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

STUDIES IN SILICO-ORGANIC COMPOUNDS. XXIV. HYDROLYSIS AND DISPROPORTIONATION OF α- AND β-CHLOROETHYLTRIALKOXYSILANES

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INTRODUCTION

The hydrolysis of silicoörthoesters was probably first studied by von Ebelmann (6) in 1846, who reported that ethyl orthosilicate (tetraethoxysilane) reacted slowly with water forming ethanol and gelatinous silica. In 1897, Abati (7) confirmed this observation and prepared the intermediate disiloxane, hexa-*n*-propoxydisiloxane, through the medium of moist *n*-propyl alcohol and tetrachlorosilane.

Radical interchange was found to take place between two different silicoorthoesters in 1865 by Friedel and Crafts (8). Analogous reactions may be found, of later date (3–5).

DISCUSSION

The products of hydrolysis were obtained by four different routes. Water was added to chloroethyltrialkoxysilanes or to a reaction mixture containing chloroethyltrialkoxysilanes, 95% alcohol was reacted with chloroethyltrichlorosilane, absolutely dry methanol was reacted with chloroethyltrichlorosilane, or β-chloroethyltrichlorosilane was reacted with dry propanol in the presence of pyridine. In the last two cases, the disiloxane was apparently the product of the following type of reactions. These are by no means new (9). The fact that yields were never greater than 52% was ascribed to the formation of polysiloxanes in most cases.

$$ClCH_2CH_2SiCl_3 + 3\ ROH \rightarrow 3\ HCl + ClCH_2CH_2Si(OR)_3$$

$$ROH + HCl \rightarrow RCl + HOH$$

or

$$C_5H_5N + HCl \rightarrow C_5H_6NCl$$

$$C_5H_6NCl + ROH \rightarrow C_5H_5N + RCl + HOH$$

$$HOH + 2\ ClCH_2CH_2Si(OR)_3 \rightarrow 2\ ROH + [ClCH_2CH_2Si(OR)_2]_2O$$

Among the α-chloroethyl pair, the yield of disiloxane with R = CH_3 was 32% and with R = C_2H_5 11%. In the β-chloroethyl series, the yields were CH_3 32%, C_2H_5 15%, and $n\text{-}C_3H_7$ 15%.

Redistribution in the β-chloroethyltrialkoxyl series, brought about by reaction of two members having different alkoxyl groups resulted in all cases but one, in the isolation of two products. Not all of the alkoxyl was accounted for in the products, some having been lost in intermediate fractions. The following pairs interacted:

$CH_2ClCH_2Si(OCH_3)_3$ and $CH_2ClCH_2Si(OC_3H_7\text{-}n)_3$

$CH_2ClCH_2Si(OCH_3)_3$ and $CH_2ClCH_2Si(OC_4H_9\text{-}n)_3$

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$CH_2ClCH_2Si(OCH_3)_3$ and $CH_2ClCH_2Si(OC_5H_{11}\text{-}n)_3$
$CH_2ClCH_2Si(OC_2H_5)_3$ and $CH_2ClCH_2Si(OC_4H_9\text{-}n)_3$

EXPERIMENTAL

Di-α-chloroethyl-1,1,3,3-tetramethoxydisiloxane. α-Chloroethyltrichlorosilane (50 g., 0.253 mole) was allowed to react with 28 g. (0.875 mole) of methanol. After three hours of fluxing, 1.4 g. (0.078 mole) of water was added. Refluxing for about one hour was followed by fractionation yielding di-α-chloroethyl-1,1,3,3-tetramethoxydisiloxane, b.p. 105° (2 mm.), n_D^{25} 1.4284, d_4^{25} 1.176, yield 13.0 g., 32% (based on the amount of original silane used) 52% (on the water used).

TABLE I

PHYSICAL PROPERTIES OF THE α-CHLOROETHYL DISILOXANES $[CH_3CHClSi(OR)_2]_2O$

R	B.P., °C.	MM.	n_D^{25}	d_4^{25}
OCH_3	105	2	1.4284	1.176
OC_2H_5	132–133	5.5	1.4243	1.080

TABLE II

PHYSICAL PROPERTIES OF THE β-CHLOROETHYL DISILOXANES $[CH_2ClCH_2Si(OR)_2]_2O$

R	B.P., °C,	MM.	n_D^{25}	d_4^{25}
OCH_3	133	3	1.4333	1.189
OC_2H_5	134–135	1	1.4280	1.091
$OC_3H_7\text{-}n$	180–181	7	1.4330	1.045

TABLE III

PHYSICAL PROPERTIES OF THE β-CHLOROETHYLDIALKOXYALKOXYSILANES $CH_2ClCH_2Si(OR)_2OR'$

R	R′	B.P., °C.	MM.	n_D^{25}	d_4^{25}
OCH_3	$OC_3H_7\text{-}n$	102	18	1.4176	1.047
$OC_3H_7\text{-}n$	OCH_3	121.6	18	1.4196	1.006
OCH_3	$OC_4H_9\text{-}n$	103–105	10	1.4206	1.033
$OC_4H_9\text{-}n$	OCH_3	130–132	10	1.4244	0.9821
OC_2H_5	$OC_4H_9\text{-}n$	116	11	1.4193	.9828
$OC_4H_9\text{-}n$	OC_2H_5	137	11	1.4251	.9672
OCH_3	$OC_5H_{11}\text{-}n$	128.9	21	1.4245	1.029

Anal. Calc'd for $C_8H_{20}Cl_2O_5Si_2$: Si, 17.36; Cl, 21.94; M.R. 70.90.
Found: Si, 17.38, 17.59; Cl, 21.97, 22.11; M.R., 70.81.

