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Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV and S. I. SADYKH-ZADE

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Abstract

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SYNTHESIS OF SILICON-CONTAINING VINYL ETHERS

Polymers of vinyl ethers, as is known, are raw materials for the synthesis of varnishes, adhesives, synthetic leather, etc. (1). Vinyl ethers are obtained by a very simple reaction:

$$\mathrm{R{-}OH + HC{\equiv}CH \xrightarrow{KOH} R{-}OCH{=}CH_2}, \qquad (1)$$

which, however, is not applicable to silanols $>\mathrm{Si{-}OH}$ because of the greater ease of hydrolytic decomposition of both alkoxy- and alkenyloxysilanes under the influence not only of electrophilic but also of nucleophilic reagents.

Vinylation by reaction (1) could be accomplished only in the case of such a silicon-containing alcohol as γ-hydroxypropyltrimethylsilane (2), where, owing to the considerable distance of the alcohol group from silicon, the latter no longer exerts an influence on the silicon. Similar examples of strengthening the molecule of organosilicon compounds by moving the functional group away from silicon have also been observed by us. Thus, for example, α-ethynylsilane (3) could not be hydrated by Kucherov' s method, whereas γ-butynylsilane $>\mathrm{Si{-}CH_2{-}CH_2C{\equiv}CH}$ gave the corresponding ketone in high yield (4). We must also note that in the case of silicon-acetylene (and silicon-allene) hydrocarbons —quite similarly to acetylene hydrocarbons—the triple bond under heating with Na migrated from the center to the periphery:

$$>\mathrm{Si{-}C{\equiv}C{-}CH_3 \xrightarrow{Na} {>}Si{-}CH_2{-}C{\equiv}CH}$$

$$>\mathrm{Si{-}CH_2{-}CH{=}C{=}CH_2 \xrightarrow{Na} {>}Si{-}CH_2{-}CH_2{-}C{\equiv}CH}.$$

However, the reverse migration from the periphery to the center, unlike in acetylene hydrocarbons, could not be effected here even in the case of γ-butynylsilane because of its decomposition:

$$>\mathrm{Si{-}CH_2{-}CH_2{-}C{\equiv}CH \xrightarrow[KOH]{H_2O} {>}Si{-}O{-}Si{<} + CH_3{-}CH_2{-}C{\equiv}CH}.$$

We have succeeded for the first time in the present investigation in carrying out the synthesis of vinyl ethers of the type >Si−O−CH=CH−R, where R_1 is alkyl or aryl, only by means of a new reaction, specific for the chemistry of organosilicon compounds: the addition of trialkylsilanes R_3SiH in the presence of H_2PtCl_6 to α,β-unsaturated aldehydes or ketones. It turned out that the addition reaction here proceeds in the 1,4-position, with R_3Si- adding to the carbonyl oxygen.

$$\mathrm{R_3SiH} + {}^1\mathrm{CH_2}{=}{}^2\mathrm{CH}{-}{}^3\mathrm{C}(={}^4\mathrm{O})\mathrm{H} \rightarrow \mathrm{CH_3{-}CH{=}CH{-}O{-}SiR_3}, \qquad (2)$$

$$\mathrm{R_3SiH + CH_2{=}CH{-}C(=O){-}CH_3 \rightarrow CH_3{-}CH{=}C(CH_3){-}O{-}SiR_3} \qquad (3)$$

Table 1

Compounds obtained	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	MRD, found	MRD, calc.	Yield, % of theory	Found, % C	Found, % H	Found, % Si	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % Si
β-Methylvinyloxytriethylsilane $(C_2H_5)_3Si-O-CH=CH-CH_3$	49-50/6	1.4320	0.8363	53.41	53.72	70.0	62.41	11.41	16.70	$C_9H_{20}SiO$	62.77	11.63	16.29
β-Benzylvinyloxytriethylsilane $(C_2H_5)_3SiO-CH=CH-CH_2-C_6H_5$	119-120/2	1.4960	0.9267	78.28	78.39	80	72.58	9.79	11.18	$C_{15}H_{24}SiO$	72.52	9.71	11.30

