BRIEF COMMUNICATIONS

HYDROGENATION OF STABLE IMINOXYL RADICALS IN THE PRESENCE OF A COMPLEX PALLADIUM CATALYST WITH NITROGEN-CONTAINING LIGANDS

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Stable iminoxyl radicals are widely used for the stabilization of polymeric materials and dyes, and also as spin probes and labels. An analogy exists between the transfer of electrons via the conformational changes of functional groups in a mitochondrial chain and the phenomenon of a conformational electron exchange in iminoxyl biradicals [1, 2]. The conformational model of electron transport in multienzyme redox complexes, as is known, postulates an estaffete [stirrup] mechanism, which includes the successive paired approaches of the molecular fragments that bear the unpaired electrons (conformation wave of electron transfer along the chain) [3]. Previously, when studying the EPR spectra of iminoxyl biradicals, the theory was expressed that during the approaches the functional groups, bearing the unpaired electrons, undergo mutual chemical activation [4].

In this connection, it seemed of interest to study the reactivity of iminoxyl biradicals of variable structure in catalytic hydrogenation reactions. As is known, the degree of reduction of these compounds is determined by the nature of the catalytic system. Thus, when Pt black is used the end product is hydroxylamine, while amines are formed in the presence of Raney Ni [5, 6].

In the present paper the PdCl₂ complex with a tertiary amine was selected as the hydrogenation catalyst. This system exhibits catalytic activity in the selective hydrogenation of dienes and alkynes to olefins under mild conditions (20°C, H₂ pressure 300-500 torr) [7]. The biradical isomers of phthalic acid esters were taken as the model compounds, which were obtained by reacting the acid chloride of the appropriate acid with 2,2,6,6-tetramethyl-4hydroxypiperidine-l-oxyl as described in [8].

As a result, the starting compounds had the following chemical structure.



The catalyst was obtained by reacting a suspension of PdCl₂ with trioctylamine in toluene at 60°C in an argon atmosphere [7].

The hydrogenation reaction was studied using kinetic equipment, in which a constant H_2 pressure was maintained [9]. The hydrogenation was run in toluene at 22°C and an H_2 pressure of 500 torr. The selected method assured obtaining reproducible kinetic data; the deviations in parallel experiments did not exceed 3-5%.

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Fig. 1. Hydrogenation rate of biradical isomers of phthalic acid esters in presence of $PdCl_2-(C_8H_{17})_3N$ complex: 1) o-biradical; 2) m-biradical; 3) p-biradical; $[Pd] = 1 \cdot 10^{-3}$ mole/liter: $p_{H_2} = 500$ torr; t = 22°C; amount of substrate = 1.5 mmoles.

The hydrogenation rate for biradicals of variable structure is given in Fig. 1. As follows from Fig. 1, in the case of all three biradicals the hydrogenation stops after the addition of one mole of H_2 per mole of substrate, i.e., the process proceeds selectively with the formation of dihydroxylamines.

In the case of the o- and m-biradicals the hydrogenation proceeds stepwise and inflections are present on the kinetic curves, which correspond to the addition of 1 atom of H. This result indicates the variable reactivity of the mono- and biradicals toward hydrogen. In addition, the linear sections of the kinetic curves testify to the zero order of the hydrogenation reaction in both the biradical and the monoradical, i.e., to the complete filling of the active centers for the hydrogenation of both substrates. In the case of the pisomer a constant hydrogenation rate is observed only on the first section of the kinetic curve, and after the addition of one H atom the reaction rate gradually decreases.

A comparison of the hydrogenation rates of biradicals of variable structure reveals that the activity of the three studied compounds decreases in the order: ortho > meta > para. The obtained result differs from the data in [6], where the reverse relationship was established.

The higher reactivity of the o- and m-biradicals when compared with the p-isomer is most probably related to exchange effects, i.e., to the reaction of the paramagnetic centers in the biradical molecule. It is known that conformational electron exchange in the case of the obiradical occurs at $\sim 20^{\circ}$ C, whereas for the m-isomer the exchange reaction is manifested only at 140°C [10]. However, it may be assumed that under the hydrogenation conditions the coordination of the biradicals on the active centers lowers the energy barrier of this reaction.

