STUDY OF THE CATALYTIC ACTIVITY OF METAL COMPLEXES FIXED ON SOLID SUPPORTS. 8. IMMOBILIZED Rh AND Pd COMPLEXES IN THE DEHALOGENATION REACTION OF HALOGENATED DERIVATIVES OF BENZENE AND CYCLOPROPANE BY HYDROGEN TRANSFER FROM ALCOHOLS AND SODIUM BOROHYDRIDE

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New prospects for catalytic reduction of organic compounds were revealed while using chemically bound hydrogen [1]. Heterogenized metal complexes (HMC) can be used as catalysts of these processes. Rh complexes fixed to modified silica gel catalyze the transfer of hydrogen from 2-propanol (2-P) to ketones, olefins, and nitrobenzene [2, 3]. Hydrogenolysis with formation of aniline occurs upon reduction of halonitrobenzene by NaBH<sub>4</sub> in the presence of these complexes [3].

In this work, the hydrodehalogenation reaction of p-bromotoluene (p-BT) and gemdihalocyclopropanes by transfer of hydrogen from 2-P and NaBH<sub>4</sub> in the presence of Rh and Pd complexes fixed on modified silica gel and polymers is studied.

## EXPERIMENTAL

The composition of the synthesized catalysts (I)-(X) is given in Table 1. Silica gel and polymers modified by organic ligands were used as supports. The synthesis of silica gels with bound amino and aminophosphine groups ( $\gamma$ -AMBS and  $\gamma$ -AMPBS) and the immobilization of Rh complexes on them was done according to [4]. The polymeric supports (Polyorgs-IV and Polyorgs-XVI) were obtained according to [5], and (Polyorgs-XI) according to [6]. Catalysts (VII)-(X) were synthesized by treatment of the support with 0.01 M RhCl<sub>3</sub> or Na<sub>2</sub>PdCl<sub>4</sub> solutions for 1-3 h. The content of Rh and Pd in the polymer was calculated by the loss of concentration of the complexes in the solution as determined spectrophotometrically.

The purity of the compounds used in the experiments was 98% by GLC. Synthesis of the gem-dihalophenylcyclopropanes and 7,7-dichloronorcarane was done according to [7] from the corresponding styrenes and cyclohexene in CHCl<sub>3</sub> or CHBr<sub>3</sub> and NaOH using a catalytic quantity of triethylbenzylammonium chloride. The data for the gem-dichlorides and gem-dibromides coincide with those in [7-12]. The experimental method is given in [3]. The composition of the catalysate was determined by GLC on a Biochrom-21 chromatograph with a flame ionization detector at 60-200°C, N<sub>2</sub> carrier gas, a 2 m × 3 mm stainless steel column, and a liquid phase of SE-30 (15%) on Chromosorb W. The activity of catalysts was characterized by the value of the initial specific formation of products W<sup>0</sup> (mole/(g·at Rh (Pd)·min)).

## DISCUSSION

Reduction of p-BT by Hydrogen Transfer from 2-P. Preliminary experiments established that all synthesized HMC in 2-P (20-82.4°C, Ar) are inactive for reductive dehalogenation of p-BT. Formaton of toluene is observed upon introduction of KOH

$$CH_{3} - \bigcirc -Br + i - C_{3}H_{7}OH \xrightarrow{Cat, KOH} CH_{3} - \bigcirc -H + (CH_{3})_{2}CO + HBr$$
(1)

The activity of the catalysts depends on the quality of KOH in the 2-P solution.  $W^0$  increases from 0.5 to 2.0 mole/(g.at Pd.min) using (VIII) with increasing concentration in the range  $7.5 \cdot 10^{-3} - 6 \cdot 10^{-2}$  M. Data on the activity of the catalysts in reaction (1) are given below,  $(3.2-8.7) \cdot 10^{-6}$  g.at Rh(Pd),  $(6.4-17.4) \cdot 10^{-5}$  mole p-BT,  $(3.8-10.4) \cdot 10^{-4}$  mole KOH, 10 ml 2-P, 82.4°C, Ar.

