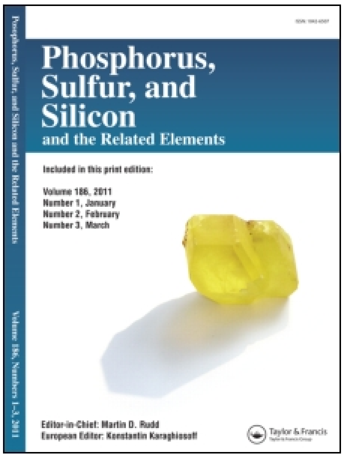

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HYDROSILYLATION OF AROMATIC AZOMETHINS

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The interaction of aromatic azomethins with methyldichlorosilane, phenyldichlorosilane, and dimethylchlorosilane has been investigated in the presence of a Speier catalyst, a Wilkinson catalyst, a Karsted catalyst, and a range of LL'PtCl$_2$ complexes. The reaction yielded the products of hydrosilylation and reduction as identified by ^{1}H NMR. The ratio of hydrosilylation / reduction products depends of the catalyst used. The higher yield of hydrosilylation products was observed with using Pt(II) complexes as a catalyst.

Keywords: Azomethins; catalysis; hydrosilanes; hydrosilylation; platinum complexes

Aromatic azomethins are important and the most available liquid crystalline compounds which can be used in optics and optoelectronics.[1] Chemical modification of these compounds is becoming increasingly important in synthetic methodology for the synthesis of new liquid crystalline materials with unusual phase behavior and desirable properties. One of the most promising methods for this seems hydrosilylation. Furthermore, this reaction has not been extensively explored.[2,3] This is due to the fact that catalytic hydrosilylation of benzylidene aniline with trialkyl- or aryl-hydrosilanes is a complex nonselective process and can include the following reactions: hydrosilylation, reduction, reduction/silylation with splitting, silylation and hydrogenolysis of *N*-benzylaniline, aniline silylation, *N*-benzylaniline hydrogenative

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silylation, *N*-silylaniline hydrogenative desilylation, etc.[4] The yield of hydrosilylation product is low. A possible solution to this problem is to search for new catalysts which make the hydrosilylation product the main reaction component.

In this paper, we describe our comparative studies of hydrosilylation of liquid crystalline azomethins I (*p*-ethoxybenzylidene *p*-methylaniline) and acetophenone aniline II containing a methyl group at C=N double bond. Available dimethylchlorosilane (DMS), methyldichlorosilane (MDS), and phenyldichlorosilane (PDS) were used. This made it possible to vary the reactivity of substrates and reagents. We used a Speier catalyst (1% of H_2PtCl_6 in isopropyl alcohol), siloxane-platinum(0) complexes (a Karsted catalyst), and a number of platinum (II) complexes $LL'PtCl_2$ which have been widely employed as catalysts for hydrosilylation of olefins, ketones, and vinylsiloxanes.[5–8] Additionally, a Wilkinson catalyst based on $(Ph_3P)_3RhCl$ was examined because Andrianov and co-workers reported it as the most selective catalyst for hydrosilylation of benzylidene aniline.[4]

Preparative isolation of hydrosilylation products with chlorohydrosilanes is hindered since they are ready hydrolyzed in the presence of moisture. In previous studies gas chromatography was used as the method for reaction products analysis.[4] A disadvantage of this method is the possibility of secondary transformations of products both in evaporator and in column during analysis. Because both substrates contain

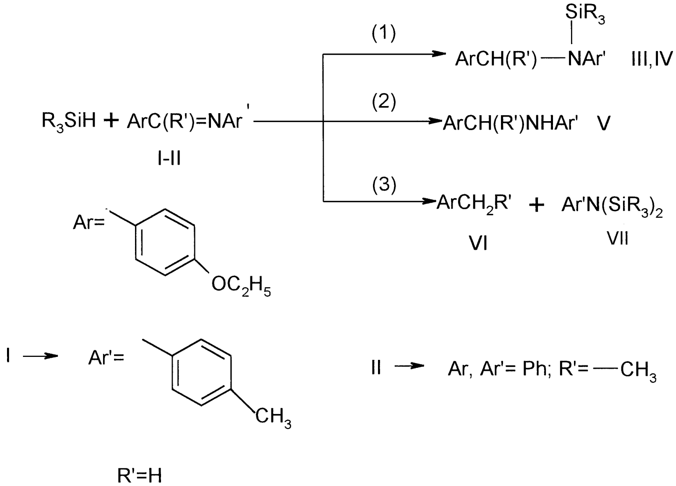
TABLE I ^{1}H NMR Parameters of Compounds I–VII