As a result, the structure of the biradical and the nature of the employed catalyst exert an important effect on the rules for the hydrogenation of stable iminoxyl biradicals.

CONCLUSIONS

1. The hydrogenation of stable iminoxyl radicals in the presence of a complex Pd catalyst, containing a tertiary amine as the ligand, proceeds selectively with the formation of dihydroxylamines.

2. The activity of the biradical isomers of the phthalic acids in the hydrogenation reaction decreases in the order: ortho > meta > para.

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SYNTHESIS OF BISALKYLTHIO DERIVATIVES OF CYCLOPENTENE AND CYCLOHEXENE

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The wide use of unsaturated sulfides in modern organic synthesis is prevented by the absence of methods for the preparation of their individual functionalized members, for example, the dialkylthiocyclenes (I) discussed below. Previously it was shown that, under the standard conditions for the synthesis of cycliè α -haloketone thioacetals, the reaction of α -haloketones with mercaptans leads to the formation of halogen-free 1,4-dithienes in moderate yields [1, 2]. We found that the related monocyclic tetrasubstituted olefins (Ia-f) can be synthesized in up to 90% yield by simply keeping a mixture of either the α -chlorocyclopentanone or α -chlorocyclohexanone and 2 mole eeuivalents of the appropriate mercaptan in cyclohexane at $\sim 25^{\circ}$ C (Table 1).* In all cases the thioacetals corresponding to the starting chloroketones were not detected in the reaction mixtures.



The structure of the previously unknown olefins (I) was confirmed by the elemental and spectral analysis data. Thus, in their IR sepctra are present the absorption bands of the C-S (520-600 cm⁻¹) and C=C (1570-1610 cm⁻¹) bonds, while the PMR spectra have the signals of the protons of all of the structural fragments of the discussed compounds. In particular, the multiplet signals of the cycloalkene allylic methylenes are located in the $\delta \sim 3$ ppm region, the remaining methylenes at $\delta \sim 2$ ppm, while the signals of the ethyl, propyl, and butyl substituents have standard tabular values.

EXPERIMENTAL

<u>1,2-Diethylthio-l-cyclopentene (Ia)</u>. To a stirred solution of 12.4 g (0.2 mole) of EtSH in 150 ml of cyclohexane at 0°C was added in 15 min a solution of 11.9 g (0.1 mole) of α -chlorocyclopentanone in 25 ml of cyclohexane. Then the reaction mass was heated to \sim 25°C and stirred for 8 h. The obtained aqueous layer was separated, the organic layer was washed with water, dried over MgSO₄, and the residue after removal of the solvent was vacuum-distilled. We obtained 14.1 g (75%) of (Ia) as a pale yellow oil, bp 90-95° (2 mm); $n_D^{2°}$ 1.5546. Found: C 57.31; H 8.43; S 33.94%. C₉H₁₆S₂. Calculated: C 57.39; H 8.56; S 34.05%.

<u>1,2-Di-n-propylthio-1-cyclopentene (Ib)</u> was obtained the same as (Ia) from n-PrSh and α -chlorocyclopentanone. Yield of (Ib) 87%, bp 105-110° (3 mm); n_D^{20} 1.5454. Found: C 61.19; H 9.24; S 29.45%. C₁₁H₂₀S₂. Calculated: C 61.05; H 9.32; S 29.63%.

1,2-Di-n-butylthio-1-cyclopentene (Ic). Similarly from 18.0 g (0.2 mole) of n-BuSH we obtained 20.7 g (85%) of (Ic), bp 140-142° (3 mm); $n_D^{2°}$ 1.5318. Found: C 63.69; H 9.81; S 26.13%. $C_{13}H_{24}S_2$. Calculated: C 63.87; H 9.90; S 26.23%. *Table 1 has apparently been omitted from the Russian - Publisher.

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