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Synthesis of Hydroxybiphenyls

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Abstract—Cyclohexylphenols were converted into hydroxybiphenyls via dehydration over large-scale palladium catalysts. The process involves slow reaction of the substrate with active centers of the catalyst with subsequent fast product formation and hydrogen desorption.

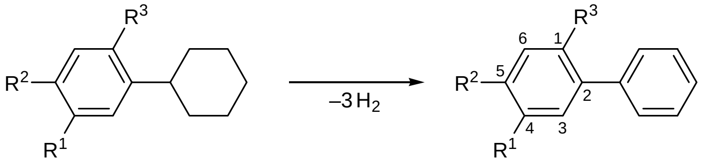
We previously developed an effective procedure for the preparation of functionalized biphenyl and terphenyl derivatives via aromatization of cyclohexyl-substituted methylbenzenes [1, 2]. These compounds are used as monomers and intermediate products in the synthesis of liquid crystalline heat-resistant polymers, biologically active substances, photographic materials, etc. [3]. However, there are almost no published data on analogous transformations of cyclohexyl-substituted phenols. Therefore, we examined liquid-phase catalytic dehydrogenation of *o*-cyclohexylphenol (**I**), *p*-cyclohexylphenol (**II**), 4-methyl-2-cyclohexylphenol (**III**), and 1,4-dihydroxy-2-cyclohexylbenzene (**IV**) with a view to obtain the corresponding hydroxybiphenyls **V**–**VIII** (Scheme 1, Table 1).

We studied the effect of catalyst, temperature, and reaction time on the substrate conversion and reaction selectivity in the dehydrogenation of *p*-cyclohexylphenol (**II**). As catalysts we used a number of industrial palladium compounds, namely Pd/C (5 and 2%), KPG, MA-15, and IK-71, taking into account their accessibility and large-scale application in petrochemical syntheses. We have found that palladium-rich catalysts (such as Pd/C, 5%) ensure 98–99% conversion of the substrate and more than 70% selectivity with respect to the target product. The nature of the support is important: In the presence of aluminum oxide-supported palladium, the conversion of **II** is only 48%, while charcoal-supported catalysts give rise to twice as large conversion (90–99%); no reaction occurs over MA-15. The best results in the dehydrogenation of compound **III** were obtained with KPG. In all cases, decrease in the weight fraction of the catalyst below 5%, as well as increase over 20%, impairs quantitative parameters of the process (i.e., the conversion and selectivity).

Thus large-scale palladium catalysts (5% Pd/C, KPG) in an amount of 20–40 wt % (with respect to the substrate) can successfully be used in the hydrogenation of cyclohexylphenols without appreciable loss in activity over 6–8 turnovers. The procedures developed for regeneration of the catalysts ensured 90–92% conversion of cyclohexylphenols **I**–**IV** and high yields (60–95%) of target compounds **V**–**VIII**.

The effect of the temperature was examined in the range from 250 to 300°C (the mixture boiled) over 5% Pd/C. Raising the temperature within the above interval resulted in increased conversion, but the yield almost did not change (Fig. 1). The hydrogenation of compound **IV** at 250–300°C was characterized by low

Scheme 1.



I–IV **V–VIII**

I, **V**, $R^1 = R^2 = H$, $R^3 = OH$; **II**, **VI**, $R^1 = R^3 = H$, $R^2 = OH$; **III**, **VII**, $R^1 = CH_3$, $R^2 = H$, $R^3 = OH$; **IV**, **VIII**, $R^1 = R^3 = OH$, $R^2 = H$.

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Table 1. Yields, melting points, and IR and ^{1}H NMR spectra of hydroxybiphenyls **V**–**VIII**

