

## THE EFFECT OF THE STRUCTURE OF SILANES ON SELECTIVITY OF HYDROSILYLATION OF 1-HEXINE

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The effect of the structure of silanes  $RR'R''SiH$  on selectivity of their orientation during hydrosilylation of 1-hexine catalysed by hexachloroplatinic acid was studied. No simple relation was found to exist between the ratio of  $\alpha$ - to  $\beta$ -adducts and structural parameters of the silane.

In the course of systematic study of hydrosilylation of acetylenic compounds  $R-C\equiv CH$  catalysed by  $H_2PtCl_6$  we observed<sup>1</sup> the relation between the ratio of  $\alpha$ - to  $\beta$ -adducts and the electronic effect of substituents  $R$ . This, in relation to generally accepted mechanism of hydrosilylation<sup>2</sup>, surprising finding could be consistent with the hypothesis that selectivity of the hydrosilylation mentioned is controlled mainly by only one reaction step. Hydrosilylation of alkynes has up to now been examined only superficially<sup>3-5</sup>. Information about the influence of electronic properties of the substituents in the silanes  $RR'R''SiH$  on selectivity of their addition to alkynes could therefore provide not only support for the hypothesis, but also additional information about the reaction mechanism of this addition.

In this work we therefore studied the influence of the structure of the silanes  $RR'R''SiH$  on selectivity of their addition in hydrosilylation of 1-hexine catalysed by hexachloroplatinic acid. This addition leads, as a rule, to a mixture of two isomeric adducts, as proved by <sup>1</sup>H-NMR and IR spectroscopy (equation (1)). The ratio of the isomers was determined by <sup>1</sup>H-NMR spectral and gas-liquid chromatographic method. As follows from Table I, the isomer with internal double bond ( $\beta$ -isomer) is favored. Contrary to the results mentioned above (ref.<sup>1</sup>), there is no simple relation between the structure of the silane  $RR'R''SiH$  (electronic and/or steric property of its substituents  $R$ ) and the ratio of  $\alpha$ - and  $\beta$ -isomers.

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TABLE I

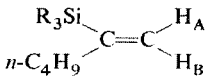
Boiling Points of the Mixtures of Isomeric  $\alpha$ - and  $\beta$ -Adducts Obtained by Hydrosilylation of 1-Hexine by the Silanes  $RR'R''SiH$  and the  $\alpha$ - to  $\beta$ -Isomer Ratio

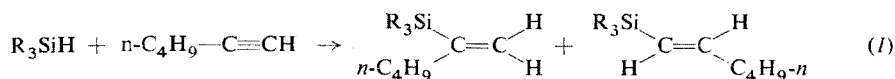
Silyl group	B.p., °C/Torr	$\alpha$ : $\beta$ mol. ratio <sup>a</sup>
$(CH_3)_2C_2H_5Si$	91—95/40	0.29
$CH_3(C_2H_5)_2Si$	74—78/8	0.25
$(C_2H_5)_3Si$	91—94/4	0.22
$(CH_3)_2[(CH_3)_3CCH_2]Si$	95—97/10	0.20
$(n-C_3H_7)_3Si$	126—129/9	0.31
$CH_3(i-C_3H_7)_2Si$	96—99/12	0.42
$CH_3(n-C_3H_7)_2Si$	97—109/8	0.38
$(i-C_4H_9)_3Si$	115—118/10	0.35
$CH_3[(CH_3)_3SiO]_2Si$	103—107/10	0.37
$C_2H_5[(CH_3)_3SiO]_2Si$	112—120/10	0.50
$ClCH_2(CH_3)_2Si$	82—84/14	0.44
$(C_2H_5O)_3Si$	92—96/8	0.25
$(C_2H_5O)_2CH_3Si$	77—80/10	0.50
$(CH_3)_2C_6H_5Si$	121—123/8	0.17
$(i-C_3H_7O)_3Si$	110—117/20	0.17

<sup>a</sup> 5% accuracy.

