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HYDROSILYLATION OF HETEROCYCLIC ALDEHYDES

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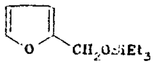
The hydrosilylation of O-, S-, and N-heterocyclic aldehydes with triethylsilane has been studied in the presence of different metal complex catalysts and the corresponding silyl ethers of hetarylcarbinols obtained. The rhodium complexes $Rh(PPh_3)_3Cl$ and $[Et_3PhCH_2N]RhCl_4$ have been found to be the most efficient catalysts for these reactions.

Hydrosilylation is a method for the preparation of organosilicon compounds. Besides this, this reaction is used in organic synthesis as an intermediate reaction, for instance, for the preparation of alcohols by the hydrosilylation of aldehydes and ketones, followed by hydrolysis [1].

So far, the hydrosilylation of heterocyclic aldehydes has not been sufficiently studied. In earlier work [2] prolonged refluxing (48-78 h) of aldehydes with triethylsilane (one of the most easily accessible hydrosilanes) in the presence of Spyer's catalyst (solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropanol) gave triethyl(furfuryloxy)silane (I), triethyl(5-methylfurfuryloxy)silane (II), and triethyl(2-thienylmethoxy)silane (III) with yields of 39, 27, and 41% respectively. The low yields demonstrate the low effeciency of the platinum catalyst in the addition of the silane to the C=O bond; besides this, as a strong acid H_2PtCl_6 enhances tar formation from the initial aldehydes.



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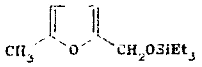

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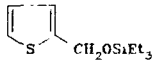

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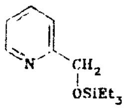

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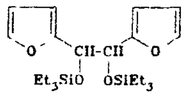

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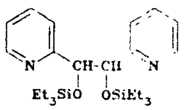

VI

The hydrosilylation of furfural and pyridine-2-aldehyde with triethylsilane in the presence of nickel chloride catalysts was carried out at 100-110° for 2-3 h [3, 4]; besides

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TABLE 1. Hydrosilylation of Furfural with Triethylsilane

Catalyst	T, °C	Time, h	Aldehyde conversion, %	Yield of ether I, % (selectivity, %)	Catalyst	T, °C	Time, h	Aldehyde conversion, %)	Yield of ether I, % (selectivity, %)
$Rh(PPh_3)_3Cl$	25	1	30	12 (40)	$[Et_3PhCH_2N]RhCl_4$	25	0,5	30	15 (50)
		1,5	50	22 (44)			1	60	43 (72)
		2	65	35 (54)			1,5	80	60 (75)
	60	1	50	32 (64)	Π-$CH_2PBu_3[RhCl_4]$	25	0,5	5	0
		2	70	49 (70)			1	10	5 (50)
	80	1	60	35 (58)			1,5	17	11 (65)
		1,5	70	37 (53)	$[Et_3PhCH_2N]FeCl_4$	100	0,5	—	0
		2	80	40 (50)	$[Et_3PhCH_2N]_2MCl_4$	100	0,5	—	0
$RhCl_3 \cdot 4H_2O$	25	0,5	40	22 (55)	(M = Ni, Cu, Zn)				
		1	80	56 (70)					

TABLE 2. Hydrosilylation of 5-Methylfurfural with Triethylsilane at 25°

Catalyst	Time, h	Aldehyde conversion, %	Yield of ether II, % (selectivity, %)
$Rh(PPh_3)_3Cl$	1	15	11 (73)
	2	25	18 (72)
$[Et_3PhCH_2N]RhCl_4$	1	90	85 (94)
	2	95	90 (94)
$[Bu_4N]_2PtCl_6$	1	7	5 (71)
	2	15	10 (67)
$[Et_3PhCH_2N]_2ZnCl_4$	1	0	0
	2	10	0

the compound I (34%) and triethyl(2-pyridylmethoxy)silane (IV) (37%), the reaction products contained the dimers (erythro- and threo-isomers) V (29%) and VI (48%).

