HYDROSILYLATION OF N- AND O-HETEROCYCLIC ALDEHYDES IN THE PRESENCE OF Rh^{I}, Ru^{II}, AND Pd^{II} COMPLEXES

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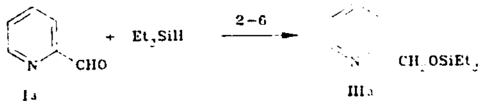
The hydrosilylation of 2-formylpyridine, 2-formyl-6-methylpyridine, 2-formylfuran, and 2-formyl-5-methylfuran with triethylsilane in the presence of $Rh(PPh_3)_3Cl$, $Rh(PPh_3)_3(CO)H$, $Rh(PPh_3)_2(CO)Cl$, $Ru(PPh_3)_3Cl_2$, $Ru(PPh_3)_2(CO)_2Cl_2$, and $Pd(PPh_3)_2Cl_2$ was studied. Silyl ethers of the corresponding hetarylcarbinols were obtained in high yields. The formation of products of dehydrocondensation of the silyl ethers is observed in the hydrosilylation of methyl-substituted aldehydes; this process does not occur in the presence of ruthenium complexes.

In our previous research [1] we studied the hydrosilylation of some heterocyclic aldehydes in the presence of primarily anionic complexes of transition metals (quaternary ammonium halometallates). In the present research in a continuation of these studies, we investigated the hydrosilylation of 2-formylpyridine (Ia), 2-formyl-6-methylpyridine (Ib), furfural (IIa), and 5-methylfurfural (IIb) with triethylsilane in the presence of neutral triphenylphosphine complexes of ruthenium and palladium: $Rh(PPh_3)_3Cl$ (1), $Rh(PPh_3)_3(CO)H$ (2), $Rh(PPh_3)_2(CO)Cl$ (3), $Ru(PPh_3)_3Cl_2$ (4), $Ru(PPh_3)_2(CO)_2Cl_2$ (5), and $Pd(PPh_3)_2Cl_2$ (6).

In [1] when we carried out the hydrosilylation of aldehyde Ia with triethylsilane (one of the most accessible hydrosilylating agents) at 130°C (most of the complex catalysts decompose at higher temperatures) in the presence of several complexes of Rh^{I}, Rh^{III}, Pt^{IV}, and Ni^{II}, we were unable to obtain a sufficiently high yield of 2-(triethylsiloxymethyl)-pyridine (IIIa) (the maximum yield was 17% in the presence of the $[Et_3NCH_2Ph][RhCl_4]$ catalyst). Since obtaining this substance as an intermediate in the synthesis of a compound of practical value — 2-pyridylcarbinol — is of interest, in the present study we undertook a search for a catalyst, the use of which would make it possible to increase the yield of silyl ether IIIa. The results obtained in an investigation of the hydrosilylation of aldehyde Ia with triethylsilane (1:1.2) at 130°C in the presence of 0.1 mole % amounts (with respect to the aldehyde) of six complexes of Rh^{I}, Ru^{II}, and Pd^{II} are presented in Table 1. In addition to ether IIIa, the disilyl (IVa) and monosilyl (Va) ethers of dipyridylethanediol and α-pyridoin (VI), the overall yield of which does not exceed 7% (on a palladium catalyst), were also detected in the reaction products by GLC, chromatographic mass spectrometry, and PMR spectroscopy. The amount of monosilyl ether Va in the catalysts was up to 2%. The PMR spectra of the α-pyridoin isolated from the reaction mixtures in the hydrosilylation of Ia provide evidence that it exists in the diol form in solution; this is due to the formation of hydrogen bonds between the ring nitrogen atoms and the hydrogen atoms of the hydroxy groups [2]. The principal reaction product on all catalysts is ether IIIa [the Wilkinson catalyst, $Rh(PPh_3)_3Cl$, is very slightly active]:



(A)

The highest yield of IIIa (37%) is observed on a ruthenium carbonyl catalyst (5). With respect to their activity in reaction (A) the investigated complexes are arranged in the following order: $Ru(PPh_3)_2(CO)_2Cl_2 > Rh(PPh_3)(CO)H > Rh(PPh_3)_2(CO)Cl > Ru(PPh_3)_3Cl_2 > Pd(PPh_3)_2Cl_2 > Rh(PPh_3)_3Cl$. The hydrosilylation rate on most of the catalysts decreases after 2 h (despite the retention in the reaction mixture of significant amounts (~60-90%, according to GLC data) of unchanged aldehyde Ia); this may constitute evidence for inhibition

