

HYDROSILYLATION OF ALLYLAMINE CATALYSED BY PLATINUM COMPLEXES*

Vlastimil VYBÍRAL, Petr SVOBODA and Jiří HETFLEŠ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

Received June 27th, 1978

Chloroplatinic acid modified with triphenylphosphine, -arsine and -stibine, some platinum-alkene and platinum-phosphine complexes were found to be efficient catalysts for the addition of triethoxysilane to allylamine yielding γ - and β -aminopropyltriethoxysilane. All the catalysts exhibited higher activity and some also higher selectivity compared to chloroplatinic acid. The effect of reaction conditions and the catalyst upon the proportion of both isomeric adducts is reported.

Hydrosilylation of allylamine by triethoxysilane represents synthetic route to γ -aminopropyltriethoxysilane. So far, several platinum compounds have been reported to be efficient catalysts for this reaction, such as chloroplatinic acid^{1,2}, $[\text{PtCl}_2 \cdot (\text{h}^2\text{-C}_2\text{H}_4) (\text{pyridine})]$ (ref.³), $[\text{PtCl}_2(\text{CH}_3\text{COCHCOCH}_3)_2]$ and related 1,3-diketones⁴ as well as $[\text{CH}_2=\text{CHCH}_2\text{NH}_3^+\text{PtCl}_3^-]$ (ref.⁵). Recently, the addition of carboxylic acids, their esters and some ketones has been claimed⁶ to enhance the catalytic activity of chloroplatinic acid.

Surprisingly, no attempt seems to have been made to utilize other platinum hydrosilylation catalysts. With the aim to ascertain the effect of the catalyst upon the course of the reaction we have examined the activity and selectivity of several catalyst systems such as chloroplatinic acid modified with addends, platinum-alkene and platinum-phosphine complexes. The results of this study are reported in the present work.

EXPERIMENTAL

Chemicals. Allylamine (Fa Berlin) was rectified and the fraction boiling at 52.5–53.5°C was used after drying over a molecular sieve. Trichlorosilane (Tesla, Rožnov) was purified by fractional distillation (b.p. 30.5–31.5°C). Other chemicals were of reagent grade purity and were used without further purification: formic, acetic, butyric, oxalic, salicylic and ascorbic acids (all Lachema Brno), trifluoroacetic acid (Fluka A.G., Buchs), cinnamic acid, ethyl formate, ethyl acetoacetate, acetone and 2,4-pentadione (all Lachema, Brno). Triphenylphosphine, triphenylarsine and triphenylstibine (all Fluka A. G., Buchs), tributylphosphine and tricyclohexylphosphine (from laboratory stock) were used without further purification, triphenylphosphine was re-

* Part LIII in the series Catalysis by Metal Complexes; Part LII: Chem. Prům. 28, 135 (1978).

crystallized from ethanol. Triethoxysilane was prepared by reported procedure⁷ and its purity was verified by gas-liquid chromatography.

Platinum compounds. Chloroplatinic acid (Kovohutě, Vestec) was used as supplied in the form of its 0.1M solution in isopropanol. $[\text{CH}_2=\text{CHCH}_2\text{NH}_3^+\text{PtCl}_3^-]$ (ref.⁸, 93% yield), $[\{\text{PtCl}_2\cdot(\text{h}^2\text{-ethylene})\}_2]$ (ref.⁹, 55% yield), $[\{\text{PtCl}_2(\text{h}^2\text{-styrene})\}_2]$ (ref.^{10,11}, 80% yield), $[\{\text{PtCl}_2(\text{h}^2\text{-4-vinylcyclohexene})\}_2]$ (ref.¹², 63% yield), $[\text{PtCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ (ref.¹³, 82% yield) and $[\text{Pt}\cdot\{\text{P}(\text{C}_6\text{H}_5)_3\}_4]$ (ref.¹³, 67% yield) were prepared by reported procedures as indicated (the yields obtained are given in parenthesis).