Di-α-chloroethyl-1,1,3,3-tetraethoxydisiloxane. In a similar manner, 30 g. (0.150 mole) of α-chloroethyltrichlorosilane was allowed to react with 19 g. (0.413 mole) of 95% ethanol. Fractionation yielded di-α-chloroethyl-1,1,3,3-tetraethoxydisiloxane, b.p. 132–133° (5.5 mm.), n_D^{25} 1.4243, d_4^{25} 1.080, yield 3.0 g., 11% (on silane used).

Anal. Calc'd for $C_{12}H_{28}Cl_2O_5Si_2$: Si, 14.79; Cl, 18.69; M.R., 89.42.
Found: Si, 14.92, 14.99; Cl, 18.63, 18.74; M.R., 89.66.

Di-β-chloroethyl-1,1,3,3-tetramethoxydisiloxane. β-Chloroethyltrichlorosilane (50 g., 0.253 mole) was reacted with 37 g. (1.16 mole) of dry methanol by refluxing for several hours. The mixture was allowed to stand for one week, then fractionated yielding di-β-chloroethyl-1,1,3,3-tetramethoxydisiloxane, b.p. 133° (3 mm.), n_D^{25} 1.4333, d_4^{25} 1.189, yield 13.0 g., 32% (based on original silane).

Anal. Calc'd for $C_8H_{20}Cl_2O_5Si_2$: Si, 17.36; Cl, 21.94; M.R., 70.90.
Found: Si, 17.41, 17.20; Cl, 21.92, 22.03; M.R., 70.70.

No monosilanes were isolable.

Di-β-chloroethyl-1,1,3,3-tetraethoxydisiloxane. In a similar manner, 30 g. (0.151 mole) of β-chloroethyltrichlorosilane and 19 g. (0.413 mole) of 95% ethanol were allowed to interact, but without standing after refluxing. Distillation gave di-β-chloroethyl-1,1,3,3-tetraethoxydisiloxane, b.p. 134–135° (1 mm.), n_D^{25} 1.4280, d_4^{25} 1.091, yield 4.3 g., 15% (based on silane used). No monosilanes were isolable.

Anal. Calc'd for $C_{12}H_{28}Cl_2O_5Si_2$: Si, 14.79; Cl, 18.69; M.R., 89.42.
Found: Si, 14.87, 14.89; Cl, 18.65, 18.68; M.R., 89.46.

Di-β-chloroethyl-1,1,3,3-tetra-n-propoxydisiloxane. β-Chloroethyltrichlorosilane (50 g., 0.253 mole) and 44 g. (0.735 mole) of propanol-1 were reacted in benzene solution, along with 60 g. (0.76 mole) of pyridine. The silane, dissolved in 75 cc. of benzene, was added over one-half hour to the alcohol-pyridine mixture in 100 cc. of benzene with stirring and immersion of the reaction flask in an ice-bath. The system was then refluxed gently for one-half hour, cooled, filtered to remove pyridine hydrochloride, and distilled, yielding di-β-chloroethyl-1,1,3,3-tetra-*n*-propoxydisiloxane, b.p. 180–181° (7 mm.), n_D^{25} 1.4330, d_4^{25} 1.045, yield 8.5 g., 15% (on original silane).

Anal. Calc'd for $C_{16}H_{36}Cl_2O_5Si_2$: Si, 12.89; Cl, 16.23: M.R., 107.94.
Found: Si, 12.84, 12.93; Cl, 15.94, 16.13; M.R., 108.2.

No monosilanes were isolable.

β-Chloroethyldimethoxy-n-propoxysilane and β-chloroethylmethoxy-di-n-propoxysilane. β-Chloroethyltrimethoxysilane (16 g., 0.086 mole) and 30 g. (0.111 mole) of β-chloroethyltri-*n*-propoxysilane were allowed to interact by keeping the temperature of the mixture at 150° for 16 hours. Fractionation yielded, in addition to the two reactants, two other compounds, β-chloroethyldimethoxy-*n*-propoxysilane, b.p. 102° (18 mm.), n_D^{25} 1.4176, d_4^{25} 1.047, yield 5.3 g., and β-chloroethylmethoxydi-*n*-propoxysilane, b.p. 121.6° (18 mm.), n_D^{25} 1.4196, d_4^{25} 1.006, 4.5 g.

