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CATALYTIC HYDROSILYLATION OF FURAN, THIOPHENE, AND PYRIDINE ALDIMINES

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The addition of hydrosilanes ($HSiEt_3$, $HSiMe_2Ph$, H_2SiPh_2) to the CH=N bond of heterocyclic azomethines has been studied in the presence of monovalent complexes of rhodium and palladium. The effect on the reaction of the CF_3 group of the aldimines, which were obtained from O-, S-, and N-heteroaromatic aldehydes and 2-trifluoromethylaniline, has been clarified, as were other regularities of the processes being studied. A series of corresponding furans, thiophenes, and pyridine amines has been synthesized.

Keywords: heterocyclic Schiff's bases, transition metal complexes, hydrosilylation, catalysis.

We have recently synthesized a series of new heterocyclic amines by the condensation of furan, thiophene, and pyridine aldehydes with 2-trifluoromethylaniline, and also with aminopyridines [1,2]. As a continuation of the previous investigation of the reaction of triethylsilane with various imines [3], the hydrosilylation of a series of new aldimines has been studied in the present work. According to the data of [3] the dimeric complexes of monovalent rhodium and palladium are the most active catalysts for these processes among the numerous organometallic compounds used. In view of these results the following compounds were used as catalysts in the present investigation: bis{[μ-chloro(cycloocta-1,5-diene)]rhodium} or $[Rh(COD)Cl]_2$ and bis{[μ-chloroallyl]palladium} or $[Pd(allyl)Cl]_2$. The interaction of triethylsilane in the presence of these complexes has been studied with N-(hetarylmethylidene)-2-trifluoromethylanilines **1a-g** (where hetaryl = 2-furyl, 5-methyl-2-furyl, 2-thienyl, 5-methyl-2-thienyl, 2-, 3-, 4-pyridyl) and N-(6-methyl-2-pyridylmethylidene)-2-aminopyridine (**1h**), and also the last imine with two other hydrosilanes $HSiMe_2Ph$ and H_2SiPh_2. The reaction was carried out in benzene on heating (65°C) or at room temperature (with H_2SiPh_2) at a molar substrate–silane ratio of 1:1.2 and a catalyst concentration of 2 mol %.

The investigations showed that in reactions of both furan imines **1a,b** with triethylsilane the rhodium catalyst was significantly more active than the palladium. However the latter catalyzes the hydrosilylation of the thiophene aldimines **1c,d** though the rhodium did not display activity in these processes (Table 1). Seemingly the thiophene substrates deactivate the rhodium complex.

After carrying out the hydrosilylation of the O- and S-heterocyclic imines the reaction mixtures were investigated by ^1H NMR. The spectra of the products (before hydrolysis) contained two sets of signals, which indicates the formation of two types of silyl products, structures **2** and **3** (Scheme 1), containing the grouping $Et_3SiCH–NH$ and $CH_2–NSiEt_3$, characterized by two doublets of protons for the CH–NH group and a singlet for CH_2 respectively (Table 1). In previous work cited in reviews [4-7] (and also in [3]) it was shown that the hydrosilylation of a CH=N double bond leads mainly to the formation of products silylated at nitrogen, which are readily hydrolyzed.