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Catalyst			Rh content, (mole/g). 10 <sup>-5</sup>	
	brand	Complex		
(I) (II) (III) (IV) (V) (V) (VI)	$\Upsilon$ -AMPBS $\Upsilon$ -AMPBS $\Upsilon$ -AMPBS $\Upsilon$ -AMBS $\Upsilon$ -AMBS $\Upsilon$ -AMBS $\Upsilon$ -AMBS	$\begin{array}{c} -O-Si(OEt)_2-(CH_2)_3-NH-PPh_2\\ -O-Si(OEt)_2-(CH_2)_3-NH-PPh_2\\ -O-Si(OEt)_2-(CH_2)_3-NH-PPh_2\\ -O-Si(OEt)_2-(CH_2)_3-NH_2\\ -O-Si(OEt)_2-(CH_2)_3-NH_2\\ -O-Si(OEt)_2-(CH_2)_3-NH_2\\ \end{array}$	[RhCl (COD) ] <sub>2</sub> RhCl (PPh <sub>3</sub> ) <sub>3</sub> RhCl <sub>3</sub> [RhCl(COD)] <sub>2</sub> RhCl(PPh <sub>3</sub> ) <sub>3</sub> RhCl <sub>3</sub>	$\begin{array}{c} 6,2 \\ 4,5 \\ 6,4 \\ 6,3 \\ 8,5 \\ 22,3 \end{array}$
(VII)	Polyorgs-IV	(Me)H $C=CH$ $C=CH$ $N=C-Me(H)$	RhCl₃	17,5
(VIII)	Polyorgs~IV	(Me)H C=CH $-CH_2-N$	Na <sub>2</sub> PdCl <sub>4</sub>	9,4
(IX)	Polyorgs-XVI	$ \begin{array}{c} & & \\ N = C - Me(H) \\ CH = CH \\ - \bigcirc - CH_2 - N \swarrow \\ CH = N \\ \end{array} $	RhCl <sub>3</sub>	19,4
(X)	Polyorgs-XI		RhCl₃	19,4
	Catalust		(11)	

TABLE 1. Immobilized Complexes of Rh and Pd

 
 Catalyst
 (I)
 (VII)
 (VIII)
 (IX)
 (X)

  $W^0 \cdot 10$ , mole/(g. at Rh (Pd)·min)
 1.8
 4.0
 20.0
 4.0
 1.8

The most active of the catalysts based on silica gel is (I) ( $W^0 = 1.8 \cdot 10^{-1} \text{ mole/(g-at Rh·min)}$ ). The reaction rate of (1) is 3-8 times smaller for samples (II)-(VI). For catalysts (VII) and (IX), (1) proceeds 2.2 times faster than for (X). The highest activity of all the studied catalysts was for (VIII) ( $W^0 = 2.0 \text{ mole/(g-at Pd·min)}$ ). The p-BT was 100% converted into toluene after 40 min using it.

<u>Reduction of p-BT by Sodium Borohydride</u>. Catalysts (I)-(X) exhibited activity for reduction reaction

$$CH_3 \longrightarrow Br \xrightarrow{Cat} CH_3 \longrightarrow + HBr$$
 (2)

(2) by sodium borohydride. The hydrodebromination of p-BT by NaBH<sub>4</sub> in 2-P solution at 82.4°C does not occur without catalyst.

It was found that the rate of reaction (2) depends on the type of support, nature of attached ligand, and immobilized compound. The Rh complexes which were fixed to the modified silica gels are placed in the order according to activity: (I) > (III)  $\approx$  (II) > (V) > (VI) > (IV). The numerical values of the rates for (2) are given below. Conditions were the same as for (1); (7.6-10.4)·10<sup>-4</sup> mole NaBH<sub>4</sub> and (1.3-5.2)·10<sup>-4</sup> mole of CaO were used.

Catalyst	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)
W <sup>0</sup> .10, mole/(g. at Rh(Pd).min)	23.6	10.2	10.4	1.5	6.1	2.5	3.2	1.6	0.2	0.3

The highest rate for (2) ( $W^0 = 3.2 \cdot 10^{-1} \text{ mole}/(g \cdot at Rh \cdot min)$ ) was attained for (VII). Note that the complexes on the polymers are less active in (2) by comparison to the complexes on silica gels, in contrast to (1).

Some features of (2) were studied based on the very active catalyst (I). As seen in Fig. 1a, the dependence of the reaction rate on the quantity of NaBH<sub>4</sub> (G) has a maximum. Upon increasing G from  $1.9 \cdot 10^{-4}$  to  $7.7 \cdot 10^{-4}$  mole, the reaction rate increases and reaches the maximal value of  $23.6 \cdot 10^{-1}$  mole/(g.at Rh.min). The rate of (2) increases sharply (Fig. 1b) with increasing temperature (50-82°C).



Fig. 1. Effect of NaBH<sub>4</sub> (G) quantity (a) and temperature (b) on the specific initial rate of hydrodehalogenation ( $W^0$ ) of p-bromotoluene using catalyst (I) (3.2·10<sup>-6</sup> g·at Rh, 6.4·10<sup>-5</sup> mole p-bromotoluene, 10 ml 2-propanol, 19.2·10<sup>-5</sup> mole CaO; a) 82.4°C; b) 7.6· 10<sup>-4</sup> mole NaBH<sub>4</sub>).

