20 mm.), n_D^{25} 1.3961, d_4^{25} 0.8627, yield 73% (without pyridine yield 63%).

Anal. Calc'd for $C_{11}H_{24}O_3Si$: Si, 12.08; M.R., 64.50 (1).
Found: Si, 11.78, 12.01; M.R., 64.74.

Vinyltri-n-butoxysilane. Dry *n*-butyl alcohol (1.00 mole) was refluxed, as above, with 0.20 mole of vinyltrichlorosilane and 0.70 mole of pyridine. Distillation produced vinyltri-*n*-butoxysilane, b.p. 141.5° (20 mm.), n_D^{25} 1.4181, d_4^{25} 0.8820, yield 64.4% (without pyridine yield 64.2%).

Anal. Calc'd for $C_{14}H_{30}O_3Si$: Si, 10.23; M.R., 78.39 (1).
Found: Si, 10.64, 10.32; M.R., 78.45.

Vinyltri-sec-butoxysilane. In similar manner, 0.51 mole of dry sec-butyl alcohol reacted with 0.30 mole of vinyltrichlorosilane and 0.48 mole of pyridine, forming vinyltri-sec-butoxysilane, b.p. 100.5° (8 mm.), n_D^{25} 1.4155, d_4^{25} 0.8767, 44 g., yield 53.5% (without pyridine yield 71.7%).

Anal. Calc'd for $C_{14}H_{30}O_3Si$: Si, 10.23; M.R., 78.39 (1).
Found: Si, 10.09; M.R., 78.25.

Vinyltriisobutoxysilane. Reacting as indicated above, 47 cc. (0.51 mole) of anhydrous isobutyl alcohol, 38 cc. (0.30 mole) of vinyltrichlorosilane and 38.2 cc. (0.48 mole) of pyridine formed vinyltriisobutoxysilane, b.p. 111.0° (6.5 mm.), n_D^{25} 1.4130, d_4^{25} 0.8718, 87.2 g., yield 63.5% (without pyridine yield 61.6%).

Anal. Calc'd for $C_{14}H_{30}O_3Si$: Si, 10.23; M.R., 78.39 (1).
Found: Si, 10.12; M.R., 78.48.

Vinyltri-n-amoxysilane. From the interaction of 1.00 mole of anhydrous *n*-amyl alcohol, 0.20 mole of vinyltrichlorosilane, and 0.70 mole of pyridine, vinyltri-*n*-amoxysilane was obtained, b.p. 147°–148° (7 mm.), n_D^{25} 1.4265, d_4^{25} 0.8797, yield 44.7% (without pyridine yield 64.5%).

Anal. Calc'd for $C_{17}H_{36}O_3Si$: Si; 8.87: M.R., 92.28 (1).
Found: Si, 9.00, 8.99; M.R., 92.31.

1,3-Divinyltetra-n-amoxydisiloxane. In addition, from the reaction above, 1,3-divinyltetra-*n*-amoxydisiloxane was isolated, b.p. 199° (7 mm.), n_D^{25} 1.4308, d_4^{25} 0.9150, 8.5 g., yield 18%.

Anal. Calc'd for $C_{24}H_{48}O_5Si_2$: Si, 11.82; M.R., 134.36 (1).
Found: Si, 11.86, 11.65; M.R., 134.29.

Alcohols were purchased, and rendered anhydrous by standard procedures. Their physical constants were satisfactory. The authors are indebted to Linde Air Products Co., for the gift of sufficient vinyltrichlorosilane.

SUMMARY

I. Anhydrous methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, sec-butyl, isobutyl and *n*-amyl alcohols have reacted with vinyltrichlorosilane in the presence of pyridine to form the corresponding vinyltrialkoxysilanes in good yields.

2. The same reaction, without pyridine gave erratic results.

3. 1,3-Divinyltetraalkoxydisiloxanes were isolated as by-products from the reactions using methyl, ethyl and *n*-amyl alcohols.

BUFFALO, N. Y.

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