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TABLE 1. Hydrosilylation of 2-Formylpyridine (Ia) with Triethylsilane in the Presence of Complex Catalysts (130°C, Ia: Et_3SiH:catalyst molar ratio = 1:1.2:0.001)

Catalyst		Yield of reaction products, % (GLC, PMR)								
		IIIa			IVa, threo + erythro			VI		
		1*	2*	3*	1	2	3	1	2	3
$Rh(PPh_3)_3Cl$	(1)	1	2	2	0	0	0	0	0	1
$Rh(PPh_3)_3(CO)H$	(2)	10	27.5	28	0	2	1	0	0	1
$Rh(PPh_3)_2(CO)Cl$	(3)	7	17.5	16	0	2	1	0	0	1
$Ru(PPh_3)_3Cl_2$	(4)	5	14	17	0	0	0	0	0.5	2
$Ru(PPh_3)_2(CO)_2Cl_2$	(5)	15	37	37	0	1	1	0	0	1
$Pd(PPh_3)_2Cl_2$	(6)	3	10	9	1	3.5	2	0	0.5	3

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*Reaction time in hours.

TABLE 2. Hydrosilylation of 2-Formyl-6-methylpyridine (Ib) with Triethylsilane in the Presence of Complex Catalysts (molar ratio 1:1.2:0.001, 130°C)

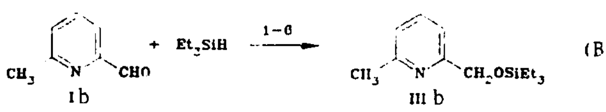
Catalyst	Yield of reaction products, %(GLC, PMR)				
	IIIb	IVb			IIIb+IVb
		threo	erythro	sum	
		Reaction time 1 h			
1	4	1	1	2	6
2	17	4	3	7	24
3	8	3	3	6	14
4	5	0	0	0	5
5	18	0	0	0	18
6	3	1	1	2	5
		Reaction time 3 h			
1	19	3	5	8	27
2	31	15	12	27	58
3	31	15	10	25	56
4	21	0	0	0	21
5	31	0	0	0	31
6	19	2	4	6	25
		Reaction time 5 h			
1	19	4	7	11	30
2	35	28	26	54	89
3	31	28	23	51	82
4	28	0	0	0	28
5	34	0	0	0	34
6	20	3	7	10	30

by the resulting ether IIIa. The latter is a stronger electron donor than the starting aldehyde Ia, and the formation of other complexes of IIIa with the catalysts and their deactivation are therefore possible. The low yields of ether IIIa in the hydrosilylation of aldehyde Ia is probably also due to this.

The results obtained in the hydrosilylation of aldehyde Ib with triethylsilane (1:1.2) at 130°C in the presence of catalysts 1–6 are presented in Table 2. The literature does not contain information on the hydrosilylation of this aldehyde. Silyl ether IIIb, the threo and erythro isomers of bis(methylpyridyl)ethanediol disilyl ether IVb, and its monosilyl ether Vb [the highest yield of the latter (8%) was observed on a Pd catalyst] were detected in the reaction products by GLC, chromatographic mass spectrometry, and PMR spectroscopy. 6,6'-Dimethyl-α-pyridoin was not detected in the reaction mixtures; this is in agreement with the literature data [3] that aldehyde Ib is less inclined to undergo autocondensation of the pyridoin type than aldehyde Ia. In the hydrosilylation of methyl-substituted aldehyde Ib (reaction (B)) the yield of silyl ether IIIb on all catalysts (except 5) is higher than the yield of ether IIIa, which is formed from aldehyde Ia. With respect to activity in the formation of IIIb catalysts 1-6 are arranged in the order $Ru(PPh_3)_2(CO)_2Cl_2$ > $Rh(PPh_3)_3(CO)H$ > $Rh(PPh_3)_2(CO)Cl$ > $Ru(PPh_3)_3Cl_2$ > $Pd(PPh_3)_2Cl_2$ > $Rh(PPh_3)_3Cl$, which is extremely similar to the order obtained in the hydrosilylation of aldehyde Ia.