The effect of solvent was studied in order to choose the optimal conditions. Evidently, the rate of (2) depends complicatedly on the nature of the alcohol and decreases in the order  $[(mole/(g \cdot at Rh \cdot min)) \cdot 10]$ : 2-propanol (23.6) > 2-butanol (6.0) > 1-propanol (2.6) > ethanol (1.1) > methanol (0.0). It should be mentioned that the rate of (2) is the same in H<sub>2</sub> as in Ar. Conducting the reaction in the presence of O<sub>2</sub> (mole ratio O<sub>2</sub>/Rh  $\approx$  400) also does not affect the catalyst activity.

Dehalogenation of Chloro and Bromo Derivatives of Cyclopropane. Rhodium complexes fixed on modified silica gels exhibit high activity toward reduction of gem-dihalocyclopropanes by transfer of hydrogen from 2-P and NaBH<sub>4</sub> (Table 2).



Only partial reduction of the starting dihalogenides occurs with use of 2-P as the hydrogen donor. Note that KOH alone in 2-P (82.4°C, Ar) does not exhibit activity in the hydrogenolysis of the C-Hal bond without catalyst.

Catalytic dehalogenation depends strongly on the nature of the halogen. Thus, the rate of dissociation of the Br atom from 1,1-dibromophenylcyclopropane is two orders of magnitude higher than for the Cl atom from the analogous chloro derivative. Decreasing the KOH content by a factor of two leads to a lowering of the rate by 1.4 times. Reduction of gem-dihalides by 2-P is characterized by predominant formation of the cis isomer (ratio of cis:trans = 2.6-1.8:1).

The nature of the hydrohalogenation process changes substantially with NaBH<sub>4</sub> as the hydrogen source. Thus, the rate of partial reduction of 1,1-dichlorophenylcyclopropane increases by 30 times. The monochloride which is formed undergoes further dehalogenation into phenylcyclopropane. The rate of substitution of the second chlorine atom is much lower than the first. The product of partial reduction accumulates in the reaction mixture as a result of this (93.3%). Phenylcyclopropane (2%) and the product of cyclopropane ring opening (4.7%) are also contained in the catalysate.

It is important to mention that NaBH<sub>4</sub> without catalyst in the 2-P solution does not reduce the chloro derivatives of cyclopropane. In order to prevent deactivation of the catalyst and opening of the three-membered ring, the HHal which is produced is neutralized by CaO.

The nature and position of the substituent in the cyclopropane has a significant effect on the rate and stereoselectivity of the reaction. Introduction of a methyl group in the o-position of the benzene moiety bonded to the cyclopropane leads to a lowering of the rate of monodechlorination from  $12 \cdot 10^{-1}$  to  $4.6 \cdot 10^{-1}$  mole/(g·at Rh·min) and a change in the stereochemistry toward the predominant formation of the trans-monochloride (ratio of cis:trans isomers = 0.8). Upon replacing a hydrogen atom by a methyl group in the cyclopro-

TABLE 2. Reduction of gem-Dihalocyclopropanes by 2-Propanol (a) and NaBH<sub>4</sub> (b).  $(3.2 \cdot 10^{-6} \text{ g} \cdot \text{at Rh}, 6.4 \cdot 10^{-5} \text{ mole substrate}, 10 ml 2-propanol, 82.4°C, Ar; a) <math>3.8 \cdot 10^{-4}$  mole KOH; b) 7.7  $\cdot 10^{-4}$  mole NaBH<sub>4</sub>,  $3.8 \cdot 10^{-4}$  mole CaO)

	Catalyst	Hydrogen donor	W0 mole/(g at	Ratio of cis/ trans isomers	
Substrate			formation of mono- halogenide	formation of hydro- carbon	genides
	(I)	2-₽ NaBH₄	0,4 12,0	0,0 0,2	1,8 1,6
Ph Cl CH <sub>3</sub> Cl	(I)	NaBH₄	5,0	0,1	trans isomer only
	(I)	NaBH₄	4,6	0,0	0,8
	(I)	NaBH4	3,3	0,0	6,7
PhBr	(I) (II) (III) (V)	2-P NaBH₄ NaBH₄ NaBH₄ NaBH₄	62 500  - -	0,0 8,4 6,3 6,4 2,3	2,6 2,1 4,0 2,1 2,7
Pin Me Br	(I)	NaBH <sub>4</sub>	-	8,4	1,3

pane ring, the rate of partial reduction also is lowered ( $W^0 = 5.0 \cdot 10^{-1} \text{ mole}/(g \cdot at Rh \cdot min)$ ). The reaction in this case occurs selectively and stereospecifically with formation of only the trans isomer (100%). The absence of a phenyl substituent in the substrate leads to deceleration of the dehalogenation reaction. Thus, monoreduction of 7,7-dichloronorcarane proceeds with a rate 3.6 times lower than for 1,1-dichlorophenylcyclopropane. The stereo-chemistry of the process is characterized by a large content in the mixture of the cis isomer (ratio cis:trans = 6.7).