Comp. no.	Yield, %	mp, °C	IR spectrum,[a] ν, cm^{-1} (substitution pattern)	^{1}H NMR spectrum, δ, ppm
V	78	60–62	755–700 (*1, 2, 1*), 3480 (OH)	9.1 s (1H, OH), 7.56–7.45 m (2H, 3-H), 7.30–7.22 m (3H, 4-H, 5-H), 7.16 d (2H, 2-H, *J* = 8 Hz), 7.98 d (2H, 1-H, *J* = 7.8 Hz)
VI	75	158–160	750 (*1*), 821 (*1, 4*), 3200 (OH)	7.64 m (2-H, 3-H), 7.47 m (4-H, 5-H), 7.37 m (6-H), 7.52 d (7-H, 8-H), 6.91 d (9-H, 10-H)
VII	97	57–60	740–700 (*1*), 870–805 (*1, 2, 4*), 3470 (OH)	2.13 s (CH_3), 8.87 s (OH), 6.47 d (3-H), 6.73 d (4-H), 6.75 s (5-H)
VIII	57	91–93	745 (*1*), 860 and 800 (*1, 2, 5*), 3300–3470 (OH)	7.64 m (2-H, 3-H), 7.47 m (4-H, 5-H), 7.37 m (6-H), 6.67 d (7-H), 6.77 d (8-H), 6.96 s (9-H)

[a] Benzene ring: ν 1610, 1570, 1500 cm^{-1}.

Table 2. Kinetic parameters of liquid-phase catalytic dehydrogenation of cyclohexylphenols **I**, **II**, and **IV**

Comp. no.	Temperature, °C	v_0, mol l^{-1} min^{-1}	E_a, kJ/mol	$1/k_2 + 1/k_3$, min	$1/k_1$, min	k_1, min^{-1}
I	250	0.0333	82.37 ± 1.73	5.50 ± 0.04	9.19 ± 0.08	0.11 ± 0.04
	270	0.0533		3.02 ± 0.05	4.12 ± 0.07	0.24 ± 0.02
	300	0.1700		0.75 ± 0.03	2.79 ± 0.08	0.36 ± 0.01
II	250	0.0520	79.34 ± 1.71	5.46 ± 0.06	6.86 ± 0.09	0.15 ± 0.03
	270	0.0960		2.28 ± 0.07	3.78 ± 0.08	0.26 ± 0.02
	300	0.2733		0.93 ± 0.04	1.89 ± 0.06	0.53 ± 0.02
IV	330	0.2500	53.74 ± 1.24	0.97 ± 0.04	2.17 ± 0.07	0.46 ± 0.03
	350	0.3700		0.78 ± 0.03	1.51 ± 0.06	0.66 ± 0.04
	370	0.4200		0.51 ± 0.02	1.41 ± 0.04	0.71 ± 0.05

efficiency: the conversion of **IV** and the yield of **VIII** did not exceed 10%. Raising the temperature to 350–370°C accelerates the process, but increases the fraction of thermal decomposition products. The maximal yield of hydroxybiphenyl **VIII** did not exceed 60%, the substrate conversion being complete.

Our results showed that liquid-phase dehydrogenation (1 atm, 250–370°C) of cyclohexylphenols **I**–**IV** over palladium catalysts gives the corresponding hydroxybiphenyls **V**–**VIII** with 100% conversion of the substrate.

In order to elucidate the mechanism of the process under study we applied previously developed kinetic model for liquid-phase catalytic dehydrogenation of cyclohexyl-substituted methylbenzenes to methylbiphenyls. We performed a series of single-factor experiments with variation of the weight fraction of the catalyst, initial concentration of cyclohexylphenol **I**–**IV**, and temperature. The reaction was found to be of first order with respect to catalyst; the order of the reaction with respect to cyclohexylphenol changed from 1 to 0, depending on the substrate concentration (Fig. 2a). The existence of a linear relation between $1/v_0$ and $1/c_0$ (Fig. 2b) provides a kinetic support for the presumed mechanism of dehydrogenation, according to which the rate-determining stage is reaction

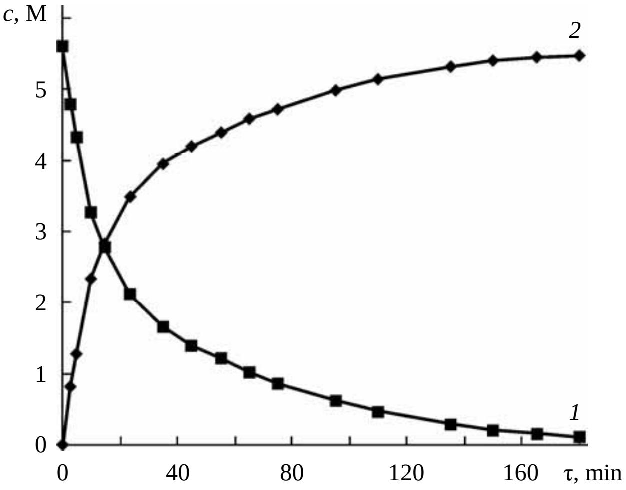

Fig. 1. Effect of the reaction time on the (*1*) consumption of *p*-cyclohexylphenol (**II**) and (*2*) accumulation of the dehydrogenation product, *p*-hydroxybiphenyl (**VI**); 300°C, c_{II} = 5.6 M, c_{cat} = 20 wt %.