TABLE 3. Hydrosilylation of Furfural (IIa) and 5-Methylfurfural (IIb) with Triethylsilane in the Presence of Complex Catalysts (molar ratio 1:1.2:0.001) at Various Temperatures

Catalyst	Reaction time, h	Yield of reaction products, %(GLC, PMR)			
		VIIa, 25 °C	VIIb, 25 °C 100 °C	VIIIb, 25 °C 100 °C	VIIb+ +VIIIb, 100 °C
1	1	12	11/37	0/12	49
2		0	—/50	0/5	55
3		7	—/34	0/27	61
4		10	—/77	0/1	78
5		0	—/72	0/2	74
6		5	—/25	0/12	37
1	2	35	18/44	0/23	67
2		0	2/49	0/30	79
3		30	34/53	0/42	95
4		25	7/68	0/2	70
5		0	2/56	0/2	58
6		8	23/32	0/29	61
1	3	55	27/39	0/35	74
2		—	3/43	0/37	80
3		—	39/52	1/45	97
4		—	18/61	0/2	63
5		—	3/48	0/3	51
6		—	34/32	0/26	58
1	4	59	33/41	2/32	73
2		8	3/44	1/32	76
3		70	46/39	2/47	86
4		58	24/—	0/—	—
5		5	3/—	0/—	—
6		24	55/27	0/27	54
1	5	60	37/—	3/—	—
2		—	3/—	2/—	—
3		—	50/—	3/—	—
4		75	30/—	0/—	—
5		—	2/—	0/—	—
6		—	58/—	2/—	—
1	6	55	42/—	4/—	—
2		12	3/—	3/—	—
3		59	54/—	5/—	—
4		73	38/—	0/—	—
5		7	2/—	0/—	—
6		27	58/—	2/—	—
1	7	—	44/—	4/—	—
3		—	56/—	7/—	—
4		—	35/—	0/—	—
6		—	48/—	5/—	—
1	8	—	45/—	5/—	—
3		—	59/—	8/—	—
4		—	35/—	0/—	—
6		—	44/—	6/—	—

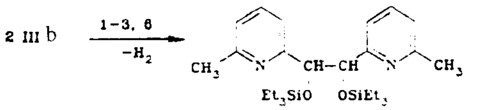


The significant differences in the hydrosilylation of aldehyde Ib and Ia consist in the formation on some of the catalysts of large amounts (up to 54 mole % based on the starting aldehyde) of the threo and erythro isomers of IVb via reaction (C). This substance is not obtained in the presence of the two ruthenium catalysts (4 and 5); consequently, a purely catalytic process that proceeds through the formation of intermediates with the participation of Rh- and Pd-containing catalysts occurs. Since a pyridoin condensation is more characteristic for aldehyde Ia than for Ib, whereas the yield of dimer IVb is much higher than the yield of IVa, it may be assumed that pyridoins are not intermediates in the formation of IVa and IVb. In other words, the hydrosilylation of aldehydes Ia and Ib to silyl ethers IIIa and IIIb occurs initially, and this is followed by the catalytic dehydrocondensation of the latter to IVa and IVb, which is particularly characteristic for ether IIIb in the presence of rhodium complexes 2 and 3 (and, to a considerably lesser extent, for rhodium complex 1 and palladium complex 6). With respect to the yield of dimer IVb the catalysts

TABLE 4. PMR Spectra of IIIb, IVb, and VIIIb

Compound	Chemical shifts, δ, ppm				
	m (Et_3Si)	s (CH_3)	s (OCH_2)	s (OCH)	m (ring protons)
IIIb	0,51 ... 1,11 (15H)	2,52 (3H)	4,80 (2H)	—	6,87 ... 7,64 (3H)
IVb, threo and erythro	0,44 ... 1,11 (30H)	2,48 (6H), threo 2,51 (6H), erythro	— —	5,09 (2H), threo 4,93 (2H), erythro	6,87 ... 7,66 (6H)
VIIIb, threo and erythro	0,42 ... 1,09 (30H)	2,18 (6H)	—	4,78 (2H), threo 4,73 (2H) erythro	5,83 ... 6,10 (4H)

are arranged in the order $Rh(PPh_3)_3(CO)H \gg Rh(PPh_3)_2(CO)Cl >> Rh(PPh_3)_3Cl \gg Pd(PPh_3)_2Cl_2$. The activity of ruthenium catalysts in reaction (C) is virtually equal to zero, evidently as a consequence of the absence of dehydrogenating ability for them. The threo and erythro isomers of IVb are formed in approximately equal amounts (Table 2).

