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Hydrosilylation of Aromatic Azomethines

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Abstract — The reactions of aromatic azomethines with methyldichlorosilane, phenyldichlorosilane, and dimethylchlorosilane, performed in the presence of Speier's, Wilkinson's, and Karstedt's catalysts and a series of Pt(II) complexes $LL'PtCl_2$, give hydrosilylation and reduction products whose ratio depends on the catalyst used. The highest yield of hydrosilylation products is attained with Pt(II) complexes as catalysts.

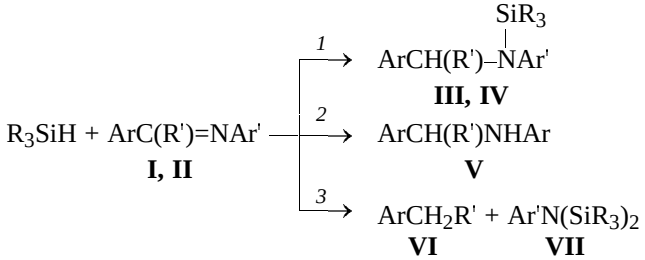
Aromatic azomethines are important and the most accessible mesomorphic compounds; they play a decisive role in development of high technologies in computer engineering and optoelectronics [1]. Modification of these compounds is a promising route to mesomorphic materials with a new phase behavior and a set of valuable properties. One of modification procedures may be hydrosilylation with various silanes. However, hydrosilylation of azomethines has been studied insufficiently [2, 3]. It is known [4] that hydrosilylation of benzalaniline with alkyl- and arylhydrosilanes in the presence of various catalysts is nonselective and is accompanied by reduction and reductive silylation followed by cleavage, silylation, and hydrogenolysis of *N*-benzylaniline, etc., with the yield of the desired hydrosilylation product being extremely low. Therefore, it is necessary to look for new catalysts allowing preparative synthesis of azomethine hydrosilylation products.

Our goal was comparative study of hydrosilylation of mesomorphic azomethine **I** (*p*-ethoxybenzylidine-*p*-methylaniline) and azomethine **II** containing a methyl substituent at the C=N bond (acetophenone anil). As hydrosilanes we used readily available dimethylchlorosilane, methyldichlorosilane, and phenyldichlorosilane, which allowed variation of the reactivity of both the substrate and reagent. As catalysts we used Speier's catalyst (1% H_2PtCl_6 in isopropyl alcohol), Pt(0) siloxane complex (so-called Karstedt's catalyst), and a series of Pt(II) complexes of the general formula $LL'PtCl_2$, tested previously in hydrosilylation of olefins, ketones, and vinylsiloxanes [5–8]. Also we tested Wilkinson's rhodium catalyst $(Ph_3P)_3RhCl$, since previous studies [2, 3] showed that this catalyst was the most selective in hydrosilylation of azomethines; it ensured predominant formation of hydrosilylation and reduction products.

Preparative isolation of hydrosilylation products obtained with chlorosilanes is complicated by their ready hydrolysis on contact with atmospheric moisture, followed by condensation. Andrianov *et al*. [4] analyzed the products of reactions of azomethines with hydrosilanes by GLC. However, a shortcoming of this method is the possibility of secondary transformations of the products in the vaporizer and column. Therefore, we chose NMR spectroscopy. Since both substrates contain methyl groups, all the transformation products can be reliably detected. The signal assignment in the NMR spectra of the substrates and hydrosilylation products in given in Table 1.

Experiments were performed at the substrate : reagent : catalyst molar ratio of 1 : 3 : 0.01. Performing the reaction at low temperatures generally leads to its higher selectivity. However, the total conversion of azomethines **I** and **II** in their reaction with methyldichlorosilane at 20°C in the presence of the Wilkinson catalyst was less than 3% in 24 h. Therefore, in the subsequent experiments the reactions were performed at 80°C for 24 h, which ensured high total conversion (Table 2).