Anal. Calc'd for $C_7H_{17}ClO_3Si$: Si, 13.19; Cl, 16.67; M.R., 51.29.
Found: Si, 13.14, 13.01; Cl, 16.68, 16.69; M.R., 51.16.

Anal. Calc'd for $C_9H_{21}ClO_3Si$: Si, 11.65; Cl, 14.72; M.R., 60.55.
Found: Si, 11.58, 11.52; Cl, 14.92, 14.93; M.R., 60.55.

β-Chloroethyldimethoxy-n-butoxysilane and β-chloroethylmethoxydi-n-butoxysilane. As described above, 8.2 g. (0.044 mole) of β-chloroethyltrimethoxysilane and 6.9 g. (0.221 mole) of β-chloroethyltri-*n*-butoxysilane interacted to form β-chloroethyldimethoxy-*n*-butoxysilane, b.p. 103–105° (10 mm.), n_D^{25} 1.4206, d_4^{25} 1.033, yield 4.7 g. and β-chloroethylmethoxydi-*n*-butoxysilane, b.p. 130–132° (10 mm.), n_D^{25} 1.4244, d_4^{25} 0.9821, yield 4.0 g.

Anal. Calc'd for $C_8H_{19}ClO_3Si$: Si, 12.37; Cl, 15.64; M.R., 55.92.
Found: Si, 12.37, 12.27; Cl, 16.00, 16.02; M.R., 55.61.

Anal. Calc'd for $C_{11}H_{25}ClO_3Si$: Si, 10.44; Cl, 13.20, M.R., 69.81.
Found: Si, 10.40, 10.45; Cl, 13.32, 13.38; M.R., 69.90.

β-Chloroethyldiethoxy-n-butoxysilane and β-chloroethylethoxydi-n-butoxysilane. In a similar manner, 9.1 g. (0.040 mole) of β-chloroethyltriethoxysilane and 25 g. (0.080 mole) β-chloroethyltri-*n*-butoxysilane were allowed to interact forming β-chloroethyldiethoxy-*n*-butoxysilane, b.p. 116° (11 mm.), n_D^{25} 1.4193, d_4^{25} 0.9828, yield 3.0 g., and β-chloroethylethoxydi-*n*-butoxysilane, b.p. 137° (11 mm.), n_D^{25} 1.4251, d_4^{25} 0.9672, yield 8.7 g.

Anal. Calc'd for $C_{10}H_{23}ClO_3Si$: Si, 11.01; Cl, 13.92; M.R., 65.18.
Found: Si, 11.07, 11.07; Cl, 13.91, 13.98; M.R., 65.50.

Anal. Calc'd for $C_{12}H_{27}ClO_3Si$: Si, 9.92; Cl, 12.54; M.R., 74.44.
Found: Si, 9.82, 10.04; Cl, 12.44, 12.37; M.R., 74.79.

β-Chloroethyldimethoxy-n-amoxysilane. Redistribution between 13.5 g. (0.073 mole) of β-chloroethyltrimethoxysilane and 13 g. (0.036 mole) of β-chloroethyltri-*n*-amoxysilane was brought about by mixing the two compounds and heating for 18 hours just below reflux temperatures. The only isolable product was β-chloroethyldimethoxy-*n*-amoxysilane, b.p. 128.9° (21 mm.), n_D^{25} 1.4245, d_4^{25} 1.029, yield 4.7 g.

Anal. Calc'd for $C_9H_{21}ClO_3Si$: Si, 11.62; Cl, 14.68; M.R., 60.55

Found: Si, 11.66, 11.62; Cl, 14.81, 14.94; M.R., 60.21.

α- and β-Chloroethyltrichlorosilanes were purchased from reputable sources and their physical constants were found to be in satisfactory agreement with values previously published (1), *Silicon* and *chlorine* were determined in accordance with methods already in the literature (1). Warrick's (2) method for the determination of molecular refractions was used.

α-Chloroethyltrialkoxysilanes and their *beta* isomers were prepared in accordance with methods already in the literature (1).

SUMMARY

1. Partial hydrolysis of α-chloroethyltrimethoxysilane and its triethoxy homolog yields the corresponding tetraalkoxydisiloxane. Three β-chloroethyl compounds, the trimethoxy, triethoxy, and tri-*n*-propoxy homologs, react in the same manner.

2. The following pairs of compounds undergo redistribution with exchange of alkoxy groups:

$CH_2ClCH_2Si(OCH_3)_3$ and $CH_2ClCH_2Si(OC_3H_7\text{-}n)_3$
$CH_2ClCH_2Si(OCH_3)_3$ and $CH_2ClCH_2Si(OC_4H_9\text{-}n)_3$
$CH_2ClCH_2Si(OCH_3)_3$ and $CH_2ClCH_2Si(OC_5H_{11}\text{-}n)_3$
$CH_2ClCH_2Si(OC_2H_5)_3$ and $CH_2ClCH_2Si(OC_4H_9\text{-}n)_3$

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