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

STUDIES IN SILICO-ORGANIC COMPOUNDS. XIX. ALKOXYALKYLTRIALKOXYSILANES

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Received September 20, 1951

DISCUSSION

Kriebel and Elliott (1) have demonstrated the occurrence of alkaline cleavage of the chloromethyl group in chloromethylpolysiloxanes. Hydrolytic cleavage of the chloromethyl group in chloromethyltrimethylsilane was found by Speier (2) not to occur to any detectable extent under the influence of sodium methoxide in boiling methanol solution. On the other hand, methoxymethyltrimethylsilane was obtained in good yields. Sodium ethoxide in boiling ethanol caused a moderate amount of cleavage (11%) along with a 70% yield of the expected ethoxy compound. Sodium *n*-butoxide in *n*-butanol caused considerable cleavage with yields of 31% of *n*-butoxytrimethylsilane and 19% of the carbon ether. Indications are that α-chloroethyl silanes have much more reactive chlorines than do the chloromethyl silanes.

It has been shown (3) that the carbon-silicon bond in β-chloroethyltrichlorosilane is cleaved in the presence of sodium hydroxide to form ethylene. This property has been referred to as *beta* elimination and not hydrolysis. Furthermore, it has been found that Grignard reagents split the compound at the carbon-silicon bond. On the other hand, α-chloroethyltrichlorosilane (4) reacts with methylmagnesium bromide to give a 53% yield of α-chloroethyltrimethylsilane.

Since the chlorine connected to the carbon atom which is directly attached to silicon has been shown to resist alkaline cleavage to a large extent when acted upon by the essentially alkaline Grignard reagents and since sodium alkoxides do not cleave this group to any extent, it was expected that the action of sodium methoxide in excess methanol on α-chloroethyltrialkoxysilanes would produce the expected α-methoxyethyltrialkoxysilanes. The action of sodium ethoxide and of sodium *n*-propoxide was also investigated.

This assumption was justified and data covering the products will be found in Table I. However, α-chloroethyltri-*n*-amoxysilane was cleaved by sodium methoxide to form, probably, methoxytri-*n*-amoxysilane which then probably disproportionated to form tetra-*n*-amoxysilane. The latter was isolated and identified. Sodium ethoxide in ethanol reacted with α-chloroethyltri-*n*-amoxysilane to form a small amount of α-ethoxyethyltri-*n*-amoxysilane.

In three cases where the alkoxide matched the alkoxy group in the silane, yields of the expected ether were high. In many runs, however, low yields left much material unaccounted for but there were always unidentifiable products which showed no definite physical constants.

It is not clear why this type of cleavage and disproportionation, as described

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

above, did not appear in other syntheses as well as the one listed. Perhaps disproportionation products formed a large part of the unidentifiable products.

EXPERIMENTAL

α-Methoxyethyltrimethoxysilane. Sodium (1.89 g., 0.082 mole) was dissolved in an excess of anhydrous methanol. This solution was slowly added to 15.2 g. (0.082 mole) of α-chloroethyltrimethoxysilane over a period of 20 minutes with stirring. The system was fractionated yielding α-methoxyethyltrimethoxysilane, b.p. 156–157° (750 mm.), n_D^{25} 1.3952, d_4^{25} 0.9936; 5.4 g., yield 36%.

Anal. Calc'd for $C_6H_{16}O_4Si$: Si, 15.57; M.R., 43.59 (6).

Found: Si, 15.52, 15.44; M.R., 43.47.

α-Methoxyethylmethoxydiethoxysilane. α-Chloroethyltriethoxysilane (25.5 g., 0.112 mole) was allowed to react, as above, with 2.6 g. of sodium (0.113 mole) in absolute methanol. The system was refluxed for three hours. There was evidence or radical interchange in that the only isolable product was α-methoxyethylmethoxydiethoxysilane, b.p. 177–178° (740 mm.), n_D^{25} 1.3979, d_4^{25} 0.9543; 12.7 g., yield 54%.

TABLE I

Physical Properties

COMPOUND	B.P., °C.	MM.	n_D^{25}	d_4^{25}	YIELD, %
$CH_3CH(OCH_3)Si(OCH_3)_3$	156–157	750	1.3952	0.9936	36
$CH_3CH(OCH_3)Si(OC_2H_5)_2OCH_3$	177–178	740	1.3979	.9543	54
$CH_3CH(OC_2H_5)Si(OC_2H_5)_3$	128.6	94	1.4000	.9237	61
$CH_3CH(OCH_3)Si(OC_3H_7\text{-}n)_3$	85–86	1	1.4084	.9124	37
	93.5–94.5	4			
$CH_3CH(OC_3H_7\text{-}n)Si(OC_3H_7\text{-}n)_3$	122–123	10	1.4112	.8975	53
$CH_3CH(OCH_3)Si(OC_4H_9\text{-}n)_3$	113–114	2	1.4178	.9051	24
	125–126	4			
$CH_3CH(OCH_3)Si(OC_4H_9\text{-}n)_2OCH_3$	83–84	1	1.4131	.9253	9
$Si(OC_5H_{11}\text{-}n)_4$	149.0–150.5	4	1.4243	.9005	26
$CH_3CH(OC_2H_5)Si(OC_5H_{11}\text{-}n)_3$	122–123	1	1.4219	.8863	13

Anal. Calc'd for $C_8H_{20}O_4Si$: Si, 13.79; M.R., 52.85 (6).

Found: Si, 13.77, 13.74; M.R., 52.67.

The experiment was repeated without refluxing with the same result, producing α-methoxyethyldiethoxymethoxysilane, yield 60%.