Compounds	^{1}H NMR spectrum ($CDCl_3$, δ, ppm, J, Hz)
I	2.37s (3H, $ArCH_3$), 1.45t (3H, $\underline{CH_3}CH_2$, J 6.7), 4.10k (2H, OCH_2, J 6.7), 8.39s (1H, CH=N)
II	2.25s (CH_3)
III($-SiCl_2CH_3$)	2.28s (3H, $ArCH_3$), 1.35t (3H, $\underline{CH_3}CH_2$, J 6.7), 3.98k (2H, OCH_2, J 6.7), 4.50s (1H, CH_2-N), 0.95s (3H, CH_3-Si)
III($-SiCl(CH_3)_2$)	2.28s (3H, $ArCH_3$), 1.34t (3H, $\underline{CH_3}CH_2$, J 6.7), 3.97k (2H, OCH_2, J 6.7), 4.52s (1H, CH_2-N), 0.82s (6H, CH_3-Si)
III($-SiCl_2Ph$)	2.28s (3H, $ArCH_3$), 1.35t (3H, $\underline{CH_3}CH_2$, J 6.7), 3.98k (2H, OCH_2, J 6.7), 4.54s (1H, CH_2-N)
IV($-SiCl_2CH_3$)	1.79 d (3H, $-CH_3$, J 7.0), 4.56k (1H, CH-N, J 7.0), 0.92s (3H, CH_3-Si)
IV($-SiCl(CH_3)_2$)	1.67 d (3H, $-CH_3$, J 7.0), 4.54k (1H, CH-N, J 7.0), 0.80s (6H, CH_3-Si)
IV($-SiCl_2Ph$)	1.57 d (3H, $-CH_3$, J 7.0), 4.60k (1H, CH-N, J 7.0)
V	2.29s (3H, $ArCH_3$), 1.37t (3H, $\underline{CH_3}CH_2$, J 6.7), 4.02k (2H, OCH_2, J 6.7), 4.29s (1H, CH_2-N), 4.80s (1H, NH)
VI	2.24s (3H, $ArCH_3$), 1.33t (3H,$\underline{CH_3}CH_2$, J 6.7), 3.96k (2H, OCH_2, J 6.7)
VII($-SiCl_2CH_3$)	2.26s (3H, $ArCH_3$), 1.16s(6H, CH_3-Si)
VII($-SiCl(CH_3)_2$)	2.26s (3H, $ArCH_3$), 1.12s (12H, CH_3-Si)
VII($-SiCl_2Ph$)	2.26s (3H, $ArCH_3$)

a methyl group, the NMR spectroscopy was chosen for identification of reaction products. The NMR data are shown in Table I.

The substrate-reagent-catalyst ratio 1:3:0.01 was chosen for the catalytic azomethins hydrosilylation. In general, if the reaction is carried out at lower temperature process selectivity is higher. However, the conversion of azomethins I and II in interaction with MDS at 20°C for 24 h was lower than 3% with a Wilkinson catalyst. Therefore, 80°C and 24 h were chosen for hydrosilylation of azomethins I and II with hydrosilanes. As shown in Table II this leads to high conversion of this reaction.

Catalytic reaction of hydrochlorosilanes with aromathic azomethins is a complex process and can include the following reactions: hydrosilylation (1), reduction (2), and reduction/silylation with splitting (3)[4]:



If the reaction was carried out in a solvent ($CDCl_3$) all three pathways 1–3 were observed independently of the catalyst used (Table II). The reaction mixture was purple colored. UV spectrum of the reaction mixture has a maximum at 355 nm which confirms the formation of azocompounds as a result of transformation of silylated amines in pathway 3. When the reaction was run without solvent pathway 3 was excluded (Table II). Therefore, it was possible to direct this process to the formation of hydrosilylation product.

As can be seen from Table II azomethins I are more reactive than II. For unsubstituted imines I the conversion is about 100% for all catalysts. For imines II with methyl substituent at C=N double bond the conversion is much lower. In this case the best catalysts were $LL'PtCl_2$ based on two-valence platinum. Some of them (e.g. $Pt(DMSO)(C_6H_5N)Cl_2$ and $Pt(DMSO)(Ph_3PSe)Cl_2$) gave the conversion

TABLE IIa Yields[1] of Products in the Hydrosilylation Reaction of Azomethins I (%)

