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Abstract

Full Text

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SYNTHESIS OF SILICON-OLEFIN OXIDES FROM CHLOROHYDRINS

The first oxide of silicon olefins (a γ,δ-secondary-primary oxide) was obtained only recently (^{1}) by the interaction of a Grignard reagent with an epichlorohydrin. The reaction here proceeded according to a very complex scheme, and the yields of the organosilicon chlorohydrin and oxide did not exceed 25–30%.

In the present investigation we have established that the interaction of Grignard reagents from silicon halides

$$\left[-\mathrm{Si} - (\mathrm{CH_2})_n\mathrm{MgX} \quad \begin{matrix} \backslash \\ \\ / \end{matrix} \right]$$

with monochloroacetone proceeds unambiguously, which made it possible for us to obtain tertiary-primary β-γ- and δ-ε-oxides already in high yield, 80–90%, according to the scheme:

$$\text{I.} \quad \mathrm{R_3Si[CH_2]_nMgX + CH_3COCH_2Cl \longrightarrow R_3Si[CH_2]_n - C(OH)(CH_3) - CH_2Cl},$$

$$\text{II.} \quad \mathrm{R_3Si(CH_2)_n{-}C(OH)(CH_3){-}CH_2{-}Cl \xrightarrow{NaOH} R_3Si{-}[CH_2]_n{-}C(CH_3)\overset{O}{\underline{\ \ }}CH_2}.$$

It is interesting to note that, in contrast to γ-δ- and δ-ε-halohydrins, β-γ-halohydrins under the action of NaOH give not oxides, but quantitatively unsaturated halides, formed according to the equation:

$$\mathrm{R_3Si{-}CH_2{-}C(OH)(CH_3){-}CH_2{-}Cl \xrightarrow{NaOH} R_3Si{-}CH_2{-}C(=CH_2){-}CH_2{-}Cl + H_2O}.$$

We succeeded in directing the reaction toward oxides here as well—either by replacing NaOH with $\mathrm{Ca(OH)_2}$, according to the reaction:

$$R_3Si-CH_2-C(OH)(CH_3)-CH_2-Cl \xrightarrow{Ca(OH)_2} R_3Si-CH_2-C(CH_3)\overset{O}{\underline{\quad}}CH_2$$

or by replacing the alkyl radical R with R_3SiO, according to the reaction:

$$R_3Si{-}O{-}Si(R)_2{-}CH_2{-}C(OH)(CH_3){-}CH_2{-}Cl \xrightarrow{NaOH} R_3Si{-}O{-}Si(R)_2{-}CH_2{-}C(CH_3)\overset{O}{\underline{\quad}}CH_2.$$

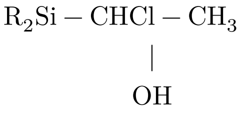
An attempt was made to obtain an α-β-bromohydrin by adding hypobromous acid to triethylvinylsilane. However, the reaction proceeded anomalously, and instead of the bromohydrin a dibromide was formed:

$$(C_2H_5)_3Si-CH=CH_2+2HOBr \longrightarrow (C_2H_5)_3Si-CHBr-CH_2Br.$$

Table 1

Substance No.	Formula	b.p., °C	Pressure, mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield, %	C, % found	C, % calc.	H, % found	H, % calc.	Si, % found	Si, % calc.	Cl, % found	Cl, % calc.	OH, % found	OH, % calc.
I	[illegible]	59–60	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.02
II	[illegible]	68–69	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
III	$CH_3(C_2H_5)_2Si-CH_2-C(OH)(CH_3)CH_2Cl$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–	–	–	[illegible]	[illegible]
IV	$(CH_3)_3Si-O-Si(CH_3)_2-CH_2-C(OH)(CH_3)-CH_2Cl$	67–67.5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–	–	–	1.06	1.03
V	[illegible]	95–95.5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
VI	[illegible]	104–105	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.01

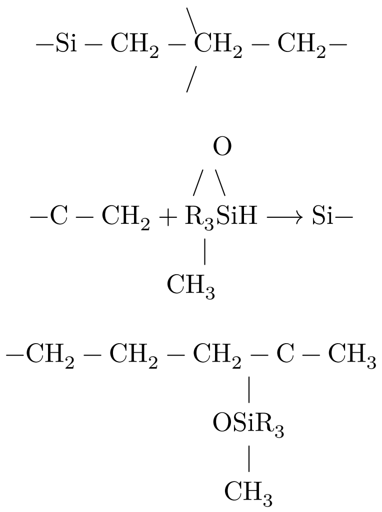
Analogous anomalous addition of HOBr was recently observed by I. N. Nazarov and A. A. Akhrem (^{2}) with 1-vinylcyclohexanol-1, which likewise formed a dibromide, whereas from the acetate of this alcohol a bromohydrin was obtained. An attempt to obtain the oxide from



$$\begin{array}{c} R_2Si-CHCl-CH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad OH \end{array}$$

also proved unsuccessful. Under the action of NaOH, hydrolysis of the Si–C bond occurred here, with formation of $R_2Si(OH)_2$; under the action of $Ca(OH)_2$ the starting compound underwent no changes and was recovered.

