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Previously [1], it was established that $[PtCl_2(SnCl_3)_2]^{2-}$ catalyzes under mild conditions, in an H₂ atmosphere, predominantly the isomerization of α -olefins, and to a lesser degree their hydrogenation. The activity of this complex as a catalyst is 1/2 to 1/10 that of $[Pt(SnCl_2X)_5]^{2+}$.

In [2] it was shown that the palladium tin halide complex $[Pd_mCl_x(SnCl_3)_y]^{-}$, stabilized with a large excess of SnCl₂ in solution (Sn:Pd = 10), in acidified methanol in either an H₂ or N₂ atmosphere, selectively catalyzes the isomerization of olefins but does not catalyze their hydrogenation.

We studied the catalytic properties of some phenylsulfone complexes of Pd, stabilized [3] by poly(vinylpyrrolidone) (PVP), in the model reaction of transforming allylbenzene.

EXPERIMENTAL

 $[Pd(C_6H_5SO_2)_2(H_2O)_2] (I) and K[Pd(C_6H_5SO_2)_2Cl(H_2O)] (II) were synthesized as described in [4]. K_2[Pd(C_6H_5SO_2)_2Cl_2] and K_2[Pd(C_6H_5SO_2)_2Br_2] were obtained by thoroughly grinding in an agate mortar stoichiometric amounts of K[Pd(C_6H_5SO_2)_2Cl(H_2O)] with KCl, and also K[Pd·(C_6H_5SO_2)_2Br(H_2O)] with KBr, moistened with a little ether. The obtained compounds were dissolved in methanol at 5-10°C, filtered, and the filtrate was evaporated to dryness at <math>\sim 20^{\circ}$ C. Found: Pd 19.4; Cl 13.5; S 11.2%. K_2[Pd(C_6H_5SO_2)_2Cl_2]. Calculated: Pd 19.8; Cl 13.2; S 11.9%. Found: Pd 16.7; Br 25.1; S 9.5%. K_2[Pd(C_6H_5SO_2)_2Br_2]. Calculated: Pd 17.0; Br 25.5; S 10.2%.

The catalytic properties of the complexes were tested in a glass reactor at 20° and atmospheric H₂ pressure, with vigorous mixing on a rocker. For experiment we took 5-7 ml of methanol, 0.005 g (\sim 0.00001 mole) of the complex, 0.05 g (0.0000044 mole) of PVP, and 0.5 g of NaBH₄. The air was displaced by hydrogen, 0.5 g of allylbenzene was added, and the rocker

TABLE 1. Transformation of Allylbenzene in Presence of Phenylsulfone Complexes of Pd, Reduced with NaBH₄ and Stabilized by PVP

	L.	Composition of catalyzate, %						
Complex	from of expe min	en-	lben-	propeny1benzenes			genatio	SI
	Time start c ment,	allylb zene	propy] zene	trans-	cis-	2-ene	Hydro; isome)	cis
$[Pd(C_6H_5SO_2)_2(H_2O)_2]$ (I)	$\begin{vmatrix} 7\\40\\52\\61 \end{vmatrix}$	94,4 66,6 57,7 49,4	1,1 5,5 7,5 8,4	3,0 19,8 24,7 29,8	1,5 8,1 10,1 12,4	4,5 27,9 34,8 42,2	$0,24 \\ 0,20 \\ 0,22 \\ 0,20$	$ \begin{array}{c c} 2,0 \\ 2,4 \\ 2,4 \\ 2,4 \\ 2,4 \end{array} $
$K[Pd(C_6H_5SO_2)_2(H_2O)Cl]$ (II)	10 32 70	89,2 75,8 54,3	3,1 7,7 12,6	4,7 11,8 22,3	3,0 4,7 10,8	7,7 16,5 33,1	0,40 0,47 0,38	1,6 2,5 2,1
$K_2[Pd(C_6H_5SO_2)_2Cl_2]$ (III)	90 130 170	89,9 84,4 81,6	1,6 2,2 2,8	6,5 10,2 11,8	2,0 3,3 3,8	8,5 13,5 15,6	0,19 0,16 0,18	3,2 3,2 3,1
$K_{2}[Pd(C_{6}H_{5}SO_{2})_{2}Br_{2}]$ (IV)	17 25 37 42	84,1 79,3 69,8 64,4	1,9 2,5 3,7 4,1	10,2 13,4 19,8 23,6	3,8 4,8 6,7 7,9	14,0 18,2 26,5 31,6	0,14 0,14 0,14 0,13	2,7 2,8 3,0 3,0

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Fig. 1: Transformation of allylbenzene in presence of [Pd(DMSO)₂Cl₂]: 1) allylbenzene; 2) n-propylbenzene; 3) transpropenylbenzene; 4) cis-propenylbenzene.

was started. Samples of the catalyzate were taken during the course of reaction for analysis by GLC.