Compounds obtained	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.	Yield, % of theory	Found, % C	Found, % H	Found, % Si	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % Si
3-Methyl-1-cyclohexenyloxytriethylsilane $(C_2H_5)_3Si—O—$[[unclear: cyclohexenyl structural formula with CH_3 substituent]]	82–83/2	1.4568	0.8823	65.54	65.48	90	67.95 68.15	11.58 11.40	12.95 13.51	$C_{12}H_{24}OSi$	67.90	11.32	13.21
2-Methyl-1-cyclohexenyloxytriethylsilane $(C_2H_5)_3Si—O—$[[unclear: cyclohexenyl structural formula with CH_3 substituent]]	82–83/2	1.4550	0.8807	65.79	65.48	70				$C_{12}H_{24}OSi$	67.90	11.32	13.21

Addition by reaction (2) was carried out with acrylic and cinnamic aldehydes, and by reaction (3) with methyl vinyl ketone and methylcyclohexenone. Silicon-containing vinyl ethers are hydrolyzed with the same ease as vinyl ethers that do not contain silicon. They can be analyzed by oximation of the aldehydes (or ketones) formed as a result of hydrolysis; in place of alcohols, hexaalkyldisiloxanes are, naturally, obtained here.

In the presence of the same catalyst it was also possible to carry out addition of $C_2H_5HSiCl_2$ to acrylic aldehyde:

$$CH_2{=}CH{-}C\left(\begin{matrix}O\\ \backslash H\end{matrix}\right) + C_2H_5SiCl_2 \longrightarrow (C_2H_5)Cl_2Si{-}O{-}CH{=}CH{-}CH_3. \quad (4)$$

However, the ethylmethylvinyloxydichlorosilane formed immediately polymerized into a thick liquid of glycerol-like consistency. On hydrolysis of this polymer, a solid infusible polycondensation product was obtained, insoluble in ether and partially soluble in benzene. In an attempt to carry out reaction (4) in pyridine, the entire contents of the flask turned into a yellowish-white mass. Partly, this apparently homogeneous product dissolved in water. An oil separated, which quickly turned into an amorphous white product.

In order to prove the structure of the silicon-containing vinyl ethers obtained, they were subjected to hydrolysis in the presence of traces of sulfuric acid with gentle heating. For example, on hydrolysis of $(C_2H_5)_3Si{-}O{-}CH{=}CH{-}CH_3$, propionic aldehyde was isolated, b.p. 49-50°, which with 2,4-dinitrophenylhydrazine gave a hydrazone with m.p. 154-155°.

Literature data (^{5}): m.p. 155°. On hydrolysis of $(C_2H_5)_3Si{-}O{-}$

$$\begin{matrix}CH_3\\ |\end{matrix}$$

2-methylcyclohexanone was obtained,

$$=O$$

the hydrazone of which had m.p. 136-137°. Literature data (^{5}): m.p. 136°.

It should be noted that the method developed by us for the synthesis of vinyl ethers is also a new method for reducing α,β-unsaturated aldehydes and ketones to the corresponding saturated compounds.

Experimental Part

β-Methylvinyloxytriethylsilane. Into a one-liter flask equipped with a reflux condenser, protected by a calcium chloride tube, and a stirrer were placed 112 g of freshly distilled acrolein and 0.5 ml of a 0.1 N solution of chloroplatinic acid in isopropyl alcohol. Then, with continuous stirring, 20 g of $(C_2H_5)_3SiH$ was first added (out of a calculated 174 g). The temperature of the reaction mixture rose spontaneously to 35°. On subsequent heating on a water bath to 60°, the temperature inside the flask rose to 110°, as a result of which cooling had to be applied. Further addition of the remaining $(C_2H_5)_3SiH$ was carried out dropwise, the rate being regulated so that the temperature did not rise above 45°. The reaction was completed by heating for one hour to 120–140°. Under atmospheric pressure, unreacted acrolein and trialkylsilane were distilled off. The residue, amounting to 260 g, was distilled in vacuum at 6 mm. A small amount of $(C_2H_5)_3Si{-}O{-}Si(C_2H_5)_3$, about 40 g of polymer (residue), and 160 g of β-methylvinyloxytriethylsilane were isolated. A series of syntheses was carried out with other α, β-unsaturated aldehydes and ketones; they proceeded

under analogous conditions, but without self-heating. The properties of the obtained alkyl(aryl)vinyloxy- and cyclohexenyloxysilanes are presented in Table 1.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.