α-Ethoxyethyltriethoxysilane. α-Chloroethyltriethoxysilane (49 g., 0.219 mole) and sodium ethoxide, containing 4.7 g. (0.205 mole) of sodium, in an excess of dry ethanol, were mixed as above then immediately fractionated yielding α-ethoxyethyltriethoxysilane, b.p. 128.6° (94 mm.), n_D^{25} 1.4000, d_4^{25} 0.9237; 25.0 g., yield 61%.

Anal. Calc'd for $C_{10}H_{24}O_4Si$: Si, 11.87; M.R., 62.21 (6).

Found: Si, 11.89, 11.86; M.R., 62.03.

α-Methoxyethyltri-n-propoxysilane. α-Chloroethyltri-*n*-propoxysilane (13.3 g., 0.050 mole) was mixed with an absolute methanolic solution of sodium methoxide containing 1.1 g., (0.048 mole) of sodium. Fractionation followed directly giving α-methoxyethyltri-*n*-propoxysilane, b.p. 85–86° (1 mm.), 93.5–94.5° (4 mm.), n_D^{25} 1.4084, d_4^{25} 0.9124; 4.8 g., yield 37%.

Anal. Calc'd for $C_{12}H_{28}O_4Si$: Si, 10.61; M.R., 71.37 (6).

Found: Si, 10.57, 10.52; M.R., 71.54.

α-n-Propoxyethyltri-n-propoxysilane. α-Chloroethyltri-*n*-propoxysilane (12.8 g., 0.047 mole) was mixed with a solution of sodium *n*-propoxide in absolute *n*-propyl alcohol containing 1.1 g. (0.048 mole) of sodium and allowed to react for 15 minutes before distillation. α-*n*-Propoxyethyltri-*n*-propoxysilane was isolated, b.p. 122–123° (10 mm.), n_D^{25} 1.4112, d_4^{25} 0.8975; 7.3 g., yield 53%.

Anal. Calc'd for $C_{14}H_{32}O_4Si$: Si, 9.59; M.R., 80.63 (6).

Found: Si, 9.61, 9.62; M.R., 80.94.

α-Methoxyethyltri-n-butoxysilane. α-Chloroethyltri-*n*-butoxysilane (33 g., 0.106 mole) reacted with 2.44 g. (0.106 mole) of sodium (as sodium methoxide in absolute methanol) forming α-methoxyethyltri-*n*-butoxysilane, b.p. 113–114° (2 mm.), 125–126° (4 mm.), n_D^{25} 1.4178, d_4^{25} 0.9051; 9.4 g., yield 24%.

Anal. Calc'd for $C_{15}H_{34}O_4Si$: Si, 9.16; M.R., 85.26 (6).

Found: Si, 9.14, 9.18; M.R., 85.29.

α-Methoxyethylmethoxydi-n-butoxysilane. Intermediate fractions from the above synthesis were redistilled yielding α-methoxyethylmethoxydi-*n*-butoxysilane, b.p. 83–84° (1 mm.), n_D^{25} 1.4131, d_4^{25} 0.9253; 2.5 g., yield 9%.

Anal. Calc'd for $C_{12}H_{28}O_4Si$: Si, 10.62; M.R., 71.37 (6).

Found: Si, 10.76, 10.81; M.R., 71.27.

Tetra-n-amoxysilane. Sodium methoxide (1 g. of sodium, 0.044 mole) in absolute methanol was reacted with 17 g. (0.048 mole) of α-chloroethyltri-*n*-amoxysilane for 20 minutes at room temperature and the system was then fractionated. The only isolable product proved to be tetra-*n*-amoxysilane, b.p. 149.0–150.5° (4 mm.); literature (5) 145–150° (3 mm.); n_D^{25} 1.4243, d_4^{25} 0.9005, literature (5), 0.8933.

Anal. Calc'd for $C_{20}H_{44}O_4Si$: Si, 8.16; M.R., 97.40 (6).

Found: Si, 8.18, 8.24; M.R., 97.51.

α-Ethoxyethyltri-n-amoxysilane. Sodium (2 g., 0.087 mole) dissolved in excess absolute ethanol was reacted with 29.4 g. (0.083 mole) of α-chloroethyltri-*n*-amoxysilane over a period of 20 minutes at room temperature. α-Ethoxyethyltri-*n*-amoxysilane was isolated, b.p. 122–123° (1 mm.), n_D^{25} 1.4219, d_4^{25} 0.8863; 4.0 g., yield 13%.

Anal. Calc'd for $C_{19}H_{42}O_4Si$: Si, 7.74; M.R., 103.78 (6).

Found: Si, 7.71, 7.81; M.R., 103.90.

α-Chloroethyltrialkoxysilanes were prepared by methods already in the literature (7).

SUMMARY

1. Eight reactions are reported in which a sodium alkoxide reacts with an α-chloroethyltrialkoxysilane. In most cases the product was $CH_3CH(OR)Si(OR')_3$.

2. Sodium methoxide reacts with α-chloroethyltri-*n*-amoxysilane to form tetra-*n*-amoxysilane, probably by disproportionation.

3. With the same relative amount of alkoxide, sodium methoxide reacts with α-chloroethyltriethoxysilane to form α-methoxyethyldiethoxymethoxysilane. α-Methoxyethyldi-*n*-butoxymethoxysilane is isolable as a by-product of the action of sodium methoxide on α-chloroethyltri-*n*-butoxysilane.

4. Optimum yields of the products $CH_3CH(OR)Si(OR')_3$ are obtained when R and R′ are the same.

BUFFALO, NEW YORK

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