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

STUDIES IN SILICO-ORGANIC COMPOUNDS. XII. THE ACTION OF CERTAIN ALIPHATIC ALCOHOLS ON TRIALKOXYSILANES[1, 2]

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INTRODUCTION

Interaction of aliphatic alcohols with polyalkoxysilanes is a common reaction (1–4). Analogous and related reactions of the trialkoxysilanes however have received only relatively slight attention (5, 6).

In this work, simple aliphatic alcohols were allowed to react with trialkoxysilanes with resultant exchange of alkoxyl radicals. In addition the hydrolysis of a few trialkoxysilanes was also studied.

DISCUSSION

True adherence to the laws of distribution would require that four different polyethers should be formed when three moles of an aliphatic alcohol are brought into contact with one mole of a trialkoxysilane. It was the purpose of this work to isolate only pure compounds from this type of reaction, hence in most runs, only one mole of alcohol was mixed with one of trialkoxysilane. The probability that interaction of ROH and $HSi(OR')_3$ in 1:1 molar proportions would produce $HSi(OR)_2OR'$ and $HSi(OR)_3$ is very low. In some runs in which two moles of alcohol were used for each mole of polyether, $HSi(OR')_2OR$ was also isolated in major quantities while in others using the same proportions, it was not possible to isolate this homolog in a pure state. In the latter case, $HSi(OR)_2OR'$ was found.

Hydrolysis, at neutrality, of triethoxysilane, tri-*n*-propoxysilane, and tri-*n*-butoxysilane produced the corresponding hexaalkoxydisiloxane in each case. Compounds of higher molecular weight, probably the tetra- and penta-siloxane, were isolated from the hydrolysis of tri-*n*-butoxysilane however in yields greater than that of the disiloxane. Tri-*n*-amoxysilane yielded only highly polymerized material. Data covering these products are recorded in Table II.

The hydrolytic systems were not homogeneous.

EXPERIMENTAL

Triethoxysilane and n-propyl alcohol. Triethoxysilane, (38 g., 0.23 mole) in 50 cc. of anhydrous ether, was treated with 14 cc. (0.23 mole) of anhydrous *n*-propyl alcohol. Protected from moisture, the mixture was refluxed for ten hours, then fractionated, yielding 7 g. of diethoxy-*n*-propoxysilane, b.p. 140–145° (750 mm.), n_D^{25} 1.3817, d_4^{25} 0.8811; yield, 17%.

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[2] Submitted by the first author to the Graduate School of Arts and Sciences of the University of Buffalo in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Anal. Calc'd for $C_7H_{18}O_3Si$: Si, 15.7; Silane H, 0.562; M.R., 46.71 (7).
Found: Si, 15.3; Silane H, 0.565; M.R., 46.92.

Repetition of the above experiment using 0.46 mole of *n*-propyl alcohol yielded 7 g. of di-*n*-propoxyethoxysilane, b.p. 162–165° (745 mm.), n_D^{25} 1.3878, d_4^{25} 0.8804; yield, 16%.

Anal. Calc'd for $C_8H_{20}O_3Si$: Si, 14.6; Silane H, 0.522; M.R., 51.34 (7).
Found: Si, 14.5; Silane H, 0.527; M.R., 51.30.

Triethoxysilane and n-butyl alcohol. The only isolable product from this reaction, carried out as above, in 1:1 molar ratio, was 7 g. of di-*n*-butoxyethoxysilane, b.p. 188–195° (742 mm.), n_D^{25} 1.3980, d_4^{25} 0.8830; yield, 14%.

TABLE I

PHYSICAL PROPERTIES

REACTANT	PRODUCT	B.P., °C.	MM.	n_D^{25}	d_4^{25}
n-C_3H_7OH	$(C_2H_5O)_2SiH(OC_3H_7$-$n)$	140–145	750	1.3817	0.8811
2 n-C_3H_7OH	$(n$-$C_3H_7O)_2SiH(OC_2H_5)$	162–165	745	1.3878	.8804
n-C_4H_9OH	$(n$-$C_4H_9O)_2SiH(OC_2H_5)$	188–195	742	1.3980	.8830
n-$C_5H_{11}OH$	$(C_2H_5O)_2SiH(OC_5H_{11}$-$n)$	153–155	747	1.3858	.8773
n-C_4H_9OH	$(n$-$C_3H_7O)_2SiH(OC_4H_9$-$n)$	210–212	744	1.3987	.8794
2 n-C_4H_9OH	$(n$-$C_4H_9O)_2SiH(OC_3H_7$-$n)$	215–217	745	1.4025	.9685
n-$C_5H_{11}OH$	$(n$-$C_3H_7O)_2SiH(OC_5H_{11}$-$n)$	212–218	741	1.4025	.8724
2 n-$C_5H_{11}OH$	$(n$-$C_5H_{11}O)_2SiH(OC_3H_7$-$n)$	230–235	728	1.4100	.8742
n-$C_5H_{11}OH$	$(n$-$C_4H_9O)_2SiH(OC_5H_{11}$-$n)$	255–260	751	1.4127	.8739
2 n-$C_5H_{11}OH$	$(n$-$C_5H_{11}O)_2Si(OC_4H_9$-$n)_2$	146–149	7	1.4169	.8922

