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SOME NEW ORGANOXY(ALKYL)ETHYNYLSILANES

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Ethynylalkoxysilanes enter into the transetherification reaction with the higher alcohols and phenols [1, 2].

In the present paper is described the acid-catalyzed reaction of dimethylethynylmethoxysilane with 1, 3dichloroisopropanol, 4-iodophenol, and 3, 5-xylenol, and also of methyl(vinyl)ethynylmethoxysilane with ethanol and n-propanol, as well as the reactions of methyldiethynylmethoxysilane with ethanol and methylethynyldimethoxysilane with n-butanol.

$$\begin{split} \text{ROH} &+ \text{CH}_{3}\text{O}(\text{CH}_{3})_{2}\text{SiC} \equiv \text{CH} \rightarrow \text{RO}(\text{CH}_{3})_{2}\text{SiC} \equiv \text{CH} \quad (I) - (III) \\ \text{R} &= (\text{CICH}_{2})_{2}\text{CH} (I), \quad 4\text{-IC}_{6}\text{H}_{4} (II), \quad 3,5\text{-}(\text{CH}_{3})_{2}\text{C}_{6}\text{H}_{3} \quad (III) \\ \text{ROH} &+ \text{CH}_{3}\text{O} (\text{CH}_{3})\text{Si}(\text{CH} = \text{CH}_{2})_{2-n} (\textbf{C} \equiv \text{CH})_{n} \rightarrow \\ & \rightarrow \text{RO}(\text{CH}_{3})\text{Si}(\text{CH} = \text{CH}_{2})_{2-n} (\textbf{C} \equiv \text{CH})_{n} (IV) - (VI) \\ \text{R} &= \text{C}_{2}\text{H}_{5} (IV), (VI), \quad \text{C}_{3}\text{H}_{7} (V); \quad n = 1 \quad (VI), \quad (V), \quad 2 \quad (VI) \\ & \quad 2\text{C}_{4}\text{H}_{9}\text{OH} + (\text{CH}_{3}\text{O})_{2}\text{Si}(\text{CH}_{3}) \quad (\textbf{C} \equiv \text{CH}) \rightarrow \\ & \rightarrow (\text{C}_{4}\text{H}_{9}\text{O})_{2}\text{Si}(\text{CH}_{3}) \quad (\textbf{C} \equiv \text{CH}) \quad (VII) \end{split}$$

The structure of the obtained compounds was confirmed by the IR spectra, in which are present the frequencies of the ethynyl group at 2045-2050 ($C \equiv C$) and 3285-3290 cm⁻¹ ($\equiv CH$), the SiC bond at 800-850 and 1250-1260 cm⁻¹, the SiOC bond at 1020 cm⁻¹ (compounds (II) and (III), and 1080-1100 cm⁻¹ [compounds (IV)-(VI)], the aromatic rings in (II) and (III) at 3070, 1580, 1475, 720-725 cm⁻¹, and the vinyl group in (IV) and (V) at 3050, 1600, 960 cm⁻¹.

Com - pound	Formula	Yield, %	bp, °C(p, mm Hg)	n _D ²⁰	d_{4}^{20}	Foun Calci C	d ilated H	, % Si	Empirical formula
						00.00	= 04	49.09	
(I)	(ClCH ₂) ₂ CHO(CH ₂) ₂ SiC=CH *	66,5	90 (20)	1,4570	1,1033	39,62	$\frac{5,01}{5,72}$	13,00	C ₇ H ₁₂ Cl ₂ OSi
(II)	4-IC ₆ H₄O(CH₃)₂SiC≡CH †	62,4	10 4 (1)	1,5580	1,4890	39,59 39,76	$\frac{3,72}{3,67}$	9,16 9,29	C ₁₀ H ₁₁ SiIO
(III)	3,5-(CH ₃) ₂ C ₆ H ₃ OSi(CH ₃) ₂ C≡CH	63,1	104 (8)	1,4925	0,9436	70,7 1 70,05	$\frac{7,78}{7,89}$	13,98 13,74	C12H18SIO
(IV)	C ₂ H ₅ OSi(CH ₃)(CH=CH ₂)C=CH	62,8	120 (740)	1,4220	0,8551	59,57 59,92	$\frac{8,72}{8,58}$	20,26	C7H12SiO
(V)	C ₂ H ₇ OSi(CH ₂)(CH=CH ₂)C=CH	68 ,1	60 (48)	1,4262	0,8446	61,39 62,23	9,15 9,26	18,33 18,20	C _s H ₃₄ SiO
(VI)	C ₂ H ₃ OSi(C=CH) ₂ CH ₃	66,1	124 (745)	1,4212	0,8664	60,50 60,83	$\frac{7,28}{7,30}$	20,03	C7H10SiO
(VII)	(C₄H₃O)₂Si(CH₃)C≡CH	68,9	74 (5)	1,4183	0,8636	61,62 61,36	10,34 10,34	13,10 13,03	C11H22SIO2

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*Found Cl 33.64%, calculated Cl 33.58%. †Found I.42.11%, calculated I 42%.

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EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrometer as a thin layer.

<u>1, 3-Dichloroisopropoxydimethylethynylsilane (I)</u>. A mixture of 6.3 g of 1, 3-dichloroisopropanol, 8 g of dimethylethynylmethoxysilane, and 0.05 g of p-toluenesulfonic acid was refluxed in the pot of a fractionating column, and the liberated methanol and excess dimethylethynylmethoxysilane were distilled off. Distillation of the residue gave 7.0 g (66.5%) of (I) (Table 1).

Compounds (II)-(VII) were obtained in a similar manner (Table 1).

CONCLUSIONS

Some ethynyl(organoxy)silanes were obtained by the transetherification of $CH_3O(CH_3)_2SiC \equiv CH$ with 1, 3dichloroisopropanol, 4-iodophenol, and 3, 5-xylenol, of $CH_3O(CH_3)Si(C \equiv CH)_2$ with ethanol, of $CH_3O(CH_3)Si(CH = CH_2)$ (C = CH) with ethanol and propanol, and of $CH_3(CH_3O)_2SiC \equiv CH$ with butanol.

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ELECTROPHILIC REACTIONS OF

3-HYDROXYISONICOTINIC ACID

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A study of the electrophilic substitution of hydroxypyridine acids is of interest for elucidating the effect of the COOH group on the reactivity of the hydroxypyridine ring and the direction of electrophilic reactions. The data given in [1-6] testify to a different reactivity of the α -, β -, and γ -hydroxypyridinecarboxylic acids. Besides this, the position of the COOH group also exerts a substantial effect on the ease with which electrophilic substitution progresses. Thus, the electrophilic reactions of 5-hydroxynicotinic acid proceed only in the 6 position [5]. At the same time, 5-hydroxypicolinic acid also forms the bis-substituted derivatives when iodinated [6].

We studied the electrophilic reactions of 3-hydroxyisonicotinic acid (I) and its ethyl ester (II). The halogenation of (I) was studied on the example of iodination, which was run in the presence of bases.

It proved that, depending on the reaction conditions and ratio of the reactants, either the mono- or diiodo derivatives of (I) can be formed. Thus, the iodination of (I) at ~20°C in aqueous ammonia solution leads mainly to iodide (III). 2,6-Diiodo-3-hydroxyisonicotinic acid (IV) is formed in high yield when (I) is heated in Na₂CO₃ solution with excess I₂ and KI. The iodination of (II) under these conditions is accompanied by saponification of the ester group. The structure of iodo derivatives (III) and (IV) was established via the NMR spectra.

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