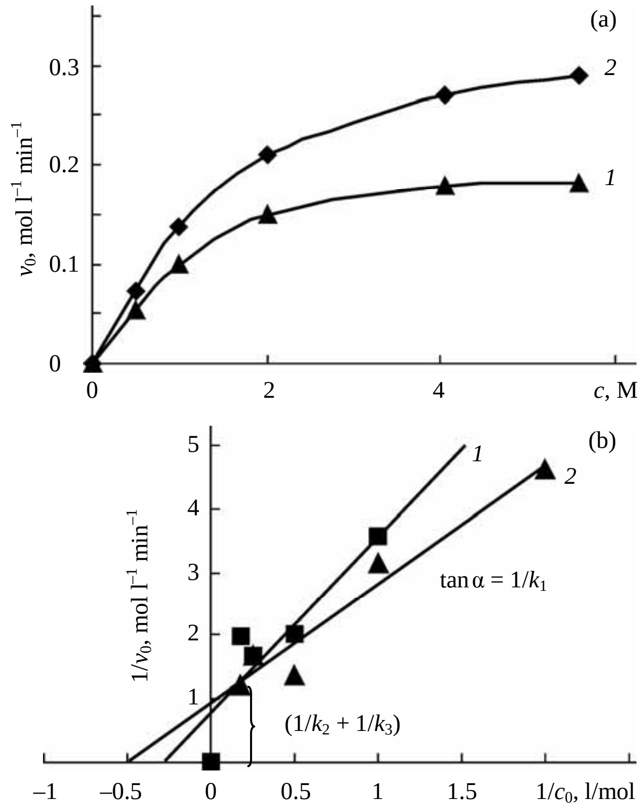

Fig. 2. Plots of the initial rates of dehydrogenation of cyclohexylphenols (*1*) **I** and (*2*) **II** versus their (a) concentration and (b) reciprocal concentration; 300°C, c_{cat} = 20 wt %.

of the substrate with active centers of the catalyst (k_1); the subsequent product formation stage (k_2), desorption of hydrogen, and regeneration of catalyst (k_3) are fast [4].

Table 2 contains the kinetic parameters for liquid-phase catalytic dehydrogenation of compounds **I**, **II**, and **IV**, which were calculated by the equation $v_0 = (1/k_2 + 1/k_3) + k_1^{-1}\, c_0^{-1}$; these values characterize the reactivity of cyclohexylphenols and are important for calculation of the reactor.

Thus we have demonstrated the possibility for synthesizing hydroxybiphenyls by dehydrogenation of cyclohexylphenols in the presence of well explored petrochemical catalysts. The yields of the products and substrate conversion are acceptable for large-scale implementation of the process.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75-IR spectrometer from samples prepared as thin films. The ^1H NMR spectra were obtained on a Tesla BS-467 instrument using acetone-d_6 as solvent and HMDS as internal reference. GLC analysis was performed on a Khrom-4 chromatograph equipped with a flame ionization detector and a 2.5-m×4-mm steel column packed with 10% of SKTFT-50Kh on Chromaton N-AW-DMCS; carrier gas nitrogen, flow rate 30 ml/min; oven temperature programming from 80 to 200°C (for the dehydrogenation products).

Cyclohexylphenols **I**–**IV** were prepared by the procedure reported in [5].

Dehydrogenation of 2-cyclohexylphenol (II). A mixture of 10 g of compound **II** and 2 g of 5% Pd/C was heated to a specified temperature. The progress of the reaction was monitored by the amount of the evolved hydrogen and the concentration of product **VI** which was determined by GLC. When the reaction was complete, the mixture was filtered from the catalyst, and hydroxybiphenyl **VI** was purified by recrystallization from petroleum ether (bp 40–70°C). Dehydrogenation of compounds **I**, **III**, and **IV** was performed in a similar way.

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