Hydrosilylation procedure. All experiments were made in a 25 ml round bottom flask equipped with a thermometer well and a reflux condenser topped with a calcium chloride tube. The flask was charged with a catalyst, allylamine (2.7 ml, 40 mmol), triethoxysilane (7.1 ml, 40 mmol) and the mixture was heated to boiling point by means of an oil bath, the temperature of which was intermittently increased to ensure 20–30°C temperature difference between the bath and the reaction mixture. The concentration of catalysts was changed within $4 \cdot 10^{-4}$ to $4 \cdot 10^{-3}$ mol/l. Chloroplatinic acid was used as 0.1M solution in isopropanol, platinum-alkene complexes were added as 0.02M solutions in allylamine, platinum-phosphine complexes as their 0.008M solutions in the same solvent. The reaction was interrupted when the reaction temperature reached 120–125°C and the samples withdrawn were subjected to analysis.

Analysis of the reaction mixture. The composition of the reaction mixture was determined by gas liquid chromatography using a Chrom 3 instrument equipped with 2 m × 3 mm column packed with 10% Silicone elastomer E 302 on Chromaton N (0.2–0.25 mm) (a thermal conductivity detector, 160°C oven temperature, 20 ml/min hydrogen flow rate). Relative amounts of individual substances were determined from the corresponding peak areas with the aid of calibration. The selectivity of catalysts was evaluated on the basis of the parameter *P* defined by expression (1) where *A* stands for tetraethoxysilane, *C* for other by-products and γ - and β - are γ - and β -aminopropyltriethoxysilane, respectively (all in mol%).

$$P = \frac{\gamma}{\beta + A + C} \quad (1)$$

RESULTS AND DISCUSSION

Before entering into a discussion of the results obtained with individual catalyst systems, several remarks concerning the reaction should be made. With all the catalysts tested, the addition of triethoxysilane to allylamine produced a mixture of both isomers, β - and γ -aminopropyltriethoxysilane, with the latter prevailing. In addition to evolution of the gas which contained hydrogen and small amounts of propylene, the main side reaction observed was the conversion of triethoxysilane into tetraethoxysilane. Other, still not fully identified, higher boiling products were formed in amounts not exceeding, with a few exceptions, several percent by weight. The presence of the products just mentioned stresses the expected similarity to the reaction course found for other platinum compounds, such as *e.g.* chloroplatinic acid¹. Because of the complexity of the reaction, the behaviour of the catalysts tested was characterized by several parameters; their activity by the reaction

time needed to achieve an arbitrary constant temperature (120°C) and by the overall yield of isomeric adducts and their selectivity by the γ - to β -isomer molar ratio, expressing the selectivity of the addition itself, and by the factor P (Eq. (1)) which gives the relative amount of triethoxysilane (used in 1 : 1 molar ratio to allylamine) consumed by the addition producing the γ -isomer.

Chloroplatinic acid with addends. As found earlier in our laboratory, the addition of Group V donors, especially tertiary phosphines, to chloroplatinic acid markedly increases the selectivity of the addition of some silicon hydrides to styrene¹⁴. A similar situation was also observed in hydrosilylation of allyl chloride¹⁵. The effect of several addends of this type upon the reaction under study is illustrated by the data presented in Table I. While triphenylphosphite and tributylphosphine slow down distinctly the reaction rate, triphenylphosphine shows rate-enhancing effect, depending somewhat on the relative amounts of both components (addend: H_2PtCl_6 mol. ratio). Besides small increase in the yield of the γ -isomer compared to the addition catalysed by chloroplatinic acid, the main advantage is the higher activity of the so formed catalyst. In contrast to triphenylphosphine, triphenylarsine and -stibine do not affect the rate of the reaction although both act similarly as tri-

TABLE I

The Effect of Group V Addends upon the Catalytic Activity of Chloroplatinic Acid in the Hydrosilylation of Allylamine by Triethoxysilane

Reaction conditions: $1.6 \cdot 10^{-5}$ mmol H_2PtCl_6 , 7.1 ml (0.04 mol) $\text{HSi}(\text{OC}_2\text{H}_5)_3$, 2.1 ml (0.04 mol) $\text{CH}_2=\text{CHCH}_2\text{NH}_2$.