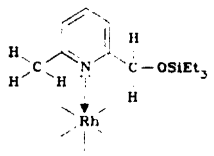


IVb

(threo and erythro)

(C)

In examining the data on the yield of silyl ether IIIb (Table 2) it may be noted that, as for ether IIIa (Table 1), a marked decrease occurs in the rate of formation of IIIb (in this case after 3 h of reaction), including those processes that occur on catalysts that do not bring about or lead to only small degrees of successive transformations of IIIb via reaction (C). It should be noted that this occurs even at low degrees of transformation of starting aldehyde Ib (∿20-30%). As in the case of the hydrosilylation of aldehyde Ia, this is apparently due to inhibition of the reaction as a consequence of deactivation of the catalysts by molecules of IIIb, which, inasmuch as they have a greater electron-donor capacity than aldehyde Ib, can form stable complexes with the catalysts, which thus lose their activity. There is, however, a certain contradiction here: IIIb molecules, which have great electron-donor capacity, deactivate the catalysts more slowly than the less electron-donor ether IIIa. This can be explained only by the fact that blind forms are formed with the participation of molecules of silyl ethers that are coordinated through the ring nitrogen atom; the introduction of a methyl group into the α'-position then can inhibit the complexing process as a consequence of the development of steric hindrance:



It might be noted that inhibition of the hydrosilylation of aldehydes Ia and Ib is least characteristic for the $Ru(PPh_3)_3Cl_2$ catalyst.

Thus in the hydrosilylation of 2-formylpyridines the reaction is inhibited after having attained certain degrees of transformation. However, almost complete conversion of the aldehyde is possible when dehydrocondensation of the resulting silyl ether is ensured. The experimental results presented in Table 2 show that this reaction proceeds rapidly with ether IIIb on rhodium complexes 2 and 3. These data confirm that deactivation of the catalysts occurs with the participation of precisely the silyl ethers of 2-pyridylcarbinols rather than other compounds such as the resinous substances that are formed in all cases when hydrosilylation is carried out at elevated temperatures; this is noted from the darkening of the reaction mixtures. The resulting blind form (which is not too stable — as in the case of ether IIIb) on rhodium catalysts 2 and 3 can undergo conversion to dimer IVb, which, because of its large size, is not retained in the coordination sphere of the metal

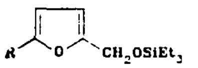
TABLE 5. Mass Spectra of the Products of Hydrosilylation of the Heterocyclic Aldehydes with Triethylsilane

Compound	m/z (relative intensity, %)*
IVa, threo	444 (M^+, 15), 415 (21), 283 (40), 223 (20), 222 (100), 194 (37), 193 (20), 136 (35), 115 (48), 87 (70), 75 (15), 59 (53)
IVa, erythro	444 (M^+, 33), 416 (15), 415 (30), 283 (26), 223 (18), 222 (100), 194 (50), 193 (37), 136 (30), 115 (52), 87 (80), 75 (17), 59 (58)
Va	301 (M^+-Et, 19), 283 (24), 223 (37), 222 (34), 207 (20), 194 (71), 136 (46), 115 (30), 107 (23), 103 (60), 93 (18), 92 (22), 87 (43), 79 (100), 77 (60), 75 (80), 55 (18), 59 (38), 53 (20), 52 (75) 51 (57)
VI	214 (M^+, 1), 212 (18), 184 (5), 156 (32), 155 (12), 129 (8), 106 (13), 78 (100), 52 (20), 51 (50)
IIIb	237 (M^+, 5), 210 (50), 209 (17), 208 (M^+-Et, 100), 150 (22), 106 (17)
IVb, threo	472 (M^+, 3), 443 (M^+-Et, 15), 311 (23), 237 (20), 236 (100), 208 (29), 184 (10), 150 (22), 115 (30), 87 (48), 59 (33)
IVb, erythro	472 (M^+, 7), 443 (M^+-Et, 10), 237 (20), 236 (100), 219 (15), 208 (22), 184 (10), 150 (18), 115 (32), 87 (48), 59 (33)
Vb	329 (M^+-Et, 38), 311 (18), 238 (20), 237 (100), 236 (62), 209 (22), 208 (92), 150 (39), 122 (57), 121 (15), 115 (41), 106 (25), 103 (17), 94 (13), 93 (36), 92 (30), 87 (65), 75 (32), 73 (20), 67 (24), 66 (29), 59 (52)
VIIIb (threo + erythro)	421 (M^+-Et, 2), 226 (18), 225 (100), 115 (13), 87 (26), 59 (14)