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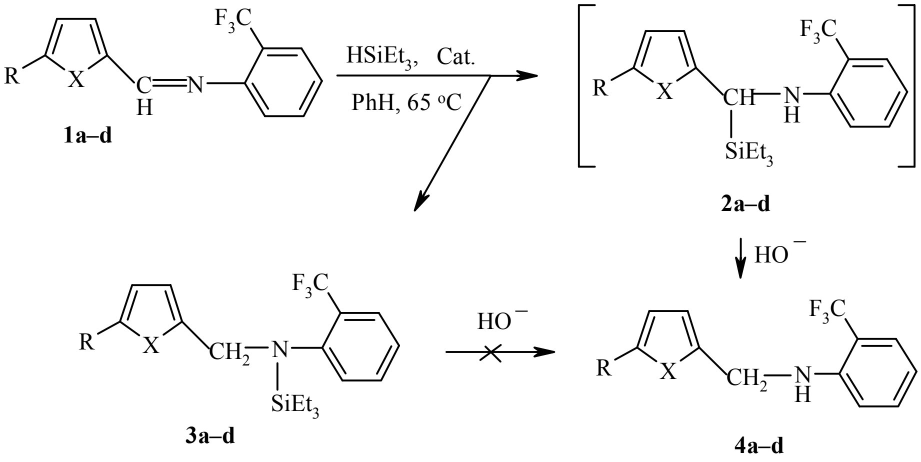
In difference to these data it was shown when investigating the hydrosilylation of imines **1a-d** that the silylated structures **2a-d** predominated in the products (80-85% of total quantity). After hydrolysis these compounds disappeared, being converted into the corresponding amines **4a-d**. Silyl products of structure **3a-d** are not hydrolyzed (even after repeating the hydrolysis procedure 2 or 3 times), and due to their stability (unlike structures **2a-d**) may be isolated using column chromatography on silica gel (Kieselgel 60). It is possible that the presence of the CF_3 group in position 2 of the aromatic ring by displaying electronic and steric factors largely directs hydrosilylation of the CH=N towards the formation of a C–Si rather than a N–Si bond. Moreover the latter bond is difficult to hydrolyze, also probably due to the effect of the neighboring CF_3 group.

Scheme 1



1-4 a, c R = H, **b, d** R = Me; **a, b** X = O, **c, d** X = S; **a, b** Cat = $(Rh(COD)Cl)_2$,
c, d Cat = $(Pd(allyl)Cl)_2$

Investigations of the interaction of triethylsilane with pyridine aldimines **1a-g** showed that substrates **1e** and **1f** did not react in practice in the presence of both catalysts $[Rh(COD)Cl]_2$ and $[Pd(allyl)Cl]_2$, only the 4-derivative **1g** was hydrosilylated (conversion was 72 and 100% respectively). After carrying out the hydrolysis the main product **4g** was isolated by column chromatography from the reaction mixture. In addition a small quantity of silyl product **3g** was also obtained (on catalysis with the palladium complex). The molecule of **3g** contains a CH_2–NSi grouping characterized by the presence in the ^{1}H NMR spectrum of a singlet at 4.89 ppm (integrating as two protons). The structure of **3g** is analogous to the structures **3a-d** isolated on silylating the furan and thiophene aldimines. The data obtained enable the assumption that, as in the hydrosilylation of O- and S-heteroaromatic azomethines **1a-d**, the process of adding hydrosilane to the N-heterocyclic imine **1g** occurs with the formation mainly of the intermediate structure **2g** which, as in the previous cases, may be caused by the effect of the 2-CF_3 group (Scheme 2).

The investigations showed that imine **1h** does not react with triethylsilane on using either the Rh or the Pd complexes. Reaction of this aldimine with two other more reactive [8] silanes ($HSiMe_2Ph$, H_2SiPh_2) is catalyzed only by the palladium complex $[Pd(allyl)Cl]_2$. In the products after hydrolysis, in difference to the silylation of all the imines obtained from 2-trifluoromethylaniline, no products of structure **3** containing a grouping with a N–Si bond were detected. Probably this is readily hydrolyzed in this case. On the other hand the corresponding compounds **2h** and **2h'** were isolated in small quantity from the reaction mixture after hydrolysis only on hydrosilylating imine **1h**. These have in their structure the SiCH–NH group characterized in the ^{1}H NMR spectra by two doublets integrating as 1H each (Scheme 3, Table 1).