Addend L	H_2PtCl_6 : L mol. ratio	Reaction- time, h ^a	Composition, % ^b					P^c
			γ -	β -	A	B	by- products	
—	—	9.7	58.2	11.3	10.7	17.8	2.2	2.4
$\text{P}(\text{OC}_6\text{H}_5)_3$	1 : 2	9.0 ^d	10.0	0	0	0	0	—
$\text{P}(\text{C}_6\text{H}_5)_3$	1 : 1	7.3	57.8	9.8	12.2	18.0	2.2	2.4
	1 : 1.5	6.9	63.6	11.2	9.1	13.4	2.8	2.8
	1 : 2	6.8	63.9	11.7	12.1	10.0	2.3	2.7
	1 : 3	6.5	61.5	10.4	10.1	15.5	2.5	2.7
$\text{P}(\text{C}_4\text{H}_9\text{-n})_3$	1 : 2	9.0 ^e	14.0	3.2	4.6	63.0	1.3	1.5
$\text{P}(\text{C}_6\text{H}_{11}\text{-cyclo})_3$	1 : 2	9.0	55.5	10.2	8.6	23.9	1.1	2.8
$\text{As}(\text{C}_6\text{H}_5)_3$	1 : 2	9.0	62.3	11.8	10.1	13.6	2.2	2.6
$\text{Sb}(\text{C}_6\text{H}_5)_3$	1 : 2	9.0	63.3	11.9	10.4	12.1	2.2	2.6

^a The time needed to achieve a temperature of 120°C . ^b γ - and β -stands for the γ - and β -isomer, A is tetraethoxysilane and B is triethoxysilane. ^c See Eq. (1). ^d After that time the temperature raised to 76°C . ^e After the time recorded the reaction mixture temperature was 87°C .

phenylphosphine concerning the proportion of both isomers produced. The difference between the behaviour of tributylphosphine and tricyclohexylphosphine demonstrates that the behaviour of catalyst systems based on modified chloroplatinic acid depends upon the electronic and steric properties of the addends in a complex way. This reflects in their efficiency which decreases in the order: $P(C_6H_5)_3 < As(C_6H_5)_3$, $Sb(C_6H_5)_3 > P(C_6H_{11}\text{-cyclo})_3$, $H_2PtCl_6 > P(C_4H_9\text{-}n)_3 > P(OC_6H_5)_2$.

Other systems based on modified chloroplatinic acid which were reported⁶ to effect hydrosilylation of allylamine contain carboxylic acids, their esters or carbonyl compounds as addends. Their efficiency is documented by the results summarized in Table II. From the inspection of the Table it is seen that not all of the addends claimed to enhance the activity do act in this way. The effect of several other acids not disclosed in the patent mentioned is shown in the last four rows of the Table.

TABLE II

The Effect of Some Carboxylic Acids, Their Esters and Some Carbonyl Compounds upon the Activity of Chloroplatinic Acid in the Hydrosilylation of Allylamine by Triethoxysilane

Reaction conditions: 7.1 ml (0.04 mol) $HSi(OC_2H_5)_3$ and 2.1 ml (0.04 mol) $CH_2=CHCH_2\cdot NH_2$, $4.2 \cdot 10^{-6}$ mol $H_2PtCl_6 \cdot 6 H_2O$.

Addend mol · 10 ³	Reaction time, h ^a	Composition, % ^b				by- products	P ^c
		γ-	β-	A	B		
—	24 ^d	41.2	8.4	6.8	42.1	1.4	2.4
Acetic acid (1.05)	21	52.4	10.6	14.7	19.6	2.7	1.9
Trifluoroacetic acid (0.87)	24	56.5	12.6	9.8	18.9	2.3	2.3
Butyric acid (9.65)	28 ^e	30.1	7.4	13.1	48.1	0.8	1.4
Benzoic acid (0.49)	21	56.4	12.7	12.2	16.8	1.9	2.1
1-Tartaric acid (1.33)	19	55.3	8.0	36.7	0	0	1.3
Citric acid (0.31)	24 ^e	27.3	5.3	10.6	54.5	1.8	1.5
Ascorbic acid (0.34)	24 ^f	43.2	11.9	19.6	20.2	5.1	1.2
Acetone (1.36)	24 ^e	30.2	8.4	13.7	45.8	1.9	1.3
Acetylacetone (0.58)	24	54.9	11.6	12.4	18.7	2.4	2.1
Ethyl acetoacetate (0.60)	24	54.0	12.2	11.6	20.1	2.1	2.1
Formic acid (2.65) ^h	24 ^{e,g}	19.4	5.1	29.8	42.3	3.0	0.5
Oxalic acid (1.11) ^h	12	51.6	8.8	30.1	7.3	2.1	1.3
Cinnamic acid (0.34) ^h	13	55.8	9.8	16.6	15.6	2.1	2.0
Salicylic acid (0.21)	19	52.4	11.1	15.4	16.6	4.4	1.7

^a The time needed to achieve a temperature of 120°C. ^b See footnote ^b in Table I. ^c See Eq. (1).

