REACTION OF TRIMETHYL(BROMOMAGNESIUMETHYNYL)SILANE WITH ORGANYLTRIALKOXYSILANES

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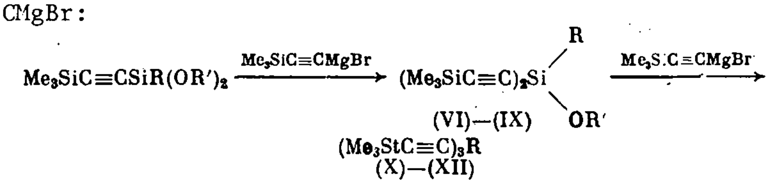
In a continuation of a study of the reactivity of ethynylsilanes [1, 2], we studied the reaction of trimethyl(bromomagnesiumethynyl)silane with organyltrialkoxysilanes. In the case of an equimolar ratio of these reagents, this reaction proceeds with the predominant formation of organyl(trimethylsilylethynyl)dialkoxysilanes in 45-55% yield:

$$\mathrm{Me_3SiC \equiv CMgBr + RSi(OR')_3 \rightarrow \underset{(I)-(V)}{Me_3SiC \equiv CSiR(OR')_2}}$$

$\mathrm{R{=}CH{=}CH_2(I), Me(II), Et(III), Ph(IV), Me_3SiCH{=}CH\ (V);\ R' = Me\ (I), (IV), (V), Et\ (II), (III).}$

The reaction mixture also yielded bis(trimethylsilylethynyl)organylalkoxysilanes in 18-20% yield and tris(trimethylsilylethynyl)organylsilanes in 14-16% yield. These compounds are the products of the reaction of the initially formed organyl(trimethylsilylethynyl)dialkoxysilanes with $\mathrm{Me_3SiC{\equiv}CMgBr}$:



$$\mathrm{Me_3SiC{\equiv}CSiR(OR')_2 \xrightarrow{Me_3SiC\equiv CMgBr} \underset{(VI)-(IX)}{(Me_3SiC{\equiv}C)_2Si(R)(OR')} \xrightarrow{Me_3SiC\equiv CMgBr} \underset{(X)-(XII)}{(Me_3StC{\equiv}C)_3R}}$$

$\mathrm{R = Me\ (VII), (X), CH{=}CH_2\ (VI), (XI), Et\ (VIII), (XII), Me_3SiCH{=}CH\ (IX);\ R' = Me\ (VI), (IX), Et\ (VII), (VIII).}$

The formation of (VI)-(IX) and (X)-(XII) may be prevented by using a twofold excess of the organyltrialkoxysilane which is quantitatively recovered upon distillation. The yields of the organyl(trimethylsilylethynyl)dialkoxysilanes in this case are increased to 70-75%.

The reaction of (II) with an equimolar amount of MeMgI smoothly proceeds to give dimethyl(trimethylsilylethynyl)ethoxysilane:

$$\mathrm{Me_3SiC \equiv CSi(OEt)_2Me + MeMgI \rightarrow \underset{(XIII)}{Me_3SiC \equiv CSiMe_2OEt}}$$

The yields, physical constants, and elemental analysis data for the compounds obtained are given in Table 1. Their structures were supported by IR spectroscopy. The triple-bond IR stretching vibrations give rise to a medium-strength band at 2115-2120 cm^{-1}, while the vinyl group in (I) and (VI) gives IR bands at 1597-1600 and 3063 cm^{-1}. The phenyl bands in (IV) are found at 706, 783, 1440, 1500, 1600, 3010, 3060, and 3080 cm^{-1}. The SiOC group gives bands at 1090-1095 cm^{-1}, while the OCH_3 group gives bands at 1190 and 2838-2845 cm^{-1}. The SiC bonds give rise to IR bands in the usual ranges at 845-850 and 1250-1255 cm^{-1}.

EXPERIMENTAL

The IR spectra were taken neat on a UR-20 spectrometer.