TABLE 1. Characteristics of the Hydrosilylation Reactions and Their Products

Initial imine	Silane	Catalyst	Temp. °C/Time, h	Conversion of imine, % (GLC)	Product		^{1}H NMR (CDCl$_3$), chemical shift, δ, ppm, *J* (Hz)					
					before hydrolysis*	after hydrolysis*^{2}	CH$_3$ (3H, s)	SiCH–NH (structure **2**)		CH$_2$–NSi (structure **3**) (2H, s)	CH$_2$–NH (structure **4**)	
								CH (d)	NH (d)		CH$_2$ (d)	NH (br. s)
1	2	3	4	5	6	7	8	9	10	11	12	13
1a	HSiEt$_3$	[Rh(COD)Cl]$_2$	65/15	85	**2a**		—	3.95 *J* = 8.0	4.53 *J* = 8.0			
					3a	**3a**	—			4.33		
						4a	—				4.18 *J* = 6.0	4.67
	HSiEt$_3$	[Pd(allyl)Cl]$_2$	65/31	10	—							
1b	HSiEt$_3$	[Rh(COD)Cl]$_2$	65/11	88	**2b**		2.26	3.95 *J* = 7.5	4.33 *J* = 7.5			
					3b	**3b**	2.27			4.32		
						4b	2.29				4.16 *J* = 6.0	4.64
	HSiEt$_3$	[Pd(allyl)Cl]$_2$	65/23	16	—							
1c	HSiEt$_3$	[Rh(COD)Cl]$_2$	65/25	~0	—							
	HSiEt$_3$	[Pd(allyl)Cl]$_2$	65/25	80	**2c**		—	4.20 *J* = 6.0	4.7 br. s			
					3c	**3c**	—			4.60		
						4c	—				4.55 *J* = 5.4	4.7
1d	HSiEt$_3$	[Rh(COD)Cl]$_2$	65/30	~0	—							
	HSiEt$_3$	[Pd(allyl)Cl]$_2$	65/30	82		**3d**	2.40	—	—	4.49		
					—*^{3}	**4d**	2.44				4.47 *J* = 5.4	4.7

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
1e	$HSiEt_3$	$[Rh(COD)Cl]_2$	65/20	~0	—							
	$HSiEt_3$	$[Pd(allyl)Cl]_2$	65/21	~0	—							
1f	$HSiEt_3$	$[Rh(COD)Cl]_2$	65/16	~0	—							
	$HSiEt_3$	$[Pd(allyl)Cl]_2$	65/21	~5	—							
1g	$HSiEt_3$	$[Rh(COD)Cl]_2$	65/20	72		**3g**	—	—	—	4.89		
	$HSiEt_3$	$[Pd(allyl)Cl]_2$	65/21	~100	—*[3]	**4g**					4.42 *J* = 6.0	5.0
1h	$HSiMe_2Ph$	$[Rh(COD)Cl]_2$	65/18	~0	—							
	$HSiMe_2Ph$	$[Pd(allyl)Cl]_2$	65/12	80		**2h**	2.42	5.43 *J* = 6.4	5.56 *J* = 6.4	—		
					—*[3]	**4h**	2.55				4.58 *J* = 5.2	5.6
	H_2SiPh_2	$[Rh(COD)Cl]_2$	20/50, 65/9	~0	—							
	H_2SiPh_2	$[Pd(allyl)Cl]_2$	20/50	77		**2h'**	2.44	5.47 *J* = 6.0	5.55 *J* = 6.0	—		
					—*[3]	**4h**	2.55				4.58 *J* = 5.2	5.6