In the presence of colloidal nickel the reaction of furfural with Et_3SiH at 110-140° leads to the formation of the addition product I (32%) and the dimer V (56%) [5]. It follows that the nickel catalysts, although active in the hydrosilylation of aldehydes, enhance the formation of dimeric dehydrocondensation products which cannot be converted to hetarylcarbinols by hydrolysis. Thus, the literature does not offer a satisfactory procedure for the hydrosilylation of heterocyclic aldehydes.

The objective of the present work was to investigate the hydrosilylation with triethylsilane of the following heterocyclic aldehydes: furfural, 5-methylfurfural, furan-2,5-dialdehyde, thiophene-2-aldehyde, three isomeric pyridine aldehydes, and pyrrole-2-aldehyde.

In agreement with the literature data on the hydrosilylation of aromatic aldehydes, good results were obtained with zinc chloride [6]; the best of the investigated catalysts for these reactions was found to be Wilkinson's catalyst $Rh(PPh_3)_3Cl$, in the presence of which (0.1-0.5%) at 20-80° in 30-60 min the hydrosilylation of some aromatic aldehydes with different silanes (molar ratio 1:1) proceeds with a yield of the corresponding siloxymethyl derivatives of 93-99% [7, 8].

Taking these data into account we have applied in our work the following rhodium complexes as catalysts for the hydrosilylation of hetarylaldehydes: $Rh(PPh_3)_3Cl$, $RhCl_3 \cdot 4H_2O$, $[Rh(phen)_2Cl_2]Cl$, $[Et_3PhCH_2N]RhCl_4$, Π-$CH_2PBu_3[RhCl_4]$. The last catalyst represents a rhodium complex, immobilized on an insoluble polymeric support, modified by quaternary phosphonium groupings. The activity of some ionic complexes of transition metals in the hydrosilylation of aldehydes was also studied which, as shown by us, act as catalysts for the hydrosilylation with different silanes at the $C{=}C$ and $C{\equiv}C$ bonds: $[Et_3PhCH_2N]FeCl_4$, $[Et_3PhCH_2N]_2CuCl_4$, $[Et_3PhCH_2N]ZnCl_4$, and $[Bu_4N]_2PtCl_6$, as well as $[Et_3PhCH_2N]_2NiCl_4$.

The hydrosilylation of the heterocylic aldehydes was carried out at 25-130°, the aldehyde and triethylsilane were taken in stoichiometric proportions, and the amount of catalyst was 0.1% in all cases.

The results obtained in the investigation of the reaction of furfural with triethylsilane in the presence of different catalysts are given in Table 1. The complexes $[Et_3PhCH_2N]$-$FeCl_4$ and $[Et_3PhCH_2N]_2MCl_4$ (M = Ni, Cu, Zn) were found to be inactive in the process. All

TABLE 3. Hydrosilylation of Thiophene-2-aldehyde with Triethylsilane

Catalyst	T, °C	Time, h	Aldehyde conversion, %	Yield of ether III, % (selectivity, %)
$Rh(PPh_3)_3Cl$	25	1	0	0
	100	2	20	15 (75)
	130	0,5	60	50 (83)
		1	68	56 (82)
		2	76	62 (81)
$[Et_3PhCH_2N]RhCl_4$	130	0,5	61	20 (33)
		1	65	23 (35)
		1,5	67	24 (34)

