

THE EFFECT OF SOLVENTS ON HYDROSILYLATION OF PHENYLALKENES CATALYSED BY $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]^*$

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Hydrosilylation of styrene, 2-phenyl-1-propene and *trans*-1-phenyl-1-propene by trialkylsilicon hydrides of the type $\text{CH}_3\text{R}_2\text{SiH}$ ($\text{R} = \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7, i\text{-C}_4\text{H}_9$) catalysed by $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ in the presence of benzene, 1,3,5-triethylbenzene, 1,2,3,4-tetraethylbenzene, pentaethylbenzene, hexaethylbenzene, 1,2,3,4-tetrahydronaphthalene, cyclohexane, tetrahydrofuran (THF), tributylphosphate (TBP), dimethylacetamide (DMA), trimethylphosphate (TMP), tributylphosphate (TBP) and hexamethylphosphorotriamide (HMPA) has been studied both in anaerobic conditions and in the presence of air oxygen. Aromatic solvents were found to affect the composition of reaction products similarly as benzene. The use of THF, TBP, TMP, DMA and HMPA as solvents for hydrosilylation of styrene by the above silanes suppresses formation of the α -adduct when the reaction is carried out under anaerobic conditions. The yields of hydrosilylation of 2-phenyl-1-propene and *trans*-1-phenyl-1-propene by $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiH}$ are decreased by the addition of THF, TBP, TMP and DMA while they are increased by using HMPA as the solvent.

As follows from the study of hydrogenation and oxidation of alkenes catalysed by $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$, solvents affect both the yield and the structure of reaction products¹⁻³. The conversion of hydrosilylation of 1-hexene by trimethylsilane or by triethoxysilane catalysed by the mentioned rhodium complex was influenced by the addition of triphenylphosphine, dimethylformamide and tetrahydrofuran⁴.

In the present work we were concerned with the effect of solvents on the selectivity of hydrosilylation of phenylalkenes by trialkylsilicon hydrides. The results of our previous work⁵ on hydrosilylation of phenylalkenes catalysed by $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ showed that the composition of the reaction mixture is strongly influenced by steric effects of substituents of the reactants. Solvent, which — similarly to reactants — interacts with the catalyst, could exert analogous effect.

Substitution of benzene by ethyl groups or by attachment of hydrogenated cycle to benzene (1,2,3,4-tetrahydronaphthalene) affects conversion of styrene and the composition of organosilicon products only very little (Table I). The conversion of styrene slightly decreases with increasing number of ethyl groups in the solvent.

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The composition of reaction products is affected so that we observe the increase in the amounts of the β -adduct and the addition-elimination product. On carrying out the reaction in tetra-, penta-, hexaethylbenzene or in cyclohexane the hydrogen evolved by the addition-elimination reaction does not react quantitatively with styrene to form ethylbenzene (compound C in Scheme 1). The lower conversion of styrene in the presence of cyclohexane indicates that the decreased yield of the α -adduct in the reaction carried out in the presence of hexaethylbenzene or cyclohexane, in which $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ does not dissolve, can be related to less efficient solvation of transient complexes rather than to the more difficult coordination of styrene caused by the bulkier aromatic solvent.

Coordinating ability of solvents can be characterized by a number of parameters. Of them, the donor number $\text{DN}_{\text{SbCl}_5}$ defined as $-\Delta H$ of dissolving SbCl_5 in a given solvent is describing best the above property of solvents. This parameter was determined for 40 solvents and varies from 0 for aromatic hydrocarbons to 38.2 for HMPA. The greater the $\text{DN}_{\text{SbCl}_5}$, the stronger the bond between solvent and the complex. The dependence of the conversion of phenylalkenes and of the composition of organosilicon products on the donor number of solvents has been followed with the use of 5 solvents of high donor number. Their presence in the reaction mixture did not cause formation of other products than those which are formed by the cor-

TABLE I

The Effect of Aromatic Solvents on Hydrosilylation of Styrene by Diethylmethylsilane Catalysed by $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$

Reaction conditions: styrene/organosilicon hydride mol. ratio = 1, $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ /styrene mol. ratio = 10^{-4} , the solvent/styrene ratio = 1 : 1 (v/v), 70°C, 6 h.