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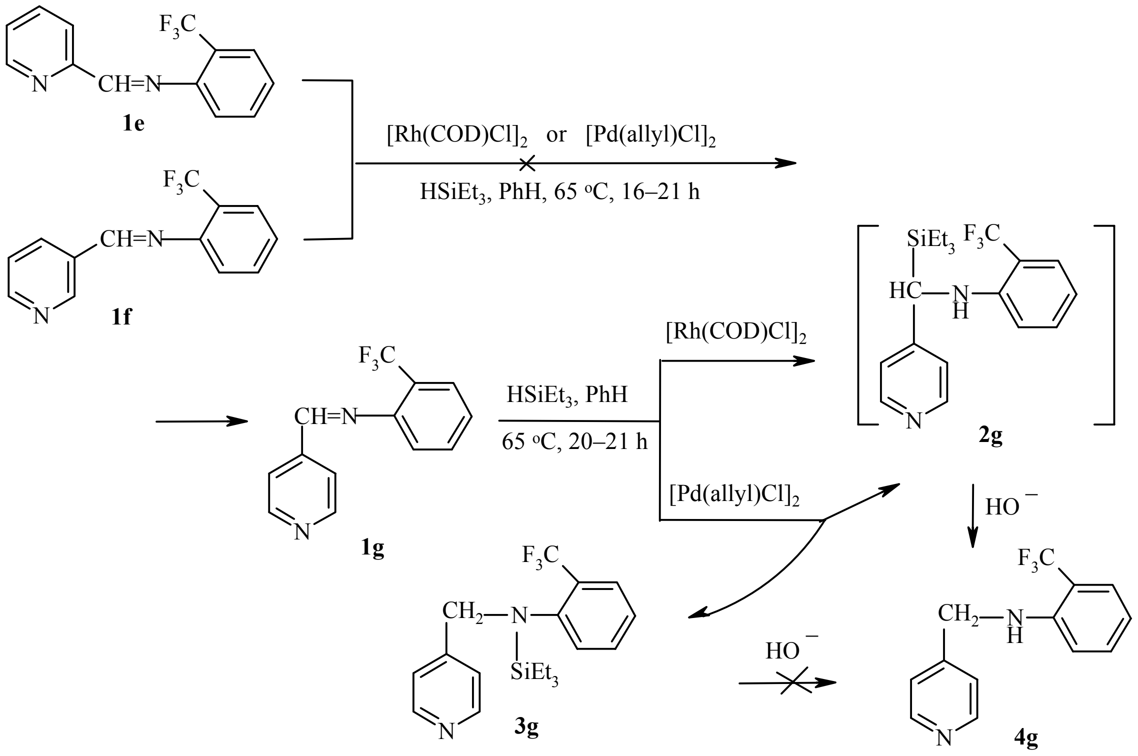
* Mixture of products according to ^1H NMR spectra.

*[2] Products were isolated by column chromatography. Eluent: benzene–ethyl acetate, 9:1 (**3a,b** and **4a,b**), benzene–ethyl acetate, 9.5:0.5 (**3c,d** and **4c,d**), chloroform–methanol, 9:1 (**3g**, **4g**, **2h**, **2h'**, **4h**).

*[3] The ^1H NMR spectra of mixtures of products were not recorded.