TABLE 4. Hydrosilylation of Pyridine Aldehydes with Triethylsilane at 130°

Aldehyde	Catalyst	Time, h	Aldehyde conversion,* %	Yield of ethers IV, IX, or X, % (selectivity, %)
Pyridine-2-aldehyde	$Rh(PPh_3)_3Cl$	2	20	2 (10)
		10	—	5
	$[Et_3PhCH_2N]RhCl_4$	1	35	12 (34)
		2	42	14 (33)
		3	44	17 (38)
	$RhCl_3 \cdot 4H_2O$	5	—	5
	$[Bu_4N]_2PtCl_6$	3	17	0,5 (3)
	$[Et_3PhCH_2N]_2NiCl_4$	3	13	0
Pyridine-3-aldehyde	$[Et_3PhCH_2N]_2ZnCl_4$	2	—	2
	$[Bu_4N]_2PtCl_6$	2	—	5
		5	—	15
		6	—	18
		7	—	21
		8	—	26
	$[Rh(phen)_2Cl_2]Cl$	2	—	0
	$[Et_3PhCH_2N]RhCl_4$	2	—	7
		3	—	15
		5	—	24
		6	—	37
		7	—	42
		8	—	42
	$Rh(PPh_3)_3Cl$	3	—	23
		5	—	30
		7	—	53
		8	—	52
Pyridine-4-aldehyde	$[Et_3PhCH_2N]RhCl_4$	1	—	3
	$Rh(PPh_3)_3Cl$	0,5	47	42 (89)
		1	76	70 (92)

*The conversion of pyridine-3-aldehyde was not determined.

rhodium complexes studied catalyze already at 20° the hydrosilylation of furfural and can be placed with respect to their activity in the order $RhCl_3 \cdot 4H_2O > [Et_3PhCH_2N]RhCl_4 > Rh(PPh_3)_3Cl > \Pi\text{-}CH_2PBu_3[RhCl_4]$. Of the rhodium contacts studied, the last catalyst has the lowest activity; this is characteristic for polymer-bound complexes and is usually attributed to sterical hindrances in the reaction of the substrates with the catalyst, due to the presence of the bulky polymer ligand. However, this catalyst can be separated from the reaction mixture by filtration and used again which is very important for a catalyst containing a noble metal.

In the presence of rhodium as well as platinum catalysts the addition proceeds already at room temperature with the formation of the ether II. The most active of the studied catalysts is $[Et_3PhCH_2N]RhCl_4$, in the presence of which the yields reach 90% (Table 2). The activity of this complex, as in the hydrosilylation of furfural, is higher than that of Wilkinson's catalyst. The reactivity of 5-methylfurfural in the hydrosilylation on the catalyst $[Et_3PhCH_2N]RhCl_4$ is higher than that of furfural, and somewhat lower on Wilkinson's catalyst.

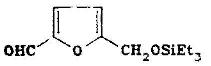
The hydrosilylation of furan-2,5-dialdehyde (which is a solid) with triethylsilane was carried out by refluxing in tetrahydrofuran and benzene in the presence of the catalyst

TABLE 5. Spectral Characteristics of the Products of Hydrosilylation of Heterocyclic Aldehydes with Triethylsilane