Hydrosilane	Solvent	Catalyst	I	III	V	VII
MDS	$CDCl_3$	Wilkinson	0.5	31.3	56.3	11.9
MDS	$CDCl_3$	Karsted	1.5	45.0	44.5	9.0
MDS	–	Wilkinson	0.1<	53.5	46.5	–
MDS	–	Karsted	0.1<	38.5	61.5	–
MDS	–	Speier	0.1<	14.0	86.0	–
MDS	–	$Pt(P\text{–}iPr_3)_2Cl_2$	0.1<	31.3	68.7	–
MDS	–	$Pt(Bz_2S)_2Cl_2$	0.1<	59.4	40.6	–
MDS	–	$Pt(DMSO)(C_6H_5N)Cl_2$	0.1<	59.25	40.75	–
MDS	–	$Pt(DMSO)(Ph_3PS)Cl_2$	0.1<	30.6	69.4	–
MDS	–	$Pt(DESO^*)_2Cl_2$	0.1<	42.4	57.6	–
MDS	–	$Pt(Ph_3As)_2Cl_2$	0.1<	55.9	44.1	–
MDS	–	$Pt(Ph_2PCH{=}CH_2)_2Cl_2$	0.1<	58.0	42.0	–
DMS	–	Wilkinson	41.55	6.25	52.5	–
DMS	–	$Pt(Ph_3Sb)_2Cl_2$	4.5	63.0	32.5	–
DMS	–	Speier	0.1<	16.0	84.0	–
DMS	–	$Pt(P\text{–}iPr_3)_2Cl_2$	0.1<	7.0	93.0	–
DMS	–	$Pt(Bz_2S)_2Cl_2$	0.1<	17.9	82.1	–
PDS	–	Wilkinson	0.1	50.8	49.2	–
PDS	–	Karsted	0.1<	60.9	39.1	–
PDS	–	Speier	0.1<	18.0	82.0	–
PDS	–	$Pt(P\text{–}iPr_3)_2Cl_2$	0.1<	41.0	59.0	–
PDS	–	$Pt(Bz_2S)_2Cl_2$	0.1<	38.5	61.5	–

*DESO-diethylsulfoxide.

[1] Yields was determined using of ^{1}H NMR spectroscopy.

about 100%. In this case the reduction products were not identified by ^{1}H NMR. Hence, pathway 2 was excluded. It provides opportunity for the preparation of optically active silylated amines by using chiral transition-metal catalysts.[9] The activity of catalysts varied depending on the hydrosilane used. However, a distinct tendency is not observed (Table II). Furthermore, it is possible to say that optimal catalyst exists for each hydrosilane.[2,3] It is of interest that the Speier catalyst is very active for hydrosilylation with such inert hydrosilane as DMS (Table II). However its use in reaction with azomethin I leads to the predominance of reduction. In this sense the Speier catalyst is less preferable. As a rule with a Wilkinson catalyst the fraction of benzylaniline IV was 50% and higher. The activity of this catalyst was low with DMS.

In conclusion, as can be seen from Table II for each hydrosilane the catalyst exists which with the yield of hydrosilylation product was higher than 50%. Hence, it becomes possible to prepare new liquid crystalline compounds by the hydrosilylation reaction.

TABLE IIb Yields[1] of Products in the Hydrosilylation Reaction of Azomethins II(%)

Hydrosilane	Catalyst	II	IV
MDS	Wilkinson	48.7	51.3
MDS	Karsted	31.6	68.4
MDS	Speier	53.8	46.2
MDS	$Pt(P–iPr_3)_2Cl_2$	16.7	83.3
MDS	$Pt(Bz_2S)_2Cl_2$	11.1	88.9
MDS	$Pt(DMSO)(C_6H_5N)Cl_2$	<1	>99
MDS	$Pt(DMSO)(Ph_3PS)Cl_2$	<1	>99
MDS	$Pt(DESO)^*{}_2Cl_2$	3.8	96.2
MDS	$Pt(Ph_3As)_2Cl_2$	7.4	92.6
MDS	$Pt(Ph_2PCH{=}CH_2)_2Cl_2$	50.6	49.4
DMS	Wilkinson	93.0	7.0
DMS	$Pt(Ph_3Sb)_2Cl_2$	92.6	7.4
DMS	Speier	53.8	46.2
DMS	$Pt(P–iPr_3)_2Cl_2$	10.7	89.3
DMS	$Pt(Bz_2S)_2Cl_2$	73.1	26.9
PDS	Wilkinson	29.3	70.7
PDS	Karsted	54.0	46.0
PDS	Speier	26.3	73.7
PDS	$Pt(P–iPr_3)_2Cl_2$	1.5	98.5
PDS	$Pt(Bz_2S)_2Cl_2$	11.5	88.5

*DESO-diethylsulfoxide.

[1] Yields was determined using of ^{1}H NMR spectroscopy.

EXPERIMENTAL PART

The NMR spectra were recorded with Bruker AC 200 spectrometer. The UV spectra were measured with Specord UV-vis spectophotometer (DDR).

PDS was prepared by method,[10] and azomethins I and II by method.[11] DMS was commercially available from Merck, MDS was a gift Reachim (Russia). Catalysts were synthesized according to[5–8] and were used as 0.1% solutions.

The hydrosilylation reaction was carried out in sealed tubes at 80°C for 24 h at azomethin-hydrosilane-catalyst ratio of 1:3:0.01.

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