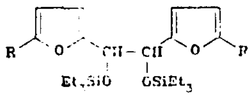
*The peaks of the M^+ ions and the ions with intensities ≥ 10% are presented.

atom of the catalyst, owing to which the catalyst is regenerated and can subsequently bring about hydrosilylation up to complete conversion of the starting aldehyde.

On virtually all of the catalysts at low degrees of conversion, when the effect of inhibition and successive processes is minimal, the reactivity of aldehyde Ib is higher than Ia, i.e., the introduction of a methyl group into the α-formylpyridine, which leads to an increase in the donor capacity of the molecule, increases the rate of hydrosilylation.



VII a,b



VIIIa,b

VII–VIII a R=H; b R=CH_3

The results of a study of the reaction with triethylsilane of furfural (IIa) at 25°C and 5-methylfurfural (IIb) at 25°C and 100°C in the presence of catalysts 1-6 are presented in Table 3 (the hydrosilylation of furfural at elevated temperatures was not carried out because of its pronounced resinification upon heating). Furfural is hydrosilylated on all of the catalysts to the corresponding furfurylcarbinol silyl ether VIIa; however, the catalysts differ markedly with respect to activity. Complexes 1, 3, and 4 display high activity: the yields of ether VIIa on them reach 60%, 70%, and 75%, respectively (Table 3). Complexes 2 and 5 are inactive; palladium catalyst 6 displays moderate activity (the yield of ether VIIa is up to 27%). Inhibition of the hydrosilylation of aldehyde IIa is not observed. After high yields of ether VIIa are reached (on catalysts 1, 3, and 4), the amount of VIIa in the reaction mixtures decreases (for reaction times greater than 4-5 h) because of successive transformations to unidentified resinous substances; this constitutes evidence for the instability of this compound. Dimer VIIIa is absent in the products of hydrosilylation of aldehyde IIa.

The reaction of aldehyde IIb with Et_3SiH at 25°C on catalysts 1, 3, 4, and 6 leads to the formation of silyl ether VIIb in up to 45%, 59%, 38%, and 58% yields, respectively (Table 3). It should be noted that palladium complex 6, under the conditions of the hydrosilylation of IIb, is reduced to palladium black (at least partially); this evidently leads to an increase in the activity of the palladium catalyst. Compound VIIb is more stable than VIIa: at reaction times up to 8 h its disappearance is observed only in the presence of catalyst 6; this process is evidently facilitated by the palladium black formed. Catalysts 2 and 5 are inactive in the hydrosilylation of aldehyde IIb (as well as IIa). In those cases in which the highest yields of ether VIIb were observed, dimer VIIIb was also detected in small amounts in the catalyzates (Table 3).

The activities of all of the catalysts in the hydrosilylation of aldehyde IIa are greater than that of IIb; complex 6 constitutes an exception; this is possibly due to its reduction in the hydrosilylation of aldehyde IIb. As in the case of IIa, inhibition by the reaction products is not observed in the hydrosilylation of IIb; this also distinguishes these processes from the hydrosilylation of formylpyridines.