Compound	Chemical shift, δ (ppm)	m/z (relative intensity, %) *
I	0,4—1,1 (m 15H, Et_3Si); 4,62 (s, 2H, CH_2O), 6,25 (m, 2H, 3-H+4-H); 7,29 (m 1H, 5-H)	184 (14), 183 (M^+−Et, 92), 155 (16), 127 (18), 125 (70), 81 (100), 75 (11), 59 (10), 53 (22), 47 (11), 45 (12)
II	0,5—1,1 (m, 15H, Et_3Si); 2,29 (d, 3H, J=1 Hz, CH_3); 4,58 (s, 2H, CH_2O); 5,89 (dd, J_1=3 Hz, J_2=1 Hz, 1H, 4-H); 6,11 (d, 1H, J=3 Hz, 3-H)	226 (M^+, 5), 198 (15), 197 (M^+−Et 90), 103 (90), 95 (100), 75 (40), 47 (11), 45 (14)
III	0,4—1,1 (m 15H, Et_3Si); 4,87 (s, 2H, CH_2O); 6,91 (m 2H, 3-H+4-H); 7,22 (m 1H, 5-H)	228 ($M^{+\cdot}$, 0,5), 191 (M^+−Et, 38), 169 (19), 136 (21), 92 (14)
IV	0,4—1,1 (m, 15H, Et_3Si); 4,82 (s, 2H, CH_2O), 7,14 (m 1H, 4-H); 7,54 (m 2H, 3-H+5-H); 8,47 (m 1H, 6-H)	223 ($M^{+\cdot}$, 2,5), 195 (16), 194 (M^+−Et, 100), 136 (21), 92 (14)
IX	0,4—1,1 (m 15H, Et_3Si); 4,74 (s, 2H, CH_2O), 7,25 (m 1H, 5-H); 7,68 (m, 1H, 4-H); 8,51 (m, 2H, 2-H+6-H)	223 ($M^{+\cdot}$, 0,7), 195 (17), 194 (M^+−Et, 100), 167 (24), 165 (10), 137 (14), 92 (25), 87 (25), 69 (13), 65 (18), 59 (23)
X	0,4—1,1 (m 15H, Et_3Si); 4,74 (s, 2H, CH_2O), 7,27 (m 2H, 3-H+5-H); 8,53 (m, 2H, 2-H+6-H)	223 ($M^{+\cdot}$, 0,7), 195 (24), 194 (M^+−Et, 100), 167 (24), 165 (10), 137 (14), 92 (25), 87 (25), 69 (13), 65 (18), 59 (23)
VII	0,4—1,1 (m, Et_3Si); 4,71 (s, 2H CH_2O); 6,45 (d, 1H, J=3,6 Hz, 3-H); 7,18 (d, 1H, J=3,6 Hz, 4-H); 9,55 (s 1H, CHO)	211 (M^+−Et, 98), 183 (11), 140 (13), 139 (100), 125 (11), 113 (13), 111 (32), 109 (48), 87 (14), 81 (46), 77 (11), 75 (31), 59 (27), 53 (76), 52 (23), 51 (16), 47 (46), 46 (49)
VIII	0,4—1,1 (m Et_3Si); 4,60 (s, 4H, CH_2O); 6,15 (s, 2H, 3-H+4-H)	327 (M^+−Et, 20), 225 (20), 217 (17), 195 (30), 189 (28), 115 (46), 107 (16), 103 (28), 95 (77), 94 (41), 93 (16), 87 (100), 75 (46), 66 (16), 65 (15), 59 (67), 53 (11), 47 (37), 45 (36), 43 (11), 40 (13)

*Given are the peaks of the characteristic ions and ions with intensities ≥10%.

$[Et_3PhCH_2N]RhCl_4$ and without a solvent on $[Bu_4N]_2PtCl_6$ as the catalyst at 130°. Under these conditions the reaction practically does not proceed. Good results were obtained when the reaction was carried out without a solvent in the presence of Wilkinson's catalyst at 130°. After 5 h a complete conversion of the dialdehyde to triethyl(5-formylfurfuryloxy)silane (VII) (~45%) and 2,5-bis(triethylsiloxymethyl)furan (VIII) (~50%) occured; tar formation was negligible. Both compounds have been prepared for the first time and have been identified by GC-mass spectrometry and from the NMR spectrum of the mixture.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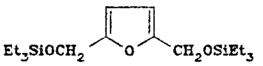
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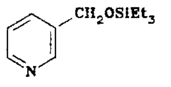
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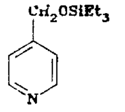
X

In the hydrosilylation of thiophene-2-aldehyde in the presence of two rhodium catalysts, better results were obtained with Wilkinson's catalyst; the selectivity of formation of the silyl ether III on $[Et_3PhCH_2N]RhCl_4$ was low (Table 3).

The data obtained in the reaction of pyridine aldehydes with Et_3SiH are given in Table 4. Attempts to obtain a product of the hydrosilylation of pyridine-2-aldehyde with a satisfactory yield were unsuccessful. The ether IV was isolated from the catalyzate by preparative gas chromatography and identified from its PMR spectrum, the parameters of which coincided with those given in [4]. The hydrosilylation of 3- and 4-pyridine aldehydes gave the ethers IX and X with yields of 50-70% when using Wilkinson's complex as the catalyst (Table 4).

The reaction of pyrrole-2-aldehyde with triethylsilane was studied at 130° in the presence of the complexes $Rh(PPh_3)_3Cl$ and $[Et_3PhCH_2N]RhCl_4$. Under these conditions the initial compounds do not undergo practically any conversions (besides some tar formed from the initial aldehyde). Evidently, the acid properties of the pyrrole aldehyde prevent hydrosilylation.