The δ,ε-oxide also readily added a silane hydride with formation of the simple ether (and not the alcohol), which was established from the negative value in the determination of the hydroxyl content:



$$-Si-CH_2-\overset{\diagdown}{\underset{/}{C}}H_2-CH_2-$$

$$\begin{array}{c} O \\ / \ \backslash \\ -C-CH_2+R_3SiH \longrightarrow Si- \\ | \\ CH_3 \end{array}$$

$$\begin{array}{c} -CH_2-CH_2-CH_2-C-CH_3 \\ | \\ OSiR_3 \\ | \\ CH_3 \end{array}$$

Experimental Part

3-Trimethylsilyl-1-chloro-2-methylpropanol-2 (I). To a Grignard reagent prepared from 24 g (1 mole) of magnesium and 122.5 g (1 mole) of α-chloromethyltrimethylsilane in 400 ml of abs. ether, at

Table 2

No. of substance	Formula	b.p., °C	Pressure, mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield, %	C, % found	C, % calc.	H, % found	H, % calc.	Si, % found	Si, % calc.
VII	[illegible]	207	755	1.4382	0.8484	57.67	57.70	80	64.25; 64.21	64.45	11.60; 11.84	11.87	15.17; 15.08	15.07
VIII	[illegible]	85– 86	3	1.4452	0.8658	62.18	62.33	90	64.88; 64.88	65.70	11.93; 11.85	12.07	14.89; 14.76	14.01
IX	[illegible]	71– 71.5	10	1.4160	0.8773	62.48	62.45	90	49.41; 49.50	49.54	10.03; 9.99	10.09	25.59; 25.94	25.68
X	[illegible]	67	10	1.4243	0.8338	44.18	43.81	52	58.01	58.30	10.93	11.11	18.89	19.44
XI	[illegible]	154	750	1.4309	0.8539	48.07	48.44	49	–	–	–	–	17.91	17.82

with cooling by ice and stirring, 92.5 g (1 mole) of freshly distilled monochloroacetone was added dropwise. The contents of the flask were then stirred for about an hour at room temperature and heated on a water bath for 2 hours. The resulting yellow product was decomposed with ice and 3% HCl. The ether layer was separated, washed twice with 3% Na_2CO_3 solution and then with water, and dried over Na_2SO_4. After distillation of the ether, the reaction product was fractionated in vacuum at 4 mm Hg: I fraction, 45-59°, 25 g; II fraction, 59-60°, 120 g; residue about 13 g (resin).

Under analogous conditions the following were obtained: 3-dimethylethylsilyl-1-chloro-2-methylpropanol-2 (II); 3-methyldiethylsilyl-1-chloro-2-methylpropanol-2 (III); 3-pentamethyldisiloxane-1-chloro-2-methylpropanol-2 (IV); 5-dimethylethylsilyl-1-chloro-2-methylpentanol-2 (V); 5-methyldiethylsilyl-1-chloro-2-methylpentanol-2 (VI). The properties of these compounds and the yields are given in Table 1.

Oxide of 5-dimethylethylsilyl-2-methylpentene-1-2 (VII). Into a 500-ml round-bottom flask equipped with a reflux condenser were placed 80 g of finely powdered NaOH, 250 ml of dry ether, and 110 g (0.58 mole). The contents of the flask were heated for 6 hours to the boiling point of the ether and were left for 12 hours, then filtered. After distillation of the ether, the reaction product was distilled on a column. 75 g of product with b.p. 85-85.5°/10 mm was isolated.

Under analogous conditions there were obtained: oxide of 5-methyldiethylsilyl-2-methylpentene-1-2 (VIII), oxide of 3-pentamethyldisiloxane-2-methylpropylene-1-2 (IX), and, under the action of $Ca(OH)_2$, oxides of trialkylsilylpropenes-1-2 (X, XI), the properties and yields of which are given in Table 2.

1-Chloro-2-methyltriethylsilylmethylpropene-1-2 (XII). 60 g of NaOH, 200 ml of dry ether, and 120 g of β-γ-chlorohydrin (III) were taken; the contents of the flask were boiled for 6 hours. 75 g of product were isolated with b.p. 205°/750 mm; n_D^{20} 1.4635; d_4^{20} 0.9085; MR_D found 57.87; MR_D calc. 57.80; yield 90%.

Found, %:	C 59.99; 57.16;	H 10.12; 10.20;	Si 15.29; 15.09
$C_9H_{19}SiCl$. Calculated, %:	C 56.69;	H 9.97;	Si 14.70

Combination light-scattering spectrum (cm^{-1}): 242 (1 sh), 380 (0), 455 (0), 484 (4), 527 (1), 580 (broad), 646 (0 sh), 665 (0 sh), 698 (1 sh), 752 (1 sh), 802 (0), 874 (0), 970 (3), 1013 (4), 1108 (5), 1132 (2), 1158 (5 sh), 1178 (3), 1194 (0), 1228 (2 sh), 1250 (1 sh), 1302 (4), 1376 (3), 1406 (3), 1436 (1), 1460 (4), 1631 (10), 2875 (8 sh), 2908 (8 sh), 2954 (6 sh), 3070 (2 sh).

Frequencies were found that occur in organosilicon compounds with an allylic position of the multiple bond at the end of the chain, namely the frequencies

1158, 1302, 1406, 1631, 3070 cm^{-1}, which make it possible to consider that the compound obtained has the structure

$$|\mathrm{CH_3}|\ |\mathrm{C_2H_5}|_2\mathrm{Si}-\mathrm{CH_2}-\mathrm{C}(=\mathrm{CH_2})-\mathrm{CH_2}-\mathrm{Cl}.$$

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Note: Figure translations are in progress. See original paper for figures.