^d 105°C. ^e 92°C. ^f 108°C. ^g The following data were obtained for the ethyl ester: 85°C, 13.8% γ-, 2.2% β-, 12.8% A, 70.3% B, 0.8% by-products, $P = 1.3$. ^h $1.07 \cdot 10^{-5}$ mol $H_2PtCl_6 \cdot 6 H_2O$.

General feature of these systems is their lower selectivity (see *P* values) due mainly to unfavourable formation of tetraethoxysilane. This limits also the usefulness of those systems with which the γ -isomer is obtained in the higher yield compared to the chloroplatinic acid catalysed addition. Furthermore, in contrast to Group V addends, in this case the behaviour of chloroplatinic acid is affected only when the above discussed compounds are used in a large excess with respect to the acid.

Platinum-alkene and platinum-phosphine complexes. As demonstrated by the results summarized in Table III, several platinum-alkene complexes are efficient catalysts for the addition studied (experiments 2-4). Compared to chloroplatinic acid (experiment 1) they exhibit both the higher activity and selectivity (measured by *P* factor). In their presence the formation of tetraethoxysilane is substantially suppressed. Similarly effective is a platinum-phosphine complex formed in situ from the platinum-alkene complex and triphenylphosphine (experiments 5-8). Confrontation of the results yields information about the nature of catalytically active species. In the case of alkenic platinum complexes their efficiency for the addition increases in dependence upon the alkene ligand in the sequence: ethylene < styrene < 4-vinylcyclohexene which parallels their increasing stability.

TABLE III

Hydrosilylation of Allylamine by Triethoxysilane Catalysed by Platinum-Alkene Complexes
For reaction conditions and denotation of the compounds see TABLE II.

No	Catalyst, (mol . 10 ⁶)	Reaction-time, h ^a	Composition, %					<i>P</i>
			γ -	β -	A	B	by-products	
1	H ₂ PtCl ₆ (16)	9.7	58.2	11.3	10.7	17.8	2.4	2.4
2	[PtCl ₂ (ethylene)] ₂ (8)	8.8	52.5	9.7	4.5	29.2	3.5	3.7
		(12)	6.8	58.8	9.8	3.4	22.2	2.5
3	[PtCl ₂ (styrene)] ₂ (8)	7.3	59.8	12.1	3.4	24.1	2.1	3.4
4	[PtCl ₂ (4-vinylcyclohexene)] ₂ (8)	7.0	67.5	12.4	5.0	13.0	2.2	3.5
		(12)	5.5	67.5	11.1	4.7	14.1	2.6
5	[PtCl ₂ (ethylene)] ₂ (8) + P(C ₆ H ₅) ₃ (12)	7.0 ^b	70.1	11.1	5.0	10.9	2.9	3.7
6	(16)	7.0 ^b	69.8	13.1	4.2	11.8	1.1	3.8
7	(24)	7.0 ^b	61.8	9.0	4.2	21.5	3.5	3.7
8	(32)	7.0 ^b	55.4	8.6	5.3	26.1	3.2	3.4

^a The time needed to achieve a temperature of 120°C. ^b The reaction carried out for a constant time.