1-Trimethylsilyl-2-dimethoxyvinylsilylacetylene (I), Bis(trimethylsilylethynyl)methoxyvinylsilane (VI), and Tris(trimethylsilylethynyl)vinylsilane (X). A sample of the Iotsich reagent prepared from 2.43 g magnesium, 10.9 g ethyl bromide, and 9.8 g $\mathrm{Me_3SiC{\equiv}CH}$ in 100 ml THF was added dropwise with stirring to 14.8 g $\mathrm{(MeO)_3SiCH{=}CH_2}$ in 25 ml THF. Then, the reflux condenser was replaced by a condenser set for distillation, and the THF was distilled off until the reaction mass became a thick mass. The precipitate was filtered off and washed on the filter with 100 ml abs. ether. The solvents were distilled off at reduced pressure. The

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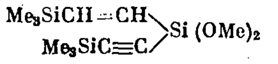
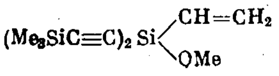
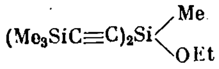
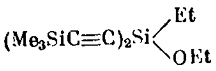
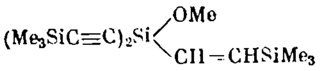
TABLE 1. Compounds Synthesized

Compound	Yield, %	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Found/Calculated, % C	H	Si	Chemical formula
$Me_3SiC{\equiv}CSi(OMe)_2CH{=}CH_2$ (I)	55,8	64 (6)	1,4360	0,9006	50,36 50,41	8,52 8,46	26,13 26,20	$C_9H_{20}Si_2O_2$
$Me_3SiC{\equiv}CSi(OEt)_2Me$ (II)	52,8	74 (10)	1,4215	0,8717	51,95 52,12	9,64 9,62	24,23 24,38	$C_{10}H_{22}Si_2O_2$
$Me_3SiC{\equiv}CSi(OEt)_2Et$ (III)	41,8	95 (13)	1,4310	0,8674	53,83 54,26	9,89 9,69	22,97 23,44	$C_{11}H_{24}Si_2O_2$
$Me_3SiC{\equiv}CSi(OMe)_2Ph$ (IV)	48,2	101 (2)	1,4860	0,9807	58,84 59,03	7,99 7,69	20,98 21,24	$C_{13}H_{20}Si_2O_2$
 $(Me_3SiCH{=}CH)(Me_3SiC{\equiv}C)Si(OMe)_2$ (V)	54,6	98 (2)	1,4471	0,8886	51,75 50,28	10,02 9,14	29,35 29,40	$C_{12}H_{26}Si_3O_2$
 $(Me_3SiC{\equiv}C)_2Si(CH{=}CH_2)(OMe)$ (VI)	18,6	103 (6)	1,4588	0,8788	55,89 55,64	8,43 8,62	30,03 30,03	$C_{13}H_{24}Si_3O$
 $(Me_3SiC{\equiv}C)_2Si(Me)(OEt)$ (VII)	18,5	86 (1)	1,4447	0,8570	55,05 55,25	9,18 9,27	28,90 29,92	$C_{13}H_{26}Si_3O$
 $(Me_3SiC{\equiv}C)_2Si(Et)(OEt)$ (VIII)	22,8	94 (1)	1,4499	0,8505	55,25 56,68	9,19 9,51	28,47 28,41	$C_{14}H_{28}Si_3O$
 $(Me_3SiC{\equiv}C)_2Si(OMe)(CH{=}CHSiMe_3)$ (IX)	28,7	130 (1) mp. 128°	–	–	54,81 54,47	8,95 9,14	33,04 31,85	$C_{16}H_{32}Si_4O$
$(Me_3SiC{\equiv}C)_3SiMe$ (X)	16,8	128 (1) mp. 64°	–	–	57,31 57,06	9,10 9,03	33,31 33,56	$C_{16}H_{30}Si_4$
$(Me_3SiC{\equiv}C)_3SiCH{=}CH_2$ (XI)	14,2	130 (1) mp 62°	–	–	58,93 58,88	8,80 8,72	32,55 32,40	$C_{17}H_{30}Si_4$
$(Me_3SiC{\equiv}C)_3SiEt$ (XII)	25,4	130 (1) 54°	–	–	58,38 58,50	9,33 9,25	32,21 32,20	$C_{17}H_{32}Si_4$

residue was distilled in vacuum to yield 11.4 g (55.8%) (I), 3.8 g (18.6%) (VI), and 2.9 g (14.2%) (X) (see Table 1).