On all of the complexes the order of the reaction in substrate was close to first. The catalytic activity of the complexes was judged by the rate of allylbenzene transformation, while the selectivity was judged by the ratio of the rates of forming propylbenzene and propenylbenzenes.

DISCUSSION OF RESULTS

All of the studied complexes are readily soluble in methanol. Like many other palladium complexes, they decompose easily when exposed to NaBH₄ and H₂ with liberation of the metal. Our experiments disclosed that the studied complexes are stabilized by PVP (mol. wt. 11,400), in whose presence the system Pd complex-NaBH₄-H₂-methanol is homogeneous.

Judging by the half-reaction time for allylbenzene (Table 1), the catalytic activity of the complexes decreased in the order:

 $[Pd(C_6H_5SO_2)_2(H_2O)_2] > K[Pd(C_6H_5SO_2)_2Cl(H_2O)] > K_2[Pd(C_6H_5SO_2)_2Br_2] > K_2[Pd(C_6H_5SO_2)_2Cl_2].$

All of the studied complexes catalyze the transformation of allylbenzene predominantly toward isomerization. The ratio of the formed trans/cis propenylbenzenes in the presence of complexes (III) and (IV) is close to the equilibrium ratio [5].

For comparison we ran experiments in the presence of the system $PdCl_2(DMSO)_2$ -NaBH₄-PVP-CH₃OH. This system is more active: the half-reaction time is $\sim 1/3$ shorter. The dimethyl sulfoxide complex catalyzes the reaction predominantly toward hydrogenation: the hydrogenationisomerization ratio ≈ 3 , i.e., one order of magnitude greater than in the presence of the sulfone complexes. In this case the composition of the formed cis- and trans-propenylbenzenes differs from the equilibrium composition (Fig. 1).

The difference established by us in the behavior of the Pd sulfone and sulfoxide complexes can be explained by the specific traits of the electronic structure of their ligands. In the sulfoxide molecule the S atom has a pair of unshared electrons, which is lacking in the sulfone molecule. According to [6], in the molecule of the complex, formed by the reduction of $PdCl_2(DMSO)_2$, the sulfoxide ligand is coordinated not only through the O atom, but also through the S atom. The sulfinate ion can also be **coordinated** with Pd through the S atom [4], but this does not refer to the low-valence state of the central atom of the complex, but **rather** to Pd(II).

CONCLUSIONS

1. When reduced with either sodium borohydride or hydrogen in methanol solution, the Pd(II) phenylsulfone complexes decompose with liberation of the metal. In the presence of poly(vinylpyrrolidone) the reduction products form a homogeneous solution.

2. The reduction products of the Pd phenylsulfone complexes predominantly catalyze the isomerization of allylbenzene; in the case of the Pd sulfoxide complex the main direction of the allylbenzene transformation is hydrogenation.

3. The composition of the formed cis- and trans-propenylbenzenes in the experiments with the Pd phenylsulfone complexes is close to the equilibrium composition, while in the

case of the sulfoxide complex it differs from the equilibrium composition.

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SYNTHESIS OF DIENIC δ -DIMETHYLAMINO- γ -METHYL(PHENYL)CARBONYL COMPOUNDS AND A STUDY OF THEIR VALENCE ISOMERISM EMPLOYING ULTRAVIOLET AND INFRARED SPECTROSCOPY

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The equilibrium valence isomerization of cis-dienes (I)D to 2H-pyrans (I)P was studied by us previously [1, 2].





It was shown that a CH_3 group in the γ position of dienone (I)D, due to strong steric interaction with the substituent at C^{α} , destabilizes the dienone and the equilibrium is shifted completely toward the 2H-pyran (I)P.

The pyran form was not detected in the previously studied [3, 4] δ -aminocarbonyl compounds of the following type:

 $\begin{array}{c} R^{2}CO \\ C = CH - CH = CR^{1} - NMe_{2}(II) \\ R^{3} \end{array}$

R¹=H, Me, Ph; R²=Me, MeO, EtO; R³=H, MeCO, MeOCO, CN, NO₂

We were able to observe both valence forms for the first time in this series on the example of ketoester (III), which contains a Me group in the γ position [5]:



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