TABLE II

<sup>1</sup>H-NMR Data on  $\alpha$ - and  $\beta$ -Adducts Obtained by Hydrosilylation of 1-Hexine by the Silanes  $RR'R''SiH$ 

$R_3Si$				
	$\tau_{H_A}$	$\tau_{H_B}$	$^2J_{AB}$	$^4J_{CH_2C=CHB}$
$C_2H_5(CH_3)_2Si$	4.71	4.44	3.0	1.5
$(C_2H_5)_2CH_3Si$	4.71	4.39	3.1	1.5
$(C_2H_5)_3Si$	4.74	4.41	3.2	—
$(CH_3)_3CCH_2(CH_3)_2Si$	4.68	4.45	3.0	1.6
$(n-C_3H_7)_3Si$	4.76	4.44	3.0	1.4
$(i-C_3H_7)_2CH_3Si$	4.71	4.35	2.8	1.7
$(n-C_3H_7)_2CH_3Si$	4.73	4.44	3.2	1.6
$(i-C_4H_9)_3Si$	4.74	4.41	3.0	1.6
$[(CH_3)_3SiO]_2CH_3Si$	4.69	4.49	3.3	1.6
$[(CH_3)_3SiO]_2C_2H_5Si$	4.61	4.45	3.0	—
$ClCH_2(CH_3)_2Si$	4.63	4.36	2.8	1.6
$(C_2H_5O)_2CH_3Si$	4.54	4.41	3.4	1.5
$(C_2H_5O)_3Si$	4.50	4.43	3.3	1.4
$C_6H_5(CH_3)_2Si$	4.60	4.33	3.0	1.6
$(i-C_3H_7O)_3Si$	4.45	4.45	—	—

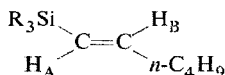


This leads us to conclude that the parallelity between the ratio of  $\alpha$ - and  $\beta$ -isomers and the electronic effect of substituents R in the alkynes  $\text{R}-\text{C}\equiv\text{CH}$  results likely from a fortuitous cancellation of many factors that can play a role in individual steps of the hydrosilylation. The reversibility of several reaction steps (see<sup>2</sup>) provides the possibility of not only the kinetic but also thermodynamic control of the reaction.

### EXPERIMENTAL

1-Hexine and the silanes<sup>6,7</sup>  $\text{RR}'\text{R}''\text{SiH}$  were prepared by reported procedures. Their purity was checked by gas-liquid chromatography and their physical constants agreed with reported data<sup>6</sup>.

Hydrosilylation reaction was carried out in the same manner as in the case of the addition of triethylsilane to 1-hexine: a mixture of 1-hexine (1.64 g), triethylsilane (2.32 g), and 0.1 ml of 0.1M solution of hexachloroplatinic acid in tetrahydrofuran was heated in a sealed tube at 100°C for 2 h. The reaction mixture was then analysed by gas-liquid chromatography (a CHL 4 chromatograph, a column filled with 15% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb W or with poly(ethylene glycol) on TND-brick; carrier gas was helium, column temperature was 130–180°C). The reactants were separated from the adducts by distillation. Boiling points of the mixtures of isomeric adducts and their composition (the ratio of both isomers) are presented in Table I.



$^4J_{\text{CH}_2\text{C}=\text{CH}_2}$	$\tau\text{H}_A$	$\tau\text{H}_B$	$^3J_{\text{AB}}$	$^3J_{\text{CH}_2\text{CHB}}$	$^4J_{\text{CH}_2\text{C}=\text{CHA}}$
1.1	4.43	4.01	18.4	5.8	1.1
1.0	4.41	3.98	18.7	6.0	1.1
1.1	4.50	4.01	18.7	6.0	1.2
1.1	4.37	4.03	18.5	5.4	1.0
0.8	4.50	4.04	18.7	5.9	1.4
1.2	4.48	3.99	18.5	6.1	1.2
1.0	4.45	4.02	18.5	5.8	1.2
1.2	4.51	4.02	18.8	6.0	1.1
1.0	4.56	3.91	18.6	6.5	1.1
1.0	4.66	3.87	18.6	6.0	1.0
1.0	4.42	3.89	18.6	5.8	1.2
1.0	4.61	3.85	18.6	6.0	1.6
1.0	4.69	3.72	18.7	6.2	1.4
1.0	4.23	3.90	18.4	5.4	0.9
—	4.68	3.73	18.5	6.2	1.3

The assignment of NMR spectra to both isomers in their mixture has been made based on our previous NMR measurement of the compounds of this type (Table II).  $^1\text{H}$ -NMR spectra were measured with Tesla BS-487 spectrometer operating at 80 MHz. Chemical shifts were determined in 30% (vol.) solutions in  $\text{CCl}_4$  with respect to tetramethylsilane as an internal standard with an accuracy of 0.01 p.p.m., the coupling constants were determined with an accuracy of 0.1 Hz.

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