Scheme 2



Scheme 3

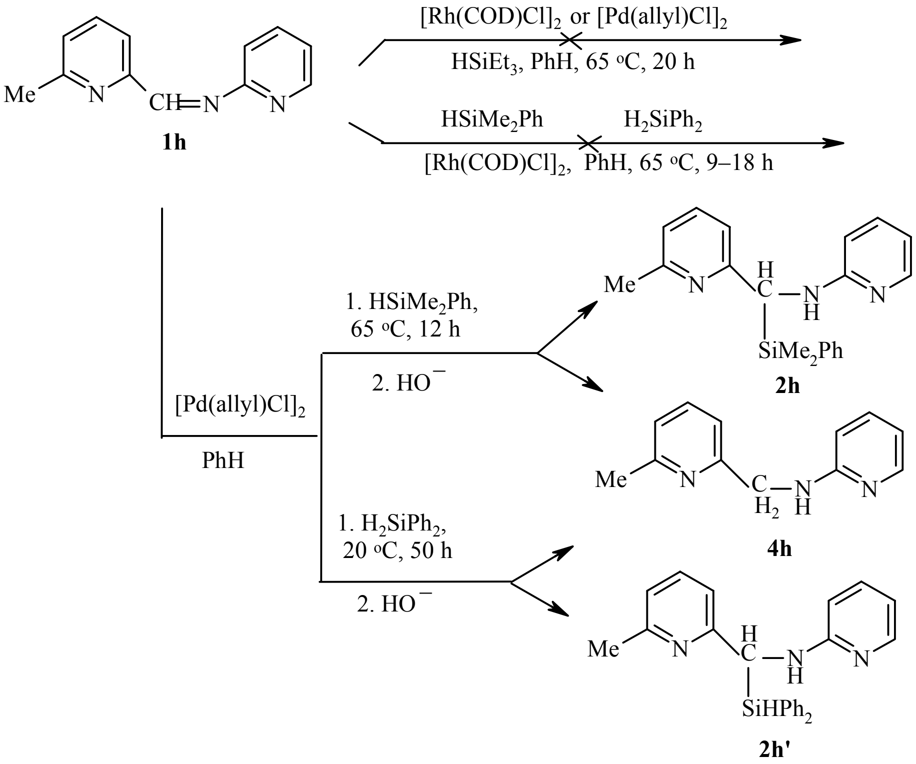


TABLE 2. Mass Spectra of the Synthesized N-(Hetarylmethyl)aromatic Amines **4a-h** and the Silyl Derivative **3g**

Compound	m/z (I_{rel}, %)*
4a	241 (33, M^+), 240 (12, $[M - H]^+$), 213 (14, $[M - CO]^+$), 202 (3), 192 (2), 182 (2), 172 (5, $[M - C_4H_3O - H_2]^+$), 165 (1), 154 (4), 145 (6, $[C_6H_4CF_3]^+$), 127 (9), 114 (6), 107 (2), 95 (4), 88 (2), 81 (100, $[C_4H_3OCH_2]^+$), 75 (7), 69 (4), 63 (4), 53 (39)
4b	255 (15, M^+), 216 (2), 202 (3), 196 (3), 185 (1), 172 (2), 154 (2), 145 (4, $[C_6H_4CF_3]^+$), 127 (8), 114 (3), 107 (2), 95 (100, $[H_3CC_4H_2OCH_2]^+$), 83 (1), 75 (4), 67 (5), 53 (6)
4c	257 (24, M^+), 218 (5), 145 (5, $[C_6H_4CF_3]^+$), 127 (9), 114 (5), 97 (100, $[C_4H_3SCH_2]^+$), 75 (4), 69 (8), 63 (6), 53 (13)
4d	271 (17, M^+), 232 (5), 202 (3), 172 (2), 154 (3), 145 (5, $[C_6H_4CF_3]^+$), 127 (11), 111 (100, $[H_3CC_4H_2SCH_2]^+$), 95 (5), 85 (2), 78 (9), 77 (10), 67 (6), 59 (5), 51 (7)
3g	366 (2, M^+), 337 (9, $[M - Et]^+$), 317 (6, $[M - Et - HF]^+$), 231 (4, $[M - SiEt_3 - HF]^+$), 214 (15), 213 (100, $[M - SiEt_3 - 2F]^+$), 193 (19, $[M - SiEt_3 - 2F - HF]^+$), 166 (5), 154 (4), 145 (2, $[C_6H_4CF_3]^+$), 127 (10, $[C_6H_5CF_2]^+$), 109 (14), 95 (11), 92 (7), 77 (31), 65 (8), 59 (9), 52 (20)
4g	253 (15, $[M + H]^+$), 252 (100, M^+), 231 (24, $[M - H - HF]^+$), 174 (25, $[M - Py]^+$), 172 (7), 154 (76, $[M - Py - HF]^+$), 145 (9, $[C_6H_4CF_3]^+$), 127 (68, $[C_6H_5CF_2]^+$), 125 (14), 107 (14, $[PyCH_2NH]^+$), 92 (27, $[PyCH_2]^+$), 80 (24), 79 (19), 78 (12, Py^+), 75 (17), 69 (8), 65 (36), 63 (20), 52 (20), 51 (10), 50 (18)
4h	200 (13, $[M + H]^+$), 199 (100, M^+), 197 (5, $[M - H_2]^+$), 196 (13), 183 (14, $[M - H - Me]^+$), 169 (7), 155 (2), 144 (1), 132 (2), 122 (6), 121 (72, $[M - Py]^+$), 119 (7, $[M - Py - H_2]^+$), 107 (39, $[PyNHCH_2]^+$), 94 (27, $[PyNH_2]^+$), 93 (7), 92 (5), 80 (8), 79 (15), 78 (24, Py^+), 65 (7), 63 (20), 52 (7), 51 (7)

