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Regiospesific Addition of Methyldichlorosilane to Styrene

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Abstract—Influence of various Pt-containing catalytic systems and additives to them on regioselectivity of styrene hydrosilylation by methyldichlorosilane was studied. The regiospesific approach to methyl(2-phenylethyl)dichlorosilane in the presence of tetrakis(triphenylphosphine)platinum Pt(0) is developed.

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Polymethyl(phenyl) siloxane rubbers are the bais of compounds, insolating and thermoprotecting (ablating) coatings characterized by high stability to radiation. These rubber coatings possess also outstanding dielectric properties and can be used in the temperature range from -70 to 300° C.

Domestic industry does not produce methylphenyldichlorosilane therefore new rubbers that would substitute imported polymethyl(phenyl)siloxane rubbers are welcome.

Methyl(2-phenylethyl)dichlorosilane (II) [hereinafter "methyl(phenethyl)dichlorosilane"] is the product of styrene hydrosilylation by methyldichlorosilane. Compound II acts as a monomer and/or comonomer for production of polymethyl(phenyl)siloxane rubbers [1, 2]. The starting materials, namely, styrene and methyldichlorosilane, are inexpensive products of Russian multi-ton technology.

The reaction results in formation of methyl(1phenylethyl)dichlorosilane (I) (α -isomer), methyl-(phenethyl)dichlorosilane (II) (β -isomer), and styrene polymerization products in accordance with the equation below.

 $(CH_3)HSiCl_2 + C_6H_5CH=CH_2$ $\rightarrow C_6H_5CH(CH_3)Si(CH_3)Cl_2 + C_6H_5CH_2CH_2(CH_3)SiCl_2$ I I + styrene polymerization products.

In the presence of the conventional platinum catalysts the addition of methyldichlorosilane to styrene results in predominant formation of compound II [3, 4]. Nickel catalysts direct this reaction towards α -isomer I [5–7].

We report here on the study of the addition reaction of methyldichlorosilane to styrene with the goal to optimize the conditions leading to compound **II** and to minimize the styrene polymerization.

Various additives to the platinum catalysts shift the ratio of products towards methyl(phenethyl)dichlorosilane **II** but do not exclude the formation of methyl(1phenylethyl)dichlorosilane (**I**) [8].

We have carried out a number of experiments in order to elucidate the influence of additives upon the yield and selectivity of the reaction. The following catalysts were used: siloxane complex of Pt(0) [9] and the Speier catalyst [4]. Platinum concentration in the catalysts was 5×10^{-5} g-atom Pt/mL and concentration of platinum with respect to styrene was 5×10^{-5} g-atom Pt/mol. The reaction progress and the ratio of isomers formed was monitored by GLC.

Experimental data are presented in the table.

The data show that the additives under study do not affect the regiospecific character of the reaction.

The next step of the study was the selection of a catalyst that would lead to high yield in the regiospecific hydrosilylation.

Phosphine complexes of Pt(0) and Pt(II) are known to act as efficient catalysts of silicon hydrides addition to olefins. The reactions in their presence proceed with an induction period and a high rate [10–13]. Kinetic data and mechanism of the process of arylalkenes hydrosilylation including that of styrene with Pt(II)

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Catalyst	Catalyst additive	Amount of additive $(\times 10^3 \text{ mol/g-atom Pt})$	Additive : catalyst (vol %)	Total yiels of I, II, %	I : II (wt %)
Speier	No additive			83	1:1
PSC ^a	No additive			85	1:1
PSC	Acetic acid	3.5	10:1	89	1:5
PSC	Acetic acid	2.1	6 : 1	93	1 : 99
PSC	Acetic acid	0.3	1:1	91	1 : 49
PSC	Triethylamine	0.3	2:1	86	1:1
Speier	Trifluoromethane sulfonic acid	0.2	1:1	92	1:2
Speier	Trifluoromethane sulfonic acid	0.3	1:1	81	1:2
Speier	Triphenylphosphine	0.1	1:1	No reaction	_
Speier	Ethyltrifluoroacetate	0.2	1:1	88	1:2

Influence of additives to the platinum catalyst on the total yield and the ratio of adducts

^a Platinum complex with siloxane.

bistriphenylphosphine complexes are reported in [12] and with Pt(0) tetrakis triphenylphosphine complexes, in [11, 13]. Hydrosilylation of styrene by various silane hydrides under the action of tetrakis(triphenylphosphine)platinum(0) proceeded regiospecifically without α -isomer formation and resulted in a high yield of compound II [10].

Our data on the styrene hydrosilylation in the presence of platinum phosphine complexes are presented below.

Catalyst	$(PPh_3)_2PtCl_2$	(PPh ₃) ₄ Pt
I : II, wt %	99:1	0:100
Yield of compound II, %	88	93
Polystyrene fraction, %	10	7

The obtained data show that the styrene hydrosilylation in the presence of all tested catalysts results in a high yield of two isomers mixture with the prevalence of compound **II**. The only catalyst that promoted regiospecific pathway of the reaction was tetrakis(triphenylphosphine)platinum.

We developed the conditions of hydrosilylation into compound **II** avoiding the induc-tion period [14]. Temperature threshold of the reaction was 90°C. Methyldichlorosilane was added slowly to the mixture of styrene and the catalyst preheated to 90°C and the reaction started upon addition of the first fraction of chlorosilane.

The study of the dependence of the product yield and the reaction time on the catalyst concentration showed that the increased catalyst concentration does not result in a higher yield and a shorter reaction time, but at the lower catalyst concentration leads to higher content of polystyrene. Longer boiling of the reaction mixture did not provide a higher yield.

It was shown recently [15] exposed that along with adducts I and II in sometimes side product formed in a pronounced yield (up to 25%) resulting from dehydrogenation, methyl(2-phenylvinyl)dichlorosilane with. GLC data show that in the process carried out according the developed procedure no side products are formed. Polystyrene is accumulated in insignificant quantity (8%).

According to ¹H NMR spectra the addition of methyldichlorosilane to styrene proceeded entirely in accordance with the Farmer rule.

EXPERIMENTAL

Chromatographic analysis of reaction products was carried out on a chromatograph LKhM-8MD, equipped with a column 2 m long of inner diameter 3 mm, stationary phase 20% SKTFT-50 on Cilite 545 (0.2–0.4 mm), carrier gas helium.

¹H and ²⁹Si NMR spectra were registered in standard 5 and 10 mm test tubes on a spectrometer Bruker Spectrospin AM-500, operating frequency 470.6 MHz with up to 1000 scans accumulation, internal reference TMS, solvent C_6D_6 .

The catalyst tetrakis(triphenylphosphine)platinum(0) was prepared by procedure [16].

Methyl(2-phenylethyl)dichlorosilane. A four neck flask equipped with a mechanical stirrer, condenser, dropping funnel, and thermometer was charged with 920 mL (8 mol) of styrene and 0.8 g (6×10^{-4} mol) of tetrakis(triphenylphosphine)platinum(0). The mixture was heated to 90°C followed by addition of 850 mL (8 mol) of methyldichlorosilane at a rate so as to maintain the reaction mixture temperature no higher than 120–130°C. Upon the end of addition of methyldichlorosilane the mixture was heated at 130°C for 2 h. The subsequent distillation in a vacuum gave 1634 g (93% yield) of methyl(phenethyl)dichlorosilane. ¹H NMR spectrum, δ , ppm: 0.9–0.95 m (3H), 1.68–1.72 m (2H), 3.05–3.09 m (2H), 7.43–7.54 m (5H). ²⁹Si NMR spectrum: 31.56 ppm.

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