In the hydrosilylation of aldehydes IIb with triethylsilane in the presence of catalysts 1-6 at 100°C (Table 3) the yield of ether VIIb increases, particularly on catalysts 2 and 5, which are virtually inactive at 25°C. The yield of dimer VIIIb increases on all of the rhodium and palladium complexes (1-3, 6) and reaches 35%, 37%, 47%, and 27%, respectively (Table 3). Since the effect of the temperature on the yield of dimer VIIIb is greater than on the yield of ether VIIb, it is apparent that the energy of activation of the dehydrocondensation is higher than that of the hydrosilylation process. Virtually no formation of dimer VIIIb occurs on ruthenium catalysts 4 and 5. This sort of behavior of the catalysts (rhodium and palladium catalysts catalyze the formation of dimers, whereas ruthenium catalysts do not) has already been noted in the hydrosilylation of formylmethylpyridine Ib. The dependence of the yield of dimer VIIIb on the time has S-shaped character (this is particularly appreciable when catalysts 2, 1, and 6 are used); this constitutes evidence for a consecutive mechanism for the formation of VIIIb from the intermediate, which, in analogy with the formation of dimer IVb in the hydrosilylation of Ib [reactions (B) and (C)], may be the more rapidly formed (inasmuch as it has a lower energy of activation) ether VIIb [reaction (D)]:

$$2\ \mathrm{IIb} \xrightarrow[\text{or } 100\,^\circ\mathrm{C}/1\text{—}6]{25\,^\circ\mathrm{C}/1;\ 3;\ 4;\ 6} 2\ \mathrm{VIIb} \xrightarrow[-\mathrm{H}_2]{100\,^\circ\mathrm{C}/1\text{—}3;\ 6} \mathrm{VIIIb} \qquad \text{(D)}$$

The formation of a dimer in the hydrosilylation process is more characteristic for 5-methylfurfural than for furfural (similar to the situation in the pyridine series). The highest overall yields of ether VIIb and dimer VIIIb were obtained on rhodium catalysts, which, with respect to activity, are arranged in the order $Rh(PPh_3)_2(CO)Cl > Rh(PPh_3)_3(CO)H > Rh(PPh_3)_3Cl$ (97%, 80%, and 74%, respectively). Somewhat lower yields were obtained on the ruthenium catalysts, but in this case their selectivity in the formation of ether VIIb is close to 100%. The palladium complex, despite its partial reduction, as evidenced by the development of palladium black in the reaction mixture, is least active in the transformation of aldehyde IIb (100°C).

The assumption regarding the successive formation of O-silylated 1,2-di(hetaryl)ethane-1,2-diols through a step involving the synthesis of silyl ethers of hetarylcarbinols in the catalytic hydrosilylation of aldehydes was checked in the case of a study of the transformations of specially prepared individual ether VIIb. In the presence of 0.1 mole % catalyst 3 at 100°C after 8 h VIIb undergoes complete conversion, and the yield of dimer VIIIb is 60 mole % (the remainder consists of resinous substances). A control experiment showed that the conversion of ether VIIb to dimer VIIIb does not occur without a catalyst under the same conditions. The results obtained constitute evidence in favor of a consecutive mechanism for the catalytic synthesis of dimeric products of hydrosilylation from the silyl ethers. A similar mechanism for the formation of the dimer was proposed in [4] in a study of the hydrosilylation of benzaldehyde in the presence of nickel catalysts.

Thus definite regularities are observed in the hydrosilylation of heterocyclic aldehydes on complex catalysts; some of them are common for all of the investigated processes, while others are in force only for aldehydes of a single series — pyridine or furan. The most common regularity is the formation of dimers as a result of the catalytic dehydrocondensation of the ethers obtained in the first step of the reaction. The process is particularly characteristic for methyl-substituted aldehydes of the pyridine and furan series; it does not occur on ruthenium catalysts.

A peculiarity of the transformation of formylpyridines is inhibition of the reaction by the hydrosilylation products — ethers IIIa and IIIb. Inhibition is not observed in the hydrosilylation of formylfurans. This means that inhibition is due to the presence of nitrogen atoms in the ring of the heterocyclic compounds undergoing hydrosilylation.