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* Signals of characteristic ions are indicated.

In the ^{1}H NMR spectra of all the silylated compounds obtained by reaction of imines with triethylsilane the $SiEt_3$ grouping is displayed as two groups of signals for the CH_2 (6H, q) and CH_3 (9H, t) protons in the range δ 0.5-1.6 ppm. The chemical shift of the signal of the $SiMe_2$ group protons in the spectrum of silylated derivative **2h** is 1.25 ppm (6H, s). The spectra in the region of the proton signals of the heterocyclic rings and aromatic azo portion of the molecules of the synthesized products were close to those reported previously [1-3].

The following amines have been synthesized in this work: N-(2-furylmethyl)-2-trifluoromethylaniline (**4a**), N-(5-methyl-2-furylmethyl)-2-trifluoromethylaniline (**4b**), N-(2-thienylmethyl)-2-trifluoromethylaniline (**4c**), N-(5-methyl-2-thienylmethyl)-2-trifluoromethylaniline (**4d**), N-(4-pyridylmethyl)-2-trifluoromethylaniline (**4g**), and N-(6-methyl-2-pyridylmethyl)-2-aminopyridine (**4h**). The yield of these amines (on using the best catalyst) was 65-70%. Only the pyridine derivative **3g**, N-(4-pyridylmethyl)-N-triethylsilyl-2-trifluoromethylaniline, proved to be thermally stable of all the heterocyclic silyl-containing compounds mentioned. Its mass spectrum was recorded (Table 2).

EXPERIMENTAL

The ^{1}H NMR spectra were investigated on Varian Mercury (200 MHz) and Bruker WH-90/DS (90 MHz) spectrometers for solutions in $CDCl_3$, internal standard was TMS. The mass spectra were obtained on an HP 6890 GC/MS chromato-mass spectrometer fitted with an HP-5 MS (30.0 m × 250 μm × 0.25 μm) capillary column, with temperature programing from 70 to 260°C (10°C/min). The benzene was distilled over CaH_2 before use. The hydrosilanes and transition metal complexes used in the work were obtained from Fluka and Acros.

General Procedure for Hydrosilylation. A Pierce 5 cm^3 capacity reaction tube was purged with argon, then dry benzene (2 ml), catalyst (0.01 mmol), and the starting imine (0.5 mmol) were placed in it, after which the contents were mixed for 30 min at room temperature. The solution was cooled with ice to 0°C and hydrosilane (0.6 mmol) was added with a syringe. Reaction was carried out at 65°C or at room temperature, periodically removing a sample and analyzing it by TLC, GLC, and GLC-MS. At the end of the silylation (the process duration is shown in Table 1) the reaction mixture was evaporated at reduced pressure (30°C/15 mm) and the ^{1}H NMR spectrum recorded. Hydrolysis was then carried out by adding methanol (2.5 ml) and 10% aqueous $NaHCO_3$ solution (0.5 ml). The mixture was extracted with ether, the extract dried over anhydrous Na_2SO_4, then filtered, and evaporated. The residue was separated by liquid chromatography on a column of silica gel (Kieselgel 60, 0.063-0.200 mesh, Merck). The eluent was benzene–ethyl acetate for the furan and thiophene derivatives and chloroform–methanol for the pyridine derivatives. All the products obtained were yellow oily substances.

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