3. The action of NH_3, $LiAlH_4$, and PCl_5 respectively gave 2-hydroxy-2-amino-3-hydroperfluorobutane, 2,3-dihydroperfluoro-2-butanol, and a mixture of 2,2,3-trichloroheptafluorobutane and 2-chloroheptafluoro-2-butene.

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REACTIONS OF AROMATIC ACETYLENIC ETHERS WITH TRIETHYLGERMANE

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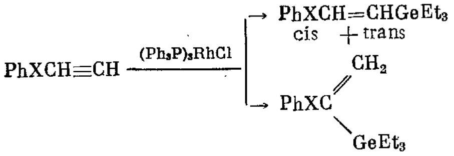
The hydrogermylation of aromatic acetylenic ethers was studied for the example of compounds of type $ArXC \equiv CH$, $ArXCH_2C \equiv CH$, $ArXC \equiv CCH_3$, and $ArXCH = C = CH_2$ (X = O, S) in the presence of Speier catalyst [1-3].

As an expansion of these studies it seemed of interest to study the stereochemical direction of the hydrogermylation of heteroatomic acetylenic compounds using triphenylphosphinerhodium chloride as another catalyst. According to [4], the latter is active in the hydrosilylation of olefins. In the present paper we used the terminal acetylenes $ArXC \equiv CH$ and $ArXCH_2C \equiv CH$ (X = O, S) as the starting compounds.

The acetylenic ether and sulfide $PhXC \equiv CH$ add Et_3GeH in the presence of the rhodium catalyst by the following scheme:



Consequently, the hydrogermylation of these compounds is both nonstereo- and nonregiospecific. In contrast to them, the propargyl ethers of phenol and of the o-bromo- and p-chloro-2,5-dimethylphenols react with hydrogermane to give the gem and trans isomers with a substantial predominance of the latter.

When compared with 3-phenoxy-1-propyne, phenyl propargyl sulfide forms the same isomers, but in reverse ratio (Table 1). For the example of these compounds it was found that replacing the Speier catalyst by $(Ph_3P)_3RhCl$ has no effect on the ratio of the isomers and the direction of the given reaction.

The structure of the obtained compounds was confirmed by elemental analysis and the PMR spectra (see

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TABLE 1

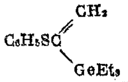
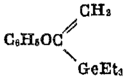
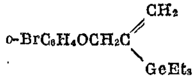
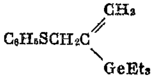
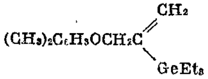
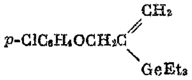
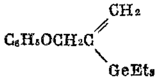
Compound	Configuration	PMR spectrum (δ, ppm; J, Hz)								Ratio
		=CH α	=CH β	Ph	Et_3Ge	$OCH_2(SCH_2)$	^3J	^2J	^4J	
$C_6H_5SCH{=}CHGeEt_3$	trans	6,52 d	5,94 d	7,20 m	1,02 m		17,5			45
	cis	7,01 d	5,93 d	7,20 m	1,02 m		11,7			50
 $C_6H_5SC(=CH_2)GeEt_3$	gem		5,02 d 5,13 d	7,20 m	0,95 m			0,5		5
$C_6H_5OCH{=}CHGeEt_3$	trans	6,35 d	5,05 d	7,15 m	1,07 m		14,0			60
	cis	4,76 d	7,15 d	6,77 m	1,07 m		7,0			30
 $C_6H_5OC(=CH_2)GeEt_3$	gem	4,65 d	4,37 d	7,15 m	0,99 m			1,5		10
 $o\text{-}BrC_6H_4OCH_2C(=CH_2)GeEt_3$	gem		5,77 t 5,97 t	7,04 m	0,97 m	4,25 d		1,5	1,5	30
$o\text{-}BrC_6H_4OCH_2CH{=}CHGeEt_3$	trans	6,08 m	6,08 m	7,04 m	0,97 m	4,50 d	2,0			70
$C_6H_5SCH_2CH{=}CHGeEt_3$	trans	5,75 m	5,75 m	7,10 m	0,90 m	3,37 d	5,0			40
 $C_6H_5SCH_2C(=CH_3)GeEt_3$	gem		5,68 d 5,12 d	7,10 m	0,90 m	3,49 s			2,2	60
 $(CH_3)_2C_6H_3OCH_2C(=CH_2)GeEt_3$	gem			5,26 m 5,75 m	6,80 m	0,94 m	4,39 d.d	2,2		10
$(CH_3)_2C_6H_3OCH_2CH{=}CHGeEt_3$	trans		6,06 m	6,06 m	6,80 m	0,94 m	4,40 d.d		1,7	90
 $p\text{-}ClC_6H_4OCH_2C(=CH_2)GeEt_3$	gem			5,26 m 5,70 m	7,00 m	0,94 m	4,38 m	2,2	1,5	30
$p\text{-}ClC{\cdot}H_4OCH_2CH{=}CHGeEt_3$	trans		6,05 m	6,05 m	7,00 m	0,94 m	4,42 d		1,8	70
 $C_6H_5OCH_2C(=CH_2)GeEt_3$	gem			5,29 t 5,86 t	7,00 m	0,98 m	4,52 d.d	2,2	1,5	20
$C_6H_5OCH_2CH{=}CHGeEt_3$	trans		6,06 m	6,06 m	7,10 m	0,98 m	4,42 d.d	1,8	1,7	80

Table 1). For the derivatives of an α-acetylenic ether and sulfide the assignment of the PMR signals to the isomers is based on the SSCC of the olefinic protons. For the phenoxypropyne and phenyl propargyl sulfide derivatives the chemical shifts of the α- and β-protons are close. The spectrum of these protons is not first order, and a determination of the SSCC without analysis on an electronic computer is difficult. To determine the configuration we calculated the chemical shifts of the olefinic protons by the additive scheme [5] with the experimentally found increments for the Et_3Ge group (δ, ppm): 0.2 (cis), 0.5 (trans), and 0.8 (gem). According to this scheme, the trans configuration is most probable, for which the difference in the shielding of the α- and β-protons is equal to 0.05 ppm, whereas for the cis configuration it is 0.35 ppm.

EXPERIMENTAL

The PMR spectra were recorded on a Tesla BS-487C spectrometer, using CCl_4 as the solvent and TMS as the internal standard.

Hydrogermylation of Phenoxyacetylene. A mixture of 3.5 g of phenoxyacetylene, 4.5 g of Et_3GeH, and 0.03 g of $(Ph_3P)_3RhCl$ was heated for 6 h at 95°C. After vacuum distillation we obtained a 40% yield (marked tarring) of a product with bp 83-89° (2 mm), in which, using the PMR spectroscopy method, were detected cis-$C_6H_5OCH = CHGeEt_3$, trans-$C_6H_5OCH = CHGeEt_3$ and gem-$C_6H_5OC = CH_2$ in a 30 :60 :10 ratio.

The reaction with phenylthioacetylene and the aryl propargyl ethers was run in a similar manner.

CONCLUSIONS

The addition of Et_3GeH to the phenoxy- and phenylthioacetylenes under the influence of $(Ph_3P)_3RhCl$ is both nonstereo- and nonregiospecific. The analogous reaction with 3-aroxy-1-propynes is stereospecific but nonregioselective.

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