5-Fluoropyrazoloanthrone (XIV). A 3.17-g (10 mmole) sample of sulfonic acid XII was heated in 30 ml of 5% nitrosylsulfuric acid at 60° for 6 h, after which the mixture was cooled and poured into 100 g of ice. The suspension was poured into 100 ml of 5 % sodium hypophosphate (NaH_2PO_2) solution at 20°. After nitrogen evolution ceased, the mixture was heated to 70°, and 70 g of sodium sulfate was added. The mixture was cooled and filtered, and the precipitate was squeezed on the filter. It was then suspended in a mixture of 100 ml of 10% HCl and 3.1 g of $KClO_3$, and the suspension was heated to 95°. A solution of 0.2 g of NH_4Cl in 5 ml of water was added dropwise at this temperature in the course of 2 h, after which the mixture was cooled and filtered. The precipitate was washed with water to remove acid, squeezed on the filter, and dried. Chloro derivative XIV was crystallized from aqueous ethanol to give yellow-orange needles.

Pyrazoloanthrone-3-diazonium Sulfate (XIII). A solution of 2.35 g (10 mmole) of amine I in 20 ml of concentrated H_2SO_4 was added to 12 ml (12 mmole) of 7% nitrosylsulfuric acid, and the mixture was stirred at 60° for 6 h. The diazo solution was cooled and poured over 200 g of ice. The aqueous mixture was filtered, and the precipitate was washed successively with 5% sulfuric acid and ether. Diazonium sulfate XIII was obtained as a red-brown powder.

3-Methylpyrazoloanthrone was obtained by a method described in [11]; 3-chloropyrazoloanthrone, in [1]; alkylamine XVII was obtained analogously by synthesis of amine I from 1-chloro-2-butylaminoanthraquinone and gave red-orange crystals on crystallization from aqueous ethanol.

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HYDROSILYLATION OF 2-VINYLQUINOLINE*

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It was found that mixtures of two isomers are formed in the hydrosilylation of 2-vinylquinoline with trialkylsilanes, triethoxysilane, ethyldichlorosilane, and pentamethyldisiloxane in the presence of $H_2PtCl_6 \cdot 6H_2O$ or $(Ph_3P)_3RhCl$. The dependence of their ratio on the structure of the silane, the nature of the solvent and catalyst, and the order of mixing of the reagents was investigated.

The hydrosilylation of hetarylalkenes usually gives a mixture of two isomers [2, 3]; however, the factors that affect their ratio have not been studied at all. We therefore undertook a systematic study of the effect of

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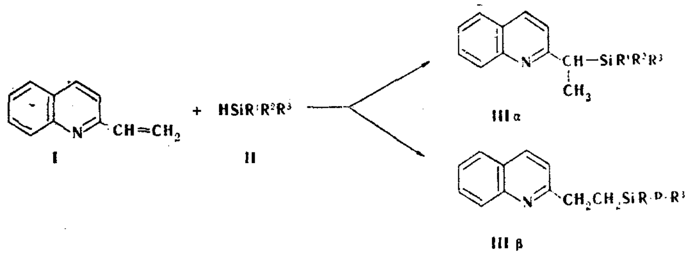
TABLE 1. (2-Quinolyl)alkylsilanes (III)