TABLE II

COMPOUNDS FORMED BY PARTIAL HYDROLYSIS

REACTANT	PRODUCT	B.P., °C.	MM.	n_D^{25}	d_4^{25}
$HSi(OC_2H_5)_3$	$[(C_2H_5O)_2SiH]_2O$	94–97	25	1.3864	0.9412
$HSi(OC_3H_7$-$n)_3$	$[(n$-$C_3H_7O)_2SiH]_2O$	131–133	13	1.4024	.9591
$HSi(OC_4H_9$-$n)_3$	$[(n$-$C_4H_9O)_2SiH]_2O$	146–150	6	1.4104	.9151
$HSi(OC_4H_9$-$n)_3$	$(n$-$C_4H_9O)_5Si_3H_3O_2$	155–160	7	1.4110	.9276
$HSi(OC_4H_9$-$n)_3$	$(n$-$C_4H_9O)_6Si_4H_4O_3$	175–179	10	1.4311	.9562

Anal. Calc'd for $C_{10}H_{24}O_3Si$: Si, 12.7; Silane H, 0.455; M.R., 60.60 (7).
Found: Si, 12.6; Silane H, 0.457; M.R., 60.09.

One fraction was collected which could have been diethoxy-*n*-butoxysilane but this could not be purified.

Triethoxysilane and n-amyl alcohol. The action of anhydrous *n*-amyl alcohol on triethoxysilane in 1:1 molar ratio formed 6 g. of diethoxy-*n*-amoxysilane, b.p. 153–155° (747 mm.), n_D^{25} 1.3858, d_4^{25} 0.8807; yield, 23%.

Anal. Calc'd for $C_9H_{22}O_3Si$: Si, 13.6; Silane H, 0.486; M.R., 55.97 (7).
Found: Si, 13.3; Silane H, 0.492; M.R., 55.19.

Reaction with double molar quantity of *n*-amyl alcohol produced nothing beyond diethoxy-*n*-amoxysilane.

Tri-n-propoxysilane and n-butyl alcohol. Equimolar amounts of these two compounds reacted, as described above, to form 10.7 g. of di-*n*-propoxy-*n*-butoxysilane, b.p. 210–212° (744 mm.), n_D^{25} 1.3987, d_4^{25} 0.8794; yield, 23%.

Anal. Calc'd for $C_{10}H_{24}O_3Si$: Si, 12.7; Silane H, 0.455; M.R., 60.62 (7).
Found: Si, 12.5; Silane H, 0.459; M.R., 60.86.

Reaction with a double quantity of *n*-butyl alcohol produced 5 g. of di-*n*-butoxy-*n*-propoxysilane, b.p. 215–217° (745 mm.), n_D^{25} 1.4025, d_4^{25} 0.8695; yield, 30%.

Anal. Calc'd for $C_{11}H_{26}O_3Si$: Si, 11.9; Silane H, 0.427; M.R., 65.23 (7).
Found: Si, 11.7; Silane H, 0.433; M.R., 65.60.

Tri-n-propoxysilane and n-amyl alcohol. Interacting as described above, in equimolar amounts, these two compounds formed 6 g. of di-*n*-propoxy-*n*-amoxysilane, b.p. 212–218° (741 mm.), n_D^{25} 1.4025, d_4^{25} 0.8724.

Anal. Calc'd for $C_{11}H_{26}O_3Si$: Si, 11.9; Silane H, 0.427; M.R., 65.23 (7).
Found: Si, 11.8; Silane H, 0.435; M.R., 65.32.

Using anhydrous *n*-amyl alcohol in double molar amounts, the product was di-*n*-amoxy-*n*-propoxysilane, 5.3 g., b.p. 235–240° (748 mm.), n_D^{25} 1.4100, d_4^{25} 0.8742; yield, 20%.

Anal. Calc'd for $C_{13}H_{20}O_3Si$: Si, 10.7; Silane H, 0.382; M.R., 74.48 (7).
Found: Si, 10.9; Silane H, 0.379; M.R., 74.40.

Tri-n-butoxysilane and n-amyl alcohol. Reacting in 1:1 molar ratio, these compounds formed 6 g. of di-*n*-butoxy-*n*-amoxysilane, b.p. 255–260° (751 mm.), n_D^{25} 1.4127, d_4^{25} 0.8739; yield, 16%.