Solvent	X^a	Composition of organosilicon products, %			A/C
		α -adduct	β -adduct	A ^b	
Benzene	100	21.5	60.1	18.4	1.0
1,3,5-Triethylbenzene	97	23.1	63.6	13.3	1.0
1,2,3,4-Tetraethylbenzene	98	20.3	69.5	10.2	1.3
Pentaethylbenzene	95	18.0	70.9	11.1	1.4
Hexaethylbenzene ^c	97	17.4	68.7	14.1	1.5
1,2,3,4-Tetrahydronaphthalene	100	20.2	63.4	16.4	1.0
Cyclohexane	87	17.9	71.0	12.1	1.5

^a X = conversion of styrene in %, ^b the addition-elimination product (Scheme 1), ^c hexaethylbenzene was dissolved in styrene such that the volume of the solution at 25°C was the same as that obtained by mixing 1,3,5-triethylbenzene and styrene (1 : 1 v/v).

responding reaction carried out in benzene. Selected solvents fulfilled also further conditions, *i.e.* the reaction mixture was homogeneous. As shown in Table II, the use of the solvent with higher DN_{SiCl_4} in place of benzene leads to decreasing styrene conversion and α -adduct formation. The composition of organosilicon products of the reaction of styrene with diisopropylmethylsilane and diisobutylmethylsilane is affected by solvents analogously to the reaction of styrene with diethylmethylsilane. While in the reaction carried out in benzene the shielding of the Si—H bond of organosilicon hydride by branched alkyl groups did not decrease the conversion of styrene⁵, the addition of the more strongly coordinating solvents decreases styrene conversion more in the case of its reaction with diisopropylmethylsilane than in the case of the reaction with diethylmethylsilane or diisobutylmethylsilane. The ratio of the β -adduct to the addition-elimination product decreases in the sequence TBP > benzene > HMPA > DMA > THF > TMP. This ratio is not, however, dependent monotonously either on dielectric constant or DN_{SiCl_4} of solvents. This indicates that interactions of solvents with reactants are so specific

TABLE II

The Effect of Solvents on Reaction of Styrene with $(\text{CH}_3)_2\text{R}_2\text{SiH}$
Reaction conditions see Table I.

Solvent (DN_{SiCl_4})	ϵ^a	R	X	Composition of organosilicon products, %		A/C
				β -adduct	A	
THF (20.0)	7.6	C_2H_5	33.0	68.3	31.7	1.0
		<i>i</i> - C_3H_7	22.0	28.0	72.0	1.0
		<i>i</i> - C_4H_9	29.3	61.6	38.4	1.0
DMA (27.8)	38.9	C_2H_5	96.2	65.7	34.3	1.1
		<i>i</i> - C_3H_7	37.7	25.4	74.6	1.1
		<i>i</i> - C_4H_9	58.3	63.6	36.4	1.1
TMP (23.0)	20.6	C_2H_5	72.8	31.9	68.1	1.0
		<i>i</i> - C_3H_7	27.6	15.1	84.9	1.0
		<i>i</i> - C_4H_9	63.2	27.3	72.7	1.0
TBP (23.7)	6.8	C_2H_5	46.3	81.7	18.3	1.0
		<i>i</i> - C_3H_7	35.4	32.4	67.7	1.0
		<i>i</i> - C_4H_9	48.7	70.1	29.9	1.0
HMPA (38.2)	30.0	C_2H_5	71.9	72.4	27.6	1.3
		<i>i</i> - C_3H_7	34.8	19.4	80.6	1.3
		<i>i</i> - C_4H_9	67.5	70.6	28.4	1.2

^a Dielectric constant.