The reaction of azomethines with hydrosilanes is a complex process involving hydrosilylation (*1*), reduction (*2*), and reduction–silylation followed by product cleavage (*3*) [4]:



When the reaction is performed in a solvent

Table 1. ^{1}H NMR spectra of **I**–**VII**

Comp. no.	Silane	δ, ppm, (*J*, Hz) ($CDCl_3$)
I		2.37 s (3H, $ArCH_3$), 1.45 t (3H, C*H*$_3$CH$_2$, *J* 6.7), 4.10 q (2H, OCH_2, *J* 6.7), 8.39 s (1H, CH=N)
II		2.25 s (CH_3)
III	$HSiCl_2CH_3$	2.28 s (3H, $ArCH_3$), 1.35 t (3H, C*H*$_3$CH$_2$, *J* 6.7), 3.98 q (2H, OCH_2, *J* 6.7), 4.50 s (1H, CH_2N), 0.95 s (3H, CH_3Si)
III	$HSiCl(CH_3)_2$	2.28 s (3H, $ArCH_3$), 1.34 t (3H, C*H*$_3$CH$_2$, *J* 6.7), 3.97 q (2H, OCH_2, *J* 6.7), 4.52 s (1H, CH_2N), 0.82 s (6H, CH_3Si)
III	$HSiCl_2Ph$	2.28 s (3H, $ArCH_3$), 1.35 t (3H, C*H*$_3$CH$_2$, *J* 6.7), 3.98 q (2H, OCH_2, *J* 6.7), 4.54 s (1H, CH_2N)
IV	$HSiCl_2CH_3$	1.79 d (3H, CCH_3, *J* 7.0), 4.56 q (1H, CHN, *J* 7.0), 0.92 s (3H, CH_3Si)
IV	$HSiCl(CH_3)_2$	1.67 d (3H, CCH_3, *J* 7.0), 4.54 q (1H, CHN, *J* 7.0), 0.80 s (6H, CH_3Si)
IV	$HSiCl_2Ph$	1.57 d (3H, CCH_3 , *J* 7.0), 4.60 q (1H, CHN, *J* 7.0)
V		2.29 s (3H, $ArCH_3$), 1.37 t (3H, C*H*$_3$CH$_2$, *J* 6.7), 4.02 q (2H, OCH_2, *J* 6.7), 4.29 s (1H, CH_2N), 4.80 s (1H, NH)
VI		2.24 s (3H, $ArCH_3$), 1.33 t (3H, C*H*$_3$CH$_2$, *J* 6.7), 3.96 q (2H, OCH_2, *J* 6.7)
VII	$HSiCl_2CH_3$	2.26 s (3H, $ArCH_3$), 1.16 s (6H, CH_3Si)
VII	$HSiCl(CH_3)_2$	2.26 s (3H, $ArCH_3$), 1.12 s (12H, CH_3Si)
VII	$HSiCl_2Ph$	2.26 s (3H, $ArCH_3$)

($CDCl_3$), all the three processes occur simultaneously, irrespective of the catalyst used (Table 2). The reaction mixture acquires a dark cherry-red color (a maximum was observed in the UV spectrum at 355 nm), suggesting partial transformation of silylated amines formed by pathway *3* into azo compounds. When the reaction is performed without a solvent, pathway *3* (cleavage of hydrosilylation–reduction products) is eliminated (Table 2), which is favorable for obtaining the desired products.

Tables 2 and 3 show that azomethines **I** and **II** strongly differ in the reactivity. Whereas the conversion of unsubstituted azomethine **I** is ~100% irrespective of the catalyst used, the total conversion of compound **II** containing a methyl substituent at the C=N bond is always considerably lower. The Pt(II)-based catalysts are optimal in this case; some of them ensure almost quantitative yield of the hydrosilylation products. At the same time, in this case virtually no reduction products are formed (as judged from the NMR spectra, sensitivity ~1%). This fact is important, as it opens prospects for preparing optically active silylated amines using chiral catalysts [9].