Anal. Calc'd for $C_{16}H_{30}O_3Si$: Si, 10.7; Silane H, 0.382; M.R., 74.48 (7).
Found: Si, 10.4; Silane H, 0.379; M.R., 74.34.

Reaction using double molar quantities of the alcohol yielded 5 g. of di-*n*-amoxy di-*n*-butoxysilane, b.p. 146–149° (7 mm.), n_D^{25} 1.4169, d_4^{25} 0.8922, 13% yield.

Anal. Calc'd for $C_{14}H_{32}O_3Si$: Si, 8.05; Silane H, 0.00; M.R., 98.14 (7).
Found: Si, 8.17; Silane H, 0.04; M.R., 98.34.

Hydrolysis of triethoxysilane. Triethoxysilane (100 g., 0.625 mole) in 100 cc. of anhydrous ether, was refluxed for 24 hours with 5 cc. (0.28 mole) of water. Distillation gave 17 g. of 1,1,3,3-tetraethoxydisiloxane, b.p. found and literature (6) 94–97° (25 mm.), n_D^{25} found 1.3864, literature (6) 1.3950, d_4^{25} 0.9412, 23% yield.

Anal. Calc'd for $C_8H_{22}O_5Si_2$: Si, 22.0; Silane H, 0.788; M.R., 61.74 (7).
Found: Si, 21.6; Silane H, 0.790; M.R., 62.54.

Hydrolysis of tri-n-propoxysilane. In the same manner and in the same molar proportions, tri-*n*-propoxysilane was hydrolyzed with water, yielding 3.8 g. of 1,1,3,3-tetra-*n*-propoxydisiloxane, b.p. 131–133° (13 mm.), n_D^{25} 1.4024, d_4^{25} 0.9591, yield, 15%.

Anal. Calc'd for $C_{12}H_{30}O_5Si_2$: Si, 18.1; Silane H, 0.646; M.R., 80.26 (7).
Found: Si, 18.5; Silane H, 0.598; M.R., 78.55.

Hydrolysis of tri-n-butoxysilane. Hydrolysis of tri-*n*-butoxysilane, under conditions identical with the preceding, produced 1,1,3,3-tetra-*n*-butoxydisiloxane, 5.5 g., b.p. 146–150° (6 mm.), n_D^{25} 1.4104, d_4^{25} 0.9151; 20% yield.

Anal. Calc'd for $C_{16}H_{38}O_5Si_2$: Si, 15.3; Silane H, 0.546; M.R., 98.78 (7).
Found: Si, 14.9; Silane H, 0.510; M.R. 99.19.

In addition there were isolated fractions which probably were higher dehydration products. Analysis was not sufficient to determine their identities with exactness. There was less than 2 g. of probable 1,1,3,5,5-penta-*n*-butoxytrisiloxane, b.p. 155–160° (7 mm.), n_D^{25} 1.4110, d_4^{25} 0.9276.

Anal. Calc'd for $C_{20}H_{48}O_7Si_3$: Si, 17.2; Silane H, 0.620; M.R., 127.0 (7).
Found: Si, 16.8; Silane H, 0.611; M.R., 129.48.

The other high-boiling compound was probably 1,1,3,5,7,7-hexa-*n*-butoxytetrasiloxane, 5 g., b.p. 175–179° (10 mm.), n_D^{25} 1.4131, d_4^{25} 0.9562, 22% yield.

Anal. Calc'd for $C_{24}H_{58}O_9Si_4$: Si, 18.6; Silane H, 0.666; M.R., 156.62 (7).
Found: Si, 18.4; Silane H, 0.663; M.R., 157.02.

Hydrolysis of tri-n-amoxysilane. Similar treatment of this compound resulted in the formation of a mixture of polymeric substances assumed to exist in various stages of hydrolysis, perhaps as far as $(HSiO_{1.5})_x$.

SUMMARY

1. It has been shown that a reaction easily takes place between the simple aliphatic alcohols and various trialkoxysilanes. Triethoxy-, tri-*n*-propoxy-, and tri-*n*-butoxy-silane have been studied. Each has been allowed to react with *n*-propyl, *n*-butyl, and *n*-amyl alcohol.

2. The three trialkoxysilanes mentioned above, plus tri-*n*-amoxysilane, have been hydrolyzed with quantitative amounts of water. Under these conditions triethoxysilane and tri-*n*-propoxysilane form the corresponding disiloxanes, tri-*n*-butoxysilane hydrolyzes to what are probably the tetra- and penta-siloxane, and tri-*n*-amoxysilane hydrolyzes to polymerized material.

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