R^1	R^2	R^3	bp, °C (nm)	d_4^{20}	n_D^{20}	Found				Empirical formula	Calculated				Isomer ratio (IIIα : IIIβ), %	Yield, %
						C, %	H, %	N, %	MR_D		C, %	H, %	N, %	MR_D		
CH_3	CH_3	C_3H_7	144—146 (1)	0,9784	1,5510	74,6	8,8	5,5	83,97	$C_{16}H_{23}NSi$	74,6	9,0	5,4	84,62	65 : 35	43
CH_3	CH_3	C_4H_9	162—164 (2)	0,9657	1,5510	75,4	8,7	5,3	89,68	$C_{17}H_{25}NSi$	75,4	9,3	5,2	89,25	68 : 32	47
CH_3	CH_3	$OSi(CH_3)_3$	132—134 (3)	0,9829	1,5250	63,4	8,3	5,6	94,63	$C_{16}H_{25}ONSi_2$	63,2	8,5	5,4	94,74	90 : 10	55
CH_3	C_2H_5	C_2H_5	156—158 (2)	0,9876	1,5625	74,9	9,1	5,5	84,60	$C_{16}H_{23}NSi$	74,6	9,0	5,4	84,62	65 : 35	44
CH_3	C_3H_7	C_3H_7	154—156 (1)	0,9658	1,5510	76,1	9,4	4,9	94,29	$C_{18}H_{27}NSi$	75,7	9,5	4,9	94,62	62 : 38	56
CH_3	C_4H_9	C_4H_9	175—177 (2)	0,9370	1,5345	76,8	9,5	4,1	104,03	$C_{20}H_{31}NSi$	76,6	9,9	4,5	103,88	67 : 33	52
C_2H_5	C_2H_5	C_2H_5	142—144 (1)	0,9841	1,5595	75,1	8,9	5,6	89,13	$C_{17}H_{25}NSi$	75,4	9,3	5,2	89,25	65 : 35	55
OC_2H_5	OC_2H_5	OC_2H_5	160—162 (1)	1,0502	1,5175	63,9	7,9	5,4	92,11	$C_{17}H_{25}O_3NSi$	63,2	7,7	5,2	92,27	50 : 50	27

the structure of the hydrosilane, the unsaturated compound, the catalyst, the nature of the solvent, and the reactions conditions on the reaction rate and direction. We selected vinylquinolines, the hydrosilylation of which has not been previously carried out, as the unsaturated compounds.



In the present research we carried out the reaction of 2-vinylquinoline with trialkylsilanes, triethoxysilane, ethyldichlorosilane, and pentamethyldisiloxane in the presence of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in absolute isopropyl alcohol (the molar ratio of the olefin and catalyst was $1:2 \cdot 10^{-5}$) at 120-160°C for 10 h. A mixture of two isomers, the ratio of which depended on the nature of the hydrosilane, was formed in all cases.

Thus, whereas the α isomer (90%) is formed in the case of pentamethyldisiloxane, primarily the β isomer (75%) is formed in the reaction with ethyldichlorosilane. A mixture of isomers with predominance of the α isomer (65%) was formed in 45-55% yield with trialkylsilanes. Triethoxysilane gave identical amounts of the α and β isomers in this reaction (Table 1).

The dependence of the direction of hydrosilylation on the reaction conditions (the solvent and the order of mixing of the reagents) was studied in the case of the reaction of 2-vinylquinoline with triethylsilane.

Little study has been devoted to the direction of hydrosilylation [4]. We observed that in the hydrosilylation of 2-vinylquinoline, nonpolar and aprotic solvents (xylene, dioxane, and diglyme) raise the yields of hydrosilylation products to 70% without affecting the isomer ratio. However, polar solvents (pyridine and quinoline) promote the formation of the β isomer, but the overall yield is reduced to 40% in this case. The reaction did not take place in dimethylformamide (DMF).

The order of mixing of the reagents with the catalyst affects the degree of its reduction, and this in turn affects the direction of hydrosilylation. We established that if a mixture of triethylsilane and the catalyst is added gradually dropwise to 2-vinylquinoline heated to 50°, primarily the α isomer (65%) is obtained. Simultaneous mixing of triethylsilane, 2-vinylquinoline, and the catalyst reduces the amount of α isomer somewhat (55%). However, in the case of addition of triethylsilane to a mixture of 2-vinylquinoline and the catalyst almost identical amounts (51 : 49) of the α and β isomers are obtained. Consequently, mostly the α isomer is formed under conditions that promote reduction of the catalyst to the maximum extent; this is in agreement with the data in [5].