The orders of activities of the catalysts are virtually identical in the hydrosilylation of both formylpyridines; in the hydrosilylation of the two formylfurans the orders of activities of the metal complexes are also extremely close to one another but differ significantly from those for formylation. This constitutes evidence that the hydrosilylation of formylpyridines and formylfurans occurs via different mechanisms.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in deuterochloroform were recorded with a Bruker WH-90/DS spectrometer with tetramethylsilane as the internal standard. The mass spectra were obtained with a Kratos MS-25 chromatographic mass spectrometer with an ionizing electron energy of 70 eV. Analysis by GLC was carried out with a Chrom-4 chromatograph with a flame-ionization detector; the column was glass (1200 by 3 mm), the sorbent was 5% OV-17 on Chromosorb W-HP (80-100 mesh), the carrier gas was helium (60 cm^3/min), and the analysis temperature was 180-220°C, depending on the composition of the reaction mixture.

The $Rh(PPh_3)_3Cl$, $Rh(PPh_3)_3(CO)H$, $Rh(PPh_3)_2(CO)Cl$, $Ru(PPh_3)_3Cl_2$, $Ru(PPh_3)_2(CO)_2Cl_2$, and $Pd(PPh_3)_2Cl_2$ were products of the Fluka company. The furfural and 5-methylfurfural were purified prior to the research by vacuum distillation. 2-Formylpyridine was obtained by hydrolysis of 2-pyridyloxy-methanesulfonic acid with concentrated HCl with subsequent extraction with chloroform, drying ($MgSO_4$), and vacuum distillation to give a product with bp 46°C (5 mm) and n_D^{20} 1.5360 (n_D^{20} 1.5360 [5]). The 2-formyl-6-methylpyridine was obtained from the Aldrich company (mp 31-33°C) and was used without additional purification.

Hydrosilylation of Heterocyclic Aldehydes (General Method). A 10^{-3} mmole sample of the catalyst was placed in a 5-cm^3 Pierce reaction test tube, 1.2 mmole of Et_3SiH and 1 mmole of the aldehyde were added, and the reaction mixture was stirred at 25-130°C (see Tables 1-3). The course of the reactions was monitored by GLC and chromatographic mass spectrometry with the periodic selection of a sample with a microsyringe. The reaction times are presented in Tables 1-3. The reaction mixtures were then diluted with a tenfold amount of hexane, the mixture was stored for a few hours in a refrigerator, the precipitates (the catalyst and resinous products) were removed by filtration, the hexane and unchanged triethylamine were removed by distillation, the unchanged starting aldehydes were removed by vacuum distillation (1 mm), and the PMR spectra were recorded.

Compounds IIIa, IVa, VIIa, b, and VIIIa are known [1, 4, 6]. The PMR spectra and mass spectra of these compounds obtained in the present research were identical to those presented in [1, 4]. α-Pyridoin (VI) was isolated from several catalyzates, and its PMR spectrum coincided with the literature data [2]. The previously unknown IIIb, IVb, and VIIIb were isolated and identified in the following way. After the complexes, resins, and unchanged Et_3SiH and aldehydes Ib (38°C/1 mm) and IIb (51°C/1 mm) were removed from the catalyzates, the PMR spectra provided evidence for the presence in the reaction mixtures of IIIb and VIIb or a mixture of IIIb and IVb (threo and erythro) and VIIb and VIIIb (threo and erythro) (Table 4). The assignment of the signals in the PMR spectra was made in analogy with [4]. According to the PMR spectral data, the indicated reaction mixtures did not contain other substances. Compound IIIb was additionally purified by vacuum distillation [bp 86-88°C (0.8 mm), yellow liquid] and was isolated by preparative GLC [Pye-Unicam 105 chromatograph, 1000 by 7 mm column, sorbent 5% SE-30 on Chromaton W-AW-MMDS (0.43-0.60 mm), temperature 200°C]. The residue after removal of ether IIIb by distillation was purified with a column packed with silica gel (Adsorbenzien Woelm, Woelm Pharma) by elution with hexane-ether (8:2) to give IVb (deliquescent crystals). Found: C 66.2; H 9.5; N 6.1%. $C_{26}H_{44}N_2O_2Si_2$. Calculated: C 66.1; H 9.3; N 5.9%. Dimer VIIIb was obtained in the form of a yellow viscous liquid after removal of silyl ether VIIb [bp 63-65°C (0.8 mm) (bp 97-98°C (5 mm) [6])] from the corresponding catalyzates by distillation and subsequent purification of the residue with a column packed with silica gel [hexane-ether (9:1) as the eluent] with subsequent isolation with a preparative chromatograph under the same conditions as indicated for ether IIIb. For the isolation of IIIb, IVb, and VIIIb in this way we recorded the PMR spectra, the parameters of which coincided with those presented in Table 4 (the ratio of the threo and erythro isomers of dimers IVb and VIIIb was ∼1:1).

