RADICAL ADDITION OF THIOLS TO DIMETHYLVINYLETHINYLCARBINOL

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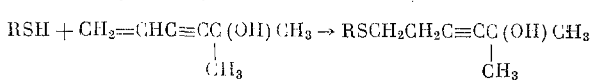
The reactions of thiols with olefins, enines, and diines have been studied in detail by a number of authors [1-6]. They noted that, in the case of olefins, thiols displayed a particular tendency to addition reactions by a free-radical mechanism [7]. This process has been widely used for obtaining sulfides of various structures [8-10].

The present paper deals with free-radical addition of thiols to dimethylvinylethinylcarbinol. For this purpose we used mercaptans of the organic type RSH ($R=C_2H_5$, C_3H_7, C_4H_9, C_6H_5, $t\text{-}C_5H_{11}$, $C_6H_5CH_2$), and organosilicon type $R_3'Si(CH_2)_nSH$ ($R'=CH_3$, C_2H_5, n=1, 2, 3). It was found that, in the presence of UV light, thiols add on to the double bond of vinylethinylcarbinol to form the corresponding mercaptohexinols :



$$RSH + CH_2{=}CHC{\equiv}C\underset{CH_3}{C}(OH)CH_3 \rightarrow RSCH_2CH_2C{\equiv}C\underset{CH_3}{C}(OH)CH_3$$

$R = C_2H_5$, C_3H_7, C_4H_9, C_6H_5,

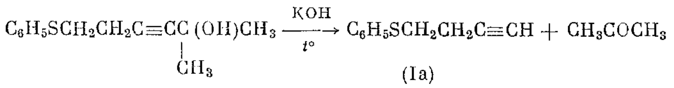
and also $R_3'Si(CH_2)_n$, where $R'=CH_3$, C_2H_5, n=1, 2, 3.

The structures of the latter are confirmed by the infrared spectra, which contain bands at 2240, 3400, and 1162 cm^{-1}, indicating the presence of $C{\equiv}C$ and OH groups in these compounds.

Note that a high-boiling by-product is formed in addition to the main product. The ultimate analysis data did not confirm the supposition of possible addition of a second mercaptan molecule at the triple bond of vinylethinylcarbinol. The ultimate analysis corresponds to the general formula $RS \cdot C_{14}H_{21}$ instead of the expected formula $(RS)_2 \cdot C_7H_{12}$.

The infrared spectra of the substances do not contain bands characteristic of the C=C bond, but contain bands at 2170 and 3298 cm^{-1}, indicating the presence of an internal triple bond and an hydroxyl group. The structures and formation mechanisms of these compounds are being studied and will form the subject of the next communication. Study of homolytic thiylation of vinylethinylcarbinol also revealed that, in the case of organosilicon mercaptans $R_3Si(CH_2)_nSH$ (n = 1, 2, 3) , α-silicon-containing thiols have minimum reactivity. This fact agrees closely with previous data [11] on the increase in nucleophilicity of organosilicon thiyl ions in the same sequence.

The 6-mercapto-2-methyl-3-hexyne-ols obtained in this work were subjected to alkaline hydrolysis [12]:



$$C_6H_5SCH_2CH_2C{\equiv}C\underset{CH_3}{C}(OH)CH_3 \xrightarrow[t^\circ]{KOH} C_6H_5SCH_2CH_2C{\equiv}CH + CH_3COCH_3$$

(Ia)

The acetone thus obtained was identified as the 2, 4-dinitrophenylhydrazone.

Study of the infrared spectra of (Ia) established that it was a mixture of the acetylene and allene isomers :

$$C_6H_5SCH_2CH_2C \equiv CH \rightleftarrows C_6H_5SCH_2CH = C = CH_2$$

This is indicated by the presence of bands at 3300 and 1960 cm^{-1}, characteristic of a terminal acetylene bond and an allene group, respectively. The presence of two isomers in the mixture was confirmed by gas-liquid and thin-layer chromatography. Therefore alkaline hydrolysis of 6-mercapto-2-methyl-3-

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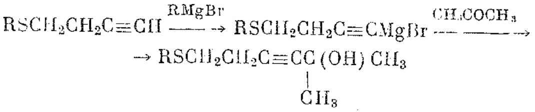
TABLE 1. Constants of Synthesized Compounds