The interaction of the silicon hydride with these complexes in the absence of allylamine leads to their decomposition to metallic platinum. The fact that these complexes are catalysts shows that the catalytically active species contains both coordinated silicon hydride and allylamine. The observed difference between the behaviour of the platinum-alkene complexes indicates, however, that at least in some species also the alkene ligand remains coordinated to the metal, as in the opposite case the above difference should hardly be expected. This assumption is also supported by the fact that no induction period has been observed in the presence of these catalysts, which excludes the different rate of the exchange of the alkene ligand for allylamine as the reason of difference in the catalytic activity. Even in the case of the platinum-(4-vinylcyclohexene) complex the alkene is not, however, bonded strongly enough to prevent decomposition of the complex which proceeds to a small extent in the course of the reaction as the result of steadily increasing reaction temperature. We believe that this is the main reason why the addition of triphenylphosphine has favourable effect, shortening the reaction time and increasing the overall yield of both isomeric adducts. This stabilizing effect of the tertiary phosphine is documented on the example of the system based on the platinum-ethylene complex (experiments 5-8). Although the activity of the platinum-ethylene + triphenylphosphine system decreases with increasing P : Pt molar ratio, only at P : Pt = 2 : 1 the system becomes comparable in its behaviour to the platinum-alkene precursor (compare experiments 2 and 5).

As expected on the basis of the results discussed above also well defined platinum-phosphine complexes act as catalysts for this addition. From Table IV it becomes

TABLE IV

Hydrosilylation of Allylamine by Triethoxysilane Catalysed by Platinum-Phosphine Complexes

For reaction conditions and denotation of the compounds see Table II ($4.0 \cdot 10^{-6}$ mol of the catalyst).

Catalyst	Reaction time, h ^a	Composition, %					P
		γ-	β-	A	B	by-products	
H ₂ PtCl ₆	24	41.2	8.4	6.8	42.1	1.4	2.4
[CH ₂ =CHCH ₂ NH ₃ ⁺ PtCl ₃ ⁻]	24	53.6	11.2	9.3	23.9	1.3	3.1
[{PtCl ₂ (ethylene)} ₂]	18	59.5	11.4	5.2	19.8	2.9	3.2
[PtCl ₂ {P(C ₆ H ₅) ₃ } ₂]	18.5	58.2	12.1	4.2	23.0	2.3	3.1
[PtI ₂ {P(C ₆ H ₅) ₃ } ₂]	18	57.5	11.5	4.2	22.5	2.3	3.2
[Pt{P(C ₆ H ₅) ₃ } ₄]	15.5	59.5	11.2	3.3	23.7	2.3	3.5

^a See footnote ^a in Table III.

evident that both Pt(II) and Pt(O) compounds are more efficient than chloroplatinic acid and allylammonium trichloroplatinate. A substantial shortening of the reaction time makes them the catalysts of choice for the hydrosilylation studied.

REFERENCES

1. Beliakova Z. V., Bochkarev V. N., Golubtsov S. A., Belikova Z. V., Yamova M. S., Ainshtein A. A., Baranova G. G., Efremova L. A., Popkov K. K.: *Zh. Obshch. Khim.* **42**, 858 (1972).
2. Nametkin N. S., Topchiev A. V., Chernysheva T. I., Liashchenko I. N.: *Dokl. Akad. Nauk SSSR* **2**, 140 (1961).
3. Chatt J., Guy R. G.: *J. Chem. Soc.* **1961**, 827.
4. Knorre H., Rothe W.: *US* 3 470 225; *Chem. Abstr.* **70**, 57 988 (1969).
5. Hetflejš J., Svoboda P., Vaisarová V.: *Czech.* **165** 746.
6. Livshits S. J., Beliakova Z. V., Belikova Z. V., Vdovenko N. N., Krivenko M. M., Mezeritkii A. M., Oleinik V. V., Yamova M. S., Chirtstov V. I.: *U.S.S.R.* **415** 268; *Chem. Abstr.* **80**, 618 (1974).
7. Kashkin I. G.: *Zh. Obshch. Khim.* **23**, 32 (1953).
8. Denning R. G., Venanzi L. M.: *J. Chem. Soc.* **1963**, 3241.
9. Řeřicha R., Čapka M.: *This Journal* **39**, 2241 (1974).
10. Joy J. R., Orchin M.: *J. Amer. Chem. Soc.* **81**, 305 (1959).
11. Anderson J. S.: *J. Chem. Soc.* **1936**, 1042.
12. Kuljian E., Fryl H.: *Z. Naturforsch.* **20b**, 204 (1965).
13. Malatesta L., Cariello C.: *J. Chem. Soc.* **1958**, 2323.
14. Čapka M., Svoboda P., Hetflejš J.: *This Journal* **38**, 3830 (1973).
15. Čapka M., Janda M.: *Czech. Appl. PV* 7277-77.

Translated by the author (J. H.).