The relative activity of the catalysts depends on particular silane, and no clear regular trends can be revealed. On the whole, for each particular silane there is a specific optimal catalyst [2, 3]. Speier's catalyst shows high activity in hydrosilylation with such an inactive hydrosilane as dichloromethylsilane (Tables 2, 3). However, when this catalyst is used with azomethine **I**, the reduction prevails. In this case, Speier's

Table 2. Product yields (%) in hydrosilylation of azomethine **I**

Catalyst	**I**	**III**	**V**
Methyldichlorosilane			
Wilkinson's	0.5[a]	31.3	56.3
Karstedt's	1.5[a]	45.0	44.5
Wilkinson's	<0.1	53.5	46.5
Karstedt's	<0.1	38.5	61.5
Speier's	<0.1	14.0	86.0
$Pt(P(i\text{-}Pr)_3)_2Cl_2$	<0.1	31.3	68.7
$Pt(Bz_2S)_2Cl_2$	<0.1	59.4	40.6
$Pt(DMSO)(C_5H_5N)Cl_2$	<0.1	59.25	40.75
$Pt(DMSO)(Ph_3PS)Cl_2$	<0.1	30.6	69.4
$Pt(DESO)_2Cl_2$	<0.1	42.4	57.6
$Pt(Ph_3As)_2Cl_2$	<0.1	55.9	44.1
Dimethyldichlorosilane			
Wilkinson's	41.55	6.25	52.5
$Pt(Ph_3Sb)_2Cl_2$	4.5	63.0	32.5
Speier's	<0.1	16.0	84.0
$Pt(P(i\text{-}Pr)_3)_2Cl_2$	<0.1	7.0	93.0
$Pt(Bz_2S)_2Cl_2$	<0.1	17.9	82.1
Phenyldichlorosilane			
Wilkinson's	<0.1	50.8	49.2
Karstedt's	<0.1	60.9	39.1
Speier's	<0.1	18.0	82.0
$Pt(P(i\text{-}Pr)_3)_2Cl_2$	<0.1	41.0	59.0
$Pt(Bz_2S)_2Cl_2$	<0.1	38.5	61.5

[a] Solvent $CDCl_3$; with Wilkinson's and Karstedt's catalyst, the yield of **VII** is 11.9 and 9.0%, respectively. No solvent in other cases.

Table 3. Product yields (%) in hydrosilylation of azomethine **II**

Catalyst	**II**	**IV**
Methyldichlorosilane		
Wilkinson's	48.7	51.3
Karstedt's	31.6	68.4
Speier's	53.8	46.2
$Pt(P(i\text{-}Pr)_3)_2Cl_2$	16.7	83.3
$Pt(Bz_2S)_2Cl_2$	11.1	88.9
$Pt(DMSO)(C_5H_5N)Cl_2$	<1	>99
$Pt(DMSO)(Ph_3PS)Cl_2$	<1	>99
$Pt(DESO)_2Cl_2$	3.8	96.2
$Pt(Ph_3As)_2Cl_2$	7.4	92.6
$Pt(Ph_2PCH{=}CH_2)_2Cl_2$	50.6	49.4
Dimethyldichlorosilane		
Wilkinson's	93.0	7.0
$Pt(Ph_3Sb)_2Cl_2$	92.6	7.4
Speier's	53.8	46.2
$Pt(P(i\text{-}Pr)_3)_2Cl_2$	10.7	89.3
$Pt(Bz_2S)_2Cl_2$	73.1	26.9
Phenyldichlorosilane		
Wilkinson's	29.3	70.7
Karstedt's	54.0	46.0
Speier's	26.3	73.7
$Pt(P(i\text{-}Pr)_3)_2Cl_2$	1.5	98.5
$Pt(Bz_2S)_2Cl_2$	11.5	88.5

catalyst is the worst. With Wilkinson's catalyst, as a rule, the yield of benzylaniline **IV** also exceeds 50%. This catalyst shows low activity with dimethylchlorosilane.

On the whole, Table 2 shows that, for each hydrosilane in the reaction with **I**, it is possible to choose a catalyst ensuring more than 50% yield of the hydrosilylation product, which opens prospects for preparative use of this reaction for synthesis of new mesomorphic compounds. In hydrosilylation of **II**, Pt(II)-based catalysts are the best.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer. The UV spectra were taken on a Specord UV-Vis spectrophotometer.

Phenyldichlorosilane was prepared as described in [10], and azomethines, as described in [11]. The catalysts were prepared according to [5–8] and used as 0.1% solutions.

Hydrosilylation was performed in sealed ampules at 80°C; the azomethine : silane : catalyst ratio was 1 : 3 : 0.01.

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