Substance	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR		Found, %				Empirical formula	Calculated, %				Yield, %
				found	calculated	C	H	Si	S		C	H	Si	S	
$C_2H_5SCH_2CH_2C{\equiv}CC(CH_3)_2OH$	115 (3,5)	1,5035	0,9811	51,95	51,69	61,46	9,41	—	19,41	$C_9H_{16}SO$	62,73	9,36	—	18,61	42,2
$C_4H_9SCH_2CH_2C{\equiv}CC(CH_3)_2OH$	109 (2)	1,4962	0,9476	61,77	60,95	66,40	10,07	—	15,93	$C_{11}H_{20}SO$	65,94	10,06	—	16,00	33,0
$C_7H_{15}SCH_2CH_2C{\equiv}CC(CH_3)_2OH$	149 (3)	1,4908	0,9308	75,40	74,84	69,13	10,79	—	13,40	$C_{14}H_{26}SO$	69,36	10,81	—	13,22	33,4
$C_2H_5(CH_3)_2CSCH_2CH_2C{\equiv}CC(CH_3)_2OH$	135 (3)	1,5040	0,9565	66,36	65,58	67,28	9,56	—	13,54	$C_{12}H_{22}SO$	67,23	10,34	—	14,95	62,5
$C_6H_5CH_2SCH_2CH_2C{\equiv}CC(CH_3)_2OH$	182 (3)	1,5610	1,0591	71,65	71,12	—	—	—	13	$C_{14}H_{18}SO$	—	—	—	13,69	80,3
$(CH_3)_3SiCH_2CH_2SCH_2CH_2C{\equiv}CC(CH_3)_2OH$	140 (1,5)	1,4912	0,9349	75,75	75,21	58,85	9,95	11,65	13,42	$C_{12}H_{24}SiSO$	58,95	9,89	11,49	13,11	37,2
$CH_3(C_2H_5)_2SiCH_2SCH_2CH_2C{\equiv}CC(CH_3)_2OH$	169 (1)	1,4963	0,9386	80,49	79,84	59,70	10,38	11,11	13,06	$C_{13}H_{26}SiSO$	60,46	10,07	10,85	12,40	16,8
$CH_3(C_2H_5)_2SiCH_2CH_2SCH_2CH_2C{\equiv}CC(CH_3)_2OH$	157 (3)	1,4975	0,9425	84,68	84,47	61,70	10,52	10,35	11,70	$C_{14}H_{28}SiSO$	61,69	10,35	10,30	11,76	60,0
$(CH_3)_3SiCH_2CH_2CH_2SCH_2CH_2C{\equiv}CC(CH_3)_2OH$	135 (1,5)	1,4904	0,9331	80,25	79,84	60,14	10,27	10,81	12,42	$C_{13}H_{26}SiSO$	60,46	10,07	10,85	12,40	51,0
$(C_2H_5)_3SiCH_2CH_2CH_2SCH_2CH_2C{\equiv}CC(CH_3)_2OH$	164 (3)	1,5018	0,9397	93,97	93,73	63,70	10,88	9,52	10,69	$C_{16}H_{32}SiSO$	63,93	10,73	9,34	10,66	22,4

hexyne-2-ols leads not only to the usual decomposition for such compounds, but also to acetylene-allene isomerization. Attempts to separate the isomers by treating the mixture with an ammoniacal solution of silver and with sodium metal did not give the desired results.

We used the ability of the acetylene isomer to form Jotsich's reagent for the alternative (check) synthesis of these thioalcohols, as follows:



$$RSCH_2CH_2C{\equiv}CH \xrightarrow{RMgBr} RSCH_2CH_2C{\equiv}CMgBr \xrightarrow{CH_3COCH_3} RSCH_2CH_2C{\equiv}C\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)CH_3$$

EXPERIMENTAL

6-Phenylmercapto-2-methyl-3-hexyne-2-ol. A mixture of 1.9 g of thiophenol and 1.19 g of dimethylvinylethinylcarbinol was placed in a Pyrex capsule and irradiated by a PRK-2 lamp for 6 h. We obtained 2.66 g (70%) of the target product; the bp was 138° (3 mm); n_D^{20} 1.5672; d_4^{20} 1.0494. Found: C 70.21; H 7.19; S 13.79%. MR 68.60. $C_{13}H_{16}SO$. Calculated: C 70.88; H 7.32; S 14.54%; MR 68.18. Other acetylene thioalcohols were obtained in the same way; their constants are given in Table 1.

To a Grignard reagent, made from 0.63 g of magnesium and 0.2 g of ethyl bromide, was added dropwise 4.25 g of 4-phenylthiobut-1-yne. To the Jotsich reagent thus obtained was added 1.52 g of absolute acetone. The contents of the flask were heated on a water bath for 6 h. The salt was carefully decomposed with water. After the usual treatment, fractional distillation gave 2.55 g (51%) of the target product with a bp of 138° (3 mm); n_D^{20} 1.5680; d_4^{20} 1.0494; found MR 68.68. Calculated MR 68.18.

Hydrolysis of 6-Phenylmercapto-2-methyl-3-hexyne-2-ol. We placed 4.19 g of mercaptoalcohol and 0.2 g of powdered KOH in a distillation flask. The mixture was heated for 1.5 h on a boiling water bath. Acetone collected in the receiver. Several crystals of hydroquinone were added to the flask and the contents distilled in vacuum. We obtained 1.46 g (47%) of the target product with a bp of 100-101° (4 mm); n_D^{20} 1.5760, d_4^{20} 1.0405. Found: C 73.20; H 6.23; S 19.27%. $C_{10}H_{10}S$. Calculated: C 74.02; H 6.21; S 19.76%. The infrared spectrum contained bands at 3310 cm^{-1} ($C{\equiv}C{-}H$ bond) and 1955 cm^{-1} ($C{=}C{=}CH_2$ bond).

By a similar procedure we hydrolyzed 18 g of 6-butylmercapto-2-methyl-3-hexyne-2-ol to 7 g of 4-butylthiobut-1-yne (see Table 1).

CONCLUSIONS

1. We have studied free-radical addition of organic and organosilicon mercaptans to dimethylvinylethinylcarbinol and have shown that photochemical addition of thiols takes place at the double bond of the latter.

2. In the case of organosilicon mercaptans, α-silicon-containing thiols exhibit minimum reactivity in this connection.

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