that the solvents can be considered in this case as cocatalysts. This assumption is substantiated also by finding that the reaction of 2-phenyl-1-propene and *trans*-1-phenyl-1-propene with diethylmethylsilane is inhibited by TMP, TBP, DMA

TABLE III

The Effect of $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ Concentration and of Hexamethylphosphorictriamide on Conversion of Phenylalkenes and Composition of Organosilicon Products

Reaction conditions: Styrene and the organosilicon hydride used in equimolar amounts, solvent to styrene ratio was 1 : 1 (v/v), $[\text{Rh}\{\text{ClP}(\text{C}_6\text{H}_5)_3\}_3]/\text{styrene}$ mol. ratio was $5 \cdot 10^{-3}$ for the reaction without solvent and 10^{-4} for the reaction in HMPA. Reaction time 6 h, inert atmosphere (argon).

Phenylalkene	Solvent/ temp., °C	Y ^a	Composition of organosilicon products, %			
			α-adduct	β-adduct	A	B
2-Phenyl-1-propene	none/60	20.0	76.3	0	8.6	15.1
	HMPA/70	45.0	94.0	94.0	0	6.0
<i>trans</i> -1-Phenyl-1-propene	none/60	16.2	64.6	36.4	0	0
	HMPA/70	39.0	12.5	87.5	0	0

^a Y = conversion of phenylalkenes in %, for designation of products see Scheme 1.

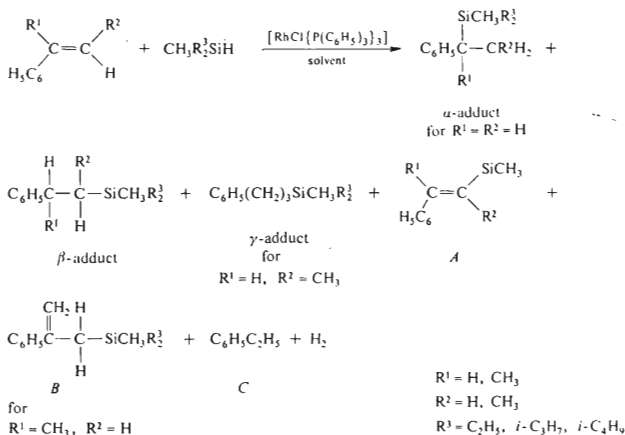
TABLE IV

The Effect of Catalyst Concentration and of Solvents on Reaction of Styrene with Diethylmethylsilane Catalysed by $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$

For reaction conditions see Table I.

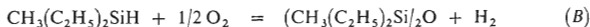
Rh complex/ styrene mol. ratio	X	Composition of organosilicon products			A/C
		α-adduct	β-adduct	A	
THF					
$1 \cdot 10^{-4}$	33.0	0	68.3	31.7	1.0
$2 \cdot 10^{-4}$	83.9	0	76.4	23.6	1.1
HMPA					
$1 \cdot 10^{-4}$	71.9	0	72.4	27.6	1.3
$2 \cdot 10^{-4}$	100.0	0	43.7	56.3	1.4

and THF, while the addition of HMPA increases conversion of both phenylalkenes (Table III). This increase is greater than that achieved by increased catalyst concentration or by carrying out the reaction without solvent⁵. Cocatalytic action of THF and HMPA confirms also the different effect of increasing catalyst concentration on the composition of organosilicon products of the reaction of styrene with diethylmethylsilane (Table IV). The presence of oxygen increases the conversion of styrene in its reaction with diethylmethylsilane and that both in the presence or absence of benzene and in the presence of the more strongly coordinating solvents such as THF, TMP, TBP, HMPA and DMA. As shown in Table V, in this case the addition products are favoured. The only exception is the reaction carried out in THF where on air the reaction products contain the addition-elimination product in greater amounts than after the reaction performed under anaerobic conditions. In the reaction of styrene with diethylmethylsilane in benzene the yield of the α -adduct increases in the presence of oxygen. On the other hand, this adduct is not formed on using HMPA, TBP and THF as solvents, and on adding TMP or DMA the adduct is formed in much lesser amounts than in the reaction in benzene under anaerobic conditions.