The mass spectra of IIIb, IVa, b, Va, b, VI, and VIIIb recorded for the first time are presented in Table 5.

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STRUCTURAL ANALYSIS OF 2,3,6-TRISUBSTITUTED 1,4-DIHYDRO-4-OXOQUINOLINES BY MEANS OF ^{13}C AND ^{15}N NMR SPECTROSCOPY

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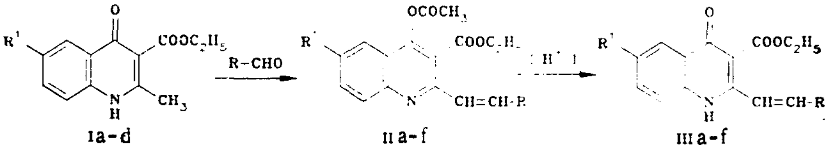
2,6-Substituted 1,4-dihydro-4-oxoquinoline-3-carboxylic acid ethyl esters were synthesized, and the effect of substituents on the migration of a hydrogen atom from the nitrogen atom to the oxygen atom was studied by ^{13}C and ^{15}N NMR spectroscopy. The presence of a 4-nitrophenylvinyl or 5-nitro-2-furylvinyl system in the 2 position of the compounds stabilizes their 4-oxoquinoline form.

Electron-acceptor substituents in the 2 position of 4-pyridones and 4-quinolones, by increasing the positive charge on the nitrogen atom, promote the migration of a hydrogen atom to the oxygen atom, and the corresponding 4-hydroxypyridines or 4-hydroxyquinolines are formed as a result [1]. A similar effect was expected from the introduction into the 2 position of 6-substituted 1,4-dihydro-4-oxoquinoline-3-carboxylic acid ethyl esters III of 4-nitrophenylvinyl and 5-nitro-2-furylvinyl systems, which have a pronounced negative conjugation effect.

However, the quinolone structure of IIIc, which was proved by PMR and IR spectroscopy [11.9 ppm (1H, s, NH) and 1630 cm^{-1} ($\nu_{C=O}$)], indicates the opposite (as compared with the expected) effect of the conjugated system containing a nitro group [2].

In order to make a detailed study of this phenomenon we synthesized IIIa-f by condensation of 2-methyl-1,4-dihydro-4-oxoquinoline-3-carboxylic acid ethyl esters Ib-d with 4-nitrobenzaldehyde and 5-nitro-2-furfural in acetic anhydride with subsequent hydrolysis of the acetyl group of the intermediate 4-acetoxy derivatives IIa-f of quinolines in an acidic medium.



I a $R^1=H$; b $R^1=OCH_3$; c $R^1=Cl$; d $R^1=Br$; II, III a $R=4\text{-}NO_2C_6H_4$, $R^1=H$; b $R=4\text{-}NO_2C_6H_4$, $R^1=OCH_3$; c $R=4\text{-}NO_2C_6H_4$, $R^1=Cl$; d $R=4\text{-}NO_2C_6H_4$, $R^1=Br$; e $R=$ 5-nitro-2-furyl, $R^1=H$; f $R=$ 5-nitro-2-furyl, $R^1=OCH_3$

The ranges of the locations of the ^{13}C signals of the quinoline ring of Ia, II, and IIIa-f and the model compound 2-methyl-1,4-dihydro-4-oxoquinoline (Table 1) correspond to the literature data for substances with similar structures. The diverse structures of the investigated compounds made it possible to refine the assignment of the chemical shifts of the $C_{(5)}$ and $C_{(8)}$ atoms, which differ from the data in [3].

The shift of the resonance signals of the $C_{(2)}$, $C_{(4)}$, and $C_{(6)}$ atoms to weak or strong field basically corresponds to the character of the inductive effect of the substituents. Thus the signal of the $C_{(4)}$ atom in Ia and IIIa-f under the influence of the oxo group is

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