Thus, the present study has shown that the furan, thiophene, and pyridine aldehydes can be converted to the silyl ethers of the corresponding alcohols with relatively high yields: furfural and 5-methylfurfural already at 20°, the other aldehydes at 130°. Of the investigated catalysts only the rhodium compounds are suited for this purpose. The most active in most cases is the complex $[Et_3PhCH_2N]RhCl_4$ and also Wilkinson's catalyst. Rhodium chloride $RhCl_3 \cdot 4H_2O$ is also active but less selective than the above complexes. Although it does not cause tar formation from the aldehydes as Spyer's catalyst does, the platinum catalyst $[Bu_4N]_2PtCl_6$ is not sufficiently active in this reaction. The investigated complexes of Fe(III), Ni(II), Cu(II), and Zn(II) do not catalyze the hydrosilylation at the C=O bond.

The spectral characteristics of the synthesized ethers of heterocyclic alcohols I-IV and VII-X are given in Table 5. PMR spectra of compounds I and IV are the same as those in [4], the others had not previously been described.

EXPERIMENTAL

The PMR spectra were taken on a Bruker WH-90/DS spectrometer in deuterochloroform, with TMS as the internal standard. The mass spectra were obtained on a Kratos MS-50 mass spectrometer-GC combination with an energy of the ionizing electrons of 70 eV. GLC analysis was carried out on a Khrom-4 chromatograph with a flame ionization detector. The glass column (1.2 × 3 mm) was packed with 5% OV-17 on Chromosorb W-HP (80-100 mesh); the carrier gas was helium (60 ml/min), the analysis temperature was 140-200°, depending on the composition of the reaction mixture.

The catalysts $Rh(PPh_3)_3Cl$ and $RhCl_3 \cdot 4H_2O$ were commercial products; $[Rh(phen)_2Cl_2]Cl$ was prepared by the procedure given in [9]. The complexes $[Et_3PhCH_2N]_2MCl_4$ (M = Ni, Cu, Zn) and $[Et_3PhCH_2N]RhCl_4$.were synthesized in the same way as $[Et_3PhCH_2N]FeCl_4$ [10] by the reactions of MCl_2 and $RhCl_3 \cdot 4H_2O$ respectively with Et_3PhCH_2NCl. The immobilized rhodium complex $\Pi\text{-}CH_2PBu_3[RhCl_4]$ was obtained by the reaction of $RhCl_3 \cdot 4H_2O$ with polymer-bonded tributylmethylphosphonium chloride $\Pi\text{-}CH_2.PBu_3Cl$ (product of the firm Fluka); it represents a transversely cross-linked copolymer of styrene with divinylbenzene, modified by quaternary phosphonium groupings. The synthesis of $[Bu_4N]_2PtCl_6$ has been described in [11].

Hydrosilylation of Heterocyclic Aldehydes (General Procedure) (Tables 1-4). A Pierce reaction test tube (volume 5 cm^3) is charged with 10^{-3} mmole catalyst, 1 mmole Et_3SiH, and 1 mmole aldehyde. The reaction mixture is stirred at 25-130°. The progress of the reaction is followed by GLC and GC-mass spectrometry by periodically taking samples with a microsyringe. In order to separate the reaction products, the mixture was diluted with the 10-fold amount of hexane, cooled in the refrigerator, and the precipitate formed filtered off (the catalyst and tarry substances). The hexane was stripped off and the starting substances removed by distillation in vacuum (1 mm). According to the PMR spectra (Table 5) the residue represented the invididual ethers I-III, IX, X, or a mixture of VII and VIII. The PMR spectrum of compound IV was recorded after isolation of the substance from the reaction mixture by preparative GLC (Pye-Unicam 105 chromatograph, column 1 m × 7 mm, sorbent 5% SE-30 on Chromaton W-AW-MMDS (0.43-0.6 mm), temperature 200°).

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