The reaction of 2-phenyl-1-propene and *trans*-1-phenyl-1-propene with diethylmethylsilane catalysed by $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ is inhibited by TBP, TMP, DMA and THF even in the presence of oxygen. In the presence of oxygen the solution of the catalyst in HMPA is the selective catalyst for hydrosilylation of styrene, 2-phenyl-

-1-propene and *trans*-1-phenyl-1-propene. At 100% conversion of the above phenylalkenes only addition products with trialkylsilyl group attached to the terminal carbon of the aliphatic chain are formed (styrene/ $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiH}$ mol. ratio = 1, the rhodium complex/styrene mol. ratio = 10^{-4} , 60°C, 6 h). In HMPA solution the reaction of 2-phenyl-1-propene and *trans*-1-phenyl-1-propene with diethylmethylsilane proceeds even at room temperature (25°C). The different coordination of diethylmethylsilane to the central rhodium atom of the complex in benzene and HMPA solutions is indicated by the different positions of the maximum of the absorption band of $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ solution ($21.3 \cdot 10^3 \text{ cm}^{-1}$ in benzene and $23.0 \cdot 10^3 \text{ cm}^{-1}$ in HMPA for volume ratio of the solvent to $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiH} = 1 : 3$ and the rhodium complex conc. = $2.18 \cdot 10^{-4} \text{ mol/l}$) which changes upon exposition of the solution to oxygen and also by faster oxidation of diethylmethylsilane in HMPA than in benzene solution. In HMPA and in the presence of $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ diethylmethylsilane reacts with air oxygen at 25°C to give $(\text{CH}_3(\text{C}_2\text{H}_5)_2\text{Si})_2\text{O}$ and hydrogen. The oxidation is quantitative after 3 days (equation (B), HMPA/ $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiH} = 1 : 1$ (v/v), $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3] : \text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiH}$ mol. ratio = 10^{-4}).



In benzene the above disiloxane is formed at a slower rate and the hydrogen evolved by the reaction has not been detected.

TABLE V

The Effect of Oxygen on Reaction of Styrene with Diethylmethylsilane Catalysed by $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ in Different Solvents

Reaction conditions: equimolar amounts of reactants, the Rh complex/styrene mol. ratio = 10^{-4} , the solvent to styrene ratio = 1 : 1 (v/v), 70°C, 6 h, on air.

Solvent	X ^a	Composition of organosilicon products, %			A/C
		α-adduct	β-adduct	A	
THF	43.6	0	59.0	41.0	1.1
DMA	100.0	9.2	70.0	20.8	1.0
TMP	84.1	3.5	52.4	44.1	1.1
TBP	79.0	0	100.0	0	—
HMPA	100.0	0	100.0	0	—

^a See Table I.

EXPERIMENTAL

Provenience and purification of organosilicon hydrides and phenylalkenes were the same as in the previous work⁵. $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ was prepared by reported procedure⁷. TMP (ref.⁸), 1,3,5-triethylbenzene⁹, 1,2,3,4-tetraethylbenzene¹⁰, pentaethylbenzene¹¹ and hexaethylbenzene¹¹ were obtained according to reported procedures. THF, DMA, HMPA and TBP were commercial products. All solvents were dried in usual way and redistilled under argon prior to use. The preparation and identification of organosilicon products was reported elsewhere⁵.

All experiments were carried out in sealed ampoules with degassed reactants and solvents. The ampoules were heated in a thermostated bath and shaken with a mechanical vibrator. After completion of the reaction, the ampoules were cooled by dry ice and analysed gas chromatographically under conditions already reported⁵. Isomerisation of organosilicon products was followed under the same conditions as hydrosilylation. The results showed that this process does not take place to the extent which would exceed experimental errors.

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