The other compounds synthesized were prepared by analogous procedures.

1-Trimethylsilyl-2-dimethylmethoxysilylacetylene (XIII). A sample of MeMgI prepared from 1.21 magnesium and 7.1 g MeI in 50 ml ether was added dropwise with stirring to 11.5 g II). The precipitate formed was filtered off, washed on the filter with ether, and the ether was distilled off. The residue was distilled in vacuum to yield 6.6 g (66%) (XIII) [4].

CONCLUSIONS

The reaction of trimethyl(bromomagnesiumethynyl)silane with organyltrialkoxysilanes gave a series of organyl(trimethylsilylethynyl)dialkoxysilanes.

LITERATURE CITED

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REACTION OF 4,4-DIMETHYL-2-PENTYN-1-AL WITH DIALKYLAMINES

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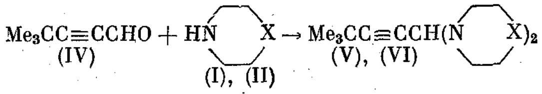
The direction of the nucleophilic addition of thiols to trimethylsilyl- and tert-butylpropynal depends significantly on the nature of the substituent at the triple bond [1]. Trimethylsilylpropynal has also been found to add cyclic dialkylamines at the C=O bond with the formation of silicoacetylenic aminals [2]. In the present work, we studied the reaction of dialkylamines (I)-(III) with 4,4-dimethyl-2-pentyn-1-al (IV).

The structure of the amine plays an important role in this reaction. Thus, morpholine and piperidine undergo only 1,2-addition, as in the case of trimethylsilylpropynal:

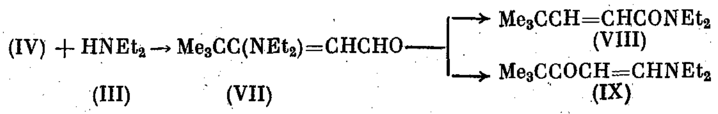


$X = CH_2$ (I), (V), O (II), (VI).

The IR spectra of acetylenic aminals (V) and (VI) have C≡C stretching bands at 2220-2230 cm^{-1}. The structure of (V) and (VI) was indicated by the PMR spectra given in Table 1 and by elemental analysis.

Diethylamine undergoes 1,4-addition to (IV). PMR monitoring of the course of this reaction showed that β-aminoacrolein (VII), which gives rise to the doublet at 5.48 ppm (=CH, J = 7 Hz) and 9.55 ppm (CHO, J = 7 Hz), is formed initially. The PMR study showed that β-diethylaminoacrolein (VII) gradually isomerizes to a compound lacking an aldehyde group. The doublets at 5.29 and 7.55 ppm (J = 13 Hz) in the PMR spectrum of the final product correspond to α- and β-olefinic protons. The isomerization of enaminoaldehyde (VII) is complete in 3 weeks at about 20°C.

In accord with literature data, the products of the isomerization of β-diethylaminoacrolein (VII) may be acrylamide (VIII) and β-enaminoketone (IX):



$$\underset{}{(IV)} + \underset{(III)}{HNEt_2} \rightarrow \underset{(VII)}{Me_3CC(NEt_2){=}CHCHO} \rightarrow \begin{cases} \underset{(VIII)}{Me_3CCH{=}CHCONEt_2} \\ \underset{(IX)}{Me_3CCOCH{=}CHNEt_2} \end{cases}$$

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