In addition to platinum catalysts, catalysts containing rhodium and palladium, particularly in the form of complexes with triphenylphosphine [6], were used for the hydrosilylation. A mixture of hydrosilylation products with, in contrast to the platinum catalyst, predominance of the β isomer (65%) is formed in 40% yield when a 0.1 M benzene solution of tris(triphenylphosphine)rhodium(I) chloride (olefin—catalyst molar ratio $1:1 \cdot 10^{-4}$) is used as the catalyst in the reaction of triethylsilane with 2-vinylquinoline (at 120-160° for 20 h). A benzene solution (0.1 M) of bis(triphenylphosphine)palladium(I) chloride (olefin—catalyst molar ratio $1:5 \cdot 10^{-5}$) was inactive in this reaction under similar conditions.

Thus it was established that vinylquinolines are sufficiently sensitive systems for a further more detailed study of the effect of various factors on their hydrosilylation.

EXPERIMENTAL

The PMR spectra of CCl_4 solutions of the compounds were recorded with a Perkin-Elmer R-12A spectrometer (60 MHz) with tetramethylsilane as the internal standard. The peaks were integrated with an accuracy of ±2.5%.

Hydrosilylation of 2-Vinylquinoline with Triethylsilane. A 6.2-g (0.04 mole) sample of 2-vinylquinoline was placed in a flask equipped with a reflux condenser, a thermometer, and a dropping funnel, and 4.6 g (0.04 mole) of triethylsilane containing 0.3 ml of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in absolute isopropyl alcohol was added gradually at 50°. The mixture was then heated for 10 h, during which the temperature was slowly raised from 120 to 160°. Vacuum distillation yielded 5.8 g (55%) of hydrosilylation products with bp 140-142° (2 mm), n_D^{20} 1.5595, and d_4^{20} 0.9841. Found: C 75.1; H 8.9, N 5.6%; MR_D 89.13. $C_{17}H_{25}NSi$. Calculated: C 75.4; H 9.3; N 5.2%; MR_D 89.25.

All of the remaining trialkyl-, triethoxy-, and dimethylsiloxysilylquinolines were similarly obtained. Their physicochemical constants and the results of analysis are presented in Table 1.

Hydrosilylation of 2-Vinylquinoline with Ethyldichlorosilane. A 6.2-g (0.04 mole) sample of 2-vinylquinoline was added dropwise to a mixture of 5 g (0.04 mole) of ethyldichlorosilane, 0.3 ml of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in absolute isopropyl alcohol, 0.1 g of hydroquinone, and 10 ml of dry dioxane, and the mixture was refluxed for 10 h. The solvent was then removed by distillation, and the residue was vacuum distilled at 150-155° (1 mm) to give 5.1 g (45%) of hydrosilylation products as a yellow oil that hydrolyzed readily in air. The structures and isomeric composition (α to β ratio 25 : 75) of the reaction products were established from the PMR spectra.

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PROTONATION OF 1,5-NAPHTHYRIDINE DERIVATIVES

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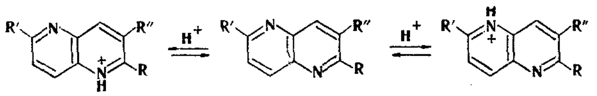
The direction of protonation (1-N or 5-N) or 2-, 2,3-, and 2,6-substituted derivatives of 1,5-naphthyridine was determined on the basis of the basicity constants.

Mono- and disubstituted 1,5-naphthyridine derivatives (R≠ R'≠ R") contain two nonequivalent basic centers – the 1-N and 5-N nitrogen atoms – the monocations formed by protonation of which may have structure a or b.



a b

I R=R'=R"=H; II R=NH_2, R'=R"=H; III R=CH_3, R'=R"=H; IV R=Cl, R'=R"=H; V R=$NHCOCH_3$, R'=R"=H; VI R=OCH_3, R'=R"=H; VII R=OH, R'=R"=H; VIII R=SH, R'=R"=H; IX R=R'=H, R"=NO_2; X R=OH, R'=H, R"=NO_2; XI R=OCH_3, R'=Cl, R"=H; XII R=$N(CH_3)_2$, R'=Cl, R"=H

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