Reduction of gem-dibromides by NaBH<sub>4</sub> using the immobilized complexes proceeds significantly more easily than for gem-dichlorides. Thus, for 1,1-dibromophenylcyclopropane, the rate of both the partial ( $W^0 = 52.8 \text{ mole}/(g \cdot at \text{ Rh} \cdot min)$ ) and total ( $W^0 = 8.4 \cdot 10^{-1} \text{ mole}/(g \cdot at \text{ Rh} \cdot min)$ ) dehalogenation increases by  $\sim 40$  times by comparison with the analogous chloro derivatives. From Table 2 it is seen that the initial rate of formation of the monobromide significantly exceeds the rate of formation of the hydrocarbon. This difference in the rates explains the high selectivity of the debromination reaction (98-99%) relative to the 2-bromophenylcyclopropane. Further reduction (2 h) leads to formation of hydrocarbon with 96% yield.

Separate experiments showed that  $NaBH_4$  without metal complex leads to monoreduction of 1,1-dibromophenylcyclopropane with  $W^0 = 9.8 \cdot 10^{-4}$  mole/min. In the presence of catalyst, the rate of partial reduction increases by 17 times, i.e., the hydrogen transfer from NaBH<sub>4</sub> to the gem-dibromide occurs primarily catalytically.

From Table 2, the order of catalysts according to the activity for complete reduction of l,l-dibromophenylcyclopropane by NaBH<sub>4</sub> is (I) > (III)  $\approx$  (II) > (V). The reaction rate depends strongly on the quantity of NaBH<sub>4</sub>. A decrease in the amount of NaBH<sub>4</sub> in the reaction mixture from 7.7 · 10<sup>-4</sup> to 3.8 · 10<sup>-4</sup> mole in the presence of (I) leads to a decrease in the rate of dehalogenation by 2.6 times.

On going from 1,1-dibrompophenylcyclopropane to 1,1-dibromo-2,2-methylphenylcyclopropane, the rate of hydrogenolysis of the C-Br bond remains constant, while the stereoselectivity switches to the side of an increased fraction of trans isomer (ratio cis:trans  $\approx$  1.3).

We note especially that reduction of gem-dichloro- and gem-dibromophenylcyclopropanes by NaBH<sub>4</sub> is accompanied by formation of only insignificant quantities of hydrogenolysis products of the cyclopropane ring (4-5%) while upon reduction by NaBH<sub>4</sub> of methyl-substituted gem-dihalocyclopropanes and use of 2-P as the hdyrogen donor the destruction of the cyclopropane fragment does not occur.

## CONCLUSIONS

1. Rhodium and palladium complexes immobilized on amino and aminophosphinated silica gels and polymers containing heterocyclic amine groups catalyze hydrodehalogenation of pbromotoluene and gem-dihalocyclopropanes by hydrogen transfer from 2-propanol and sodium borohydride.

2. Only partial dehalogenation of gem-dihalogenides occurs with rhodium complexes and 2-propanol. For NaBH, successive substitution of two halogen atoms occurs. Reduction of gem-dibromides is easier than that of gem-dichlorides. The reaction rate and stereoselectivity depend on the nature and position of the substituent in the cyclopropane.

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CATALYTIC ACTIVITY OF NICKEL COMPLEXES IN VINYL HYDROGEN SUBSTITUTION REACTIONS AND STYRENE DIMERIZATION

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Condensation of arylhalogenides with styrene is an effective method for synthesis of stilbene and its derivatives [1]. The complex  $NiCl_2L_2$  (I) (L = tertiary phosphine) in MeCN with a stoichiometric quantity of Zn [2] can be used as a catalyst for this reaction

$$ArX + PhCH = CH_2 \xrightarrow{(1)/2n} PhCH = CHAr$$
 (1)

Zn reduces complex (I) into the active Ni(0) compound (presumably NiL<sub>2</sub>), oxidative addition of which to ArX and formation of ArNiXL<sub>2</sub> (II) are the first steps in the catalytic process. Decomposition of the addition product of the intermediate (II) to styrene by  $\beta$ elimination leads to formation of stilbene and the hydride complex (III).

> $Ph-CH-CH_2-Ar \rightarrow PhCH=CHAr + HNiXL_2$ (2)NiXL<sub>2</sub> (III)

The complex (III) catalyzes the dimerization side reaction of styrene [3], as a result of which 1,3-diphenyl-l-butene (DPB) is obtained.

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