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CATALYTIC PROPERTIES OF CHLORO-TRIS[TRI(2-THIENYL)PHOSPHINE]-RHODIUM(I) IN HYDROGENATION OF UNSATURATED COMPOUNDS

Ya. L. Gol'dfarb, E. I. Klabunovskii, A. A. Dudinov,
L. N. Sukhobok, V. A. Pavlov, B. D. Polkovnikov,
and V. P. Litvinov

UDC 541.128:542.941.7:
547.361

The concept of isosterism as a phenomenon that is manifested in a close proximity of the chemical and physical properties of compounds, belonging to various chemical types [1], has obtained wide development in the series of benzene and thiophene derivatives. In studying the biological properties of these derivatives it was concluded that comparable compounds of this series have nearly the same efficiency, and this was explained within the concepts of isosterism. The generalized data on this problem are given in the review [2].

In particular, a close proximity of the physical properties of isosteres is manifested in an analogous arrangement of the electrons and geometric properties. In this connection, we will state that an analogy in the steric structure of the Pd complexes of tri(2-thienyl)-phosphine and triphenylphosphine was recently shown by us [3]. It may be assumed that a similar analogy also exists in the Rh complexes of trithienylphosphine and triphenylphosphine; the crystal and molecular structure of the latter was described in [4].

It seemed expedient to study as a possible homogeneous hydrogenation catalyst an analog of the Wilkinson catalyst, in which the triphenylphosphine ligand is replaced by the trithienylphosphine ligand. In the present communication we limit ourselves to several hydrogenation examples, hoping to substantially expand their number in the near future.

EXPERIMENTAL

Tri(2-thienyl)phosphine was obtained as described in [5], bp 146-150° (0.06-0.07 mm). After sublimation, mp 34-35°C. Chloro-tris[tri(2-thienyl)phosphine]rhodium(I) (I) was obtained as a dark yellow amorphous powder by the method described in [6]. Found: C 44.18; H 3.08; S 29.28; Cl 3.60; P 9.35; Rh 10.36%. $C_{36}H_{27}ClP_3S_9Rh$. Calculated: C 44.15; H 2.78; S 29.46; Cl 3.62; P 9.49; Rh 10.51%; mp more than 116° (with decomp.). Ultraviolet spectrum (nm) in CH_2Cl_2: λ_{max} 240 (log ε 4.72) and 327 (log ε 4.17). All of the reagents and solvents were carefully dehydrated, the peroxides were removed, distilled in an argon stream, and stored over molecular sieves 4 Å in an argon atmosphere. The hydrogenation was run with hydrogen that had been freed of O_2 ($\leqslant 3 \cdot 10^{-8}$%) and water ($\leqslant 5 \cdot 10^{-3}$%).

Hydrogenation Method. a) In a glass reactor of the "duck" type was placed 5 mmoles of (I), the reactor was sealed tightly, blown with argon, and 20 ml of a 1:1 benzene–methanol mixture, through which argon had previously been bubbled, was added. After all of the catalyst had dissolved the argon was replaced by H_2. If $NaBH_4$ was used to activate the catalyst, then 1.3 mmoles of $NaBH_4$ in 1 ml of MeOH was added to the catalyst solution. The solution was kept for 30 min in an H_2 atmosphere and then 20 mmoles of allylbenzene and dodecane (internal standard) were added from a syringe. For the hydrogenation of allyl alcohol we used 50 mmoles of allyl alcohol and butyl alcohol as the internal standard. The hydrogenation

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1880-1883, August, 1983. Original article submitted November 16, 1982.

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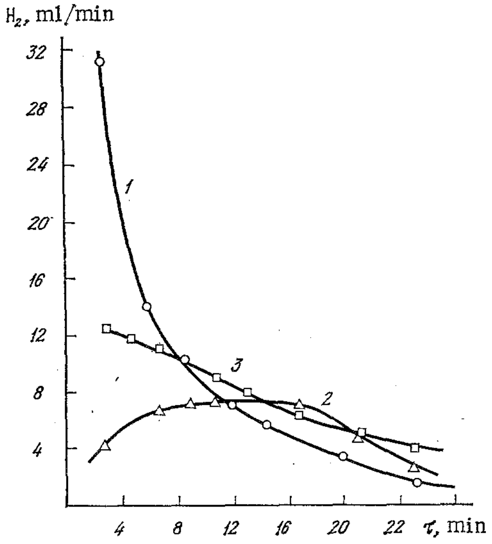

Fig. 1. Hydrogenation of allylbenzene in presence of compounds: 1) (II); 2) (I); 3) (I), treated with $NaBH_4$.

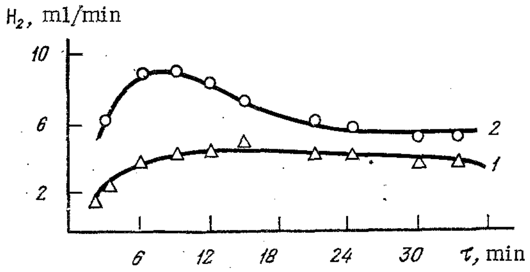

Fig. 2

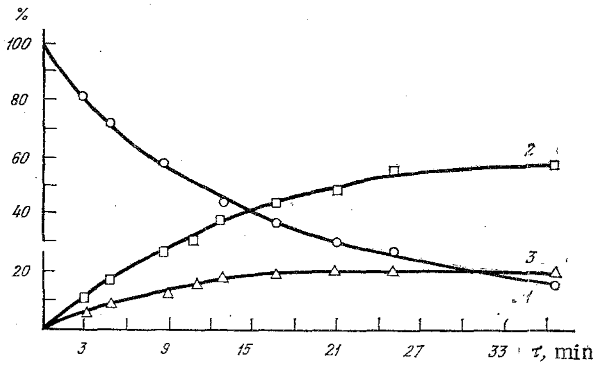

Fig. 3

Fig. 2. Hydrogenation of allyl alcohol in presence of compounds: 1) (I); 2) (I), treated with $NaBH_4$.

Fig. 3. Change in catalysate composition during hydrogenation of allylbenzene in the presence of (I), treated with $NaBH_4$ (53 mg of catalyst, 20 ml of a 1:1 benzene–methanol mixture, and 50 mg of $NaBH_4$ in 1 ml of MeOH): 1) allylbenzene; 2) propylbenzene; 3) trans-propenylbenzene. The amount of cis-propenylbenzene in the catalysate after 36 min is less than 3%.

was run at about 20° and 0.1 MPa with vigorous shaking (350-400 double swings/min). The catalysate was analyzed on a Chrom-41 chromatograph, using a 0.3 × 370 cm column packed with 15% PEG-600 + 1% KOH deposited on Celite 545, N_2, and a flame-ionization detector.

b) To a glass hydrogenation reactor, equipped with a magnetic stirrer, in an H_2 atmosphere, were added from a syringe a solution of 0.11 mmole of the catalyst in 25 ml of benzene and then a solution of 2.94 mmoles of α-acetamidocinnamic acid in 25 ml of anhydrous EtOH. The hydrogenation was run with stirring at about 20° and 0.1 MPa. At the end of H_2 absorption the solvent was distilled off on a rotor evaporator, the residue was dissolved in 20 ml of water and made alkaline with NaOH, filtered, and the filtrate was extracted with $CHCl_3$. The aqueous solution from the extraction was passed through a column packed with ion-exchange resin Dowex 50w × 8 (as the H^+ form), acidified to pH 4, and evaporated to 10 ml. The obtained crystals were dried and analyzed. For the preliminary analysis we used GLC (Biochrom-1 chromatograph, 0.25 mm × 54 m capillary column packed with N-decanoyl-L-valine tert-butylamide, N_2, and a flame-ionization detector). The reaction products were identified (as the methyl esters) to be a mixture of N-acetylphenylalanine and unreacted α-acetamidocinnamic acid. The degree of conversion in the experiments was checked by spectrophotometry, using the difference in the molar extinction coefficients of α-acetamidocinnamic acid and N-acetylphenylalanine at 280 nm (ε = 16,500 and $\varepsilon \approx 0$, respectively).

DISCUSSION OF RESULTS

A comparative study of the catalytic properties of (I) and chloro-tris(triphenylphosphine)rhodium(I) (II) shows that the initial rate for the hydrogenation of allylbenzene (method a) in the presence of (I) is 2-2.5 times slower than in the presence of (II) (Fig. 1). From Fig. 1 it can also be seen that (I) is less active but more stable than (II), which quickly loses its initial high activity. In the presence of both (I) and (II) the isomerization of allylbenzene to propenylbenzene is slight and the total amount of the cis and trans isomers does not exceed 3%. An increase in the initial hydrogenation rate of both allylbenzene (see Fig. 1) and allyl alcohol (Fig. 2) is observed after the prior treatment of (I) with $NaBH_4$, in which connection there is a change in the shape of the H_2 absorption rate curves and a sharp change in the selectivity of the catalyst effect: besides hydrogenation, a substantial isomerization of allylbenzene to trans-propenylbenzene occurs (amount of cis isomer less than 3%) (Fig. 3).

The hydrogenation of α-acetamidocinnamic acid (method b) in the presence of (I) is also slower than in the presence of (II) ($\tau_{1/2} = 230$ and $\tau_{1/2} = 140$ min, respectively). However, in this case, the treatment of (I) with $NaBH_4$ fails to have a noticeable accelerating effect. The addition of 0.6 mmole of thiophene to the reaction mixture inhibits the catalytic effect of (I) ($\tau_{1/2} = 450$ min), while the hydrogenation of α-acetamidocinnamic acid does not go in the presence of 1.2 mmoles of thiophene. This fact cannot be explained within the framework of thiophene and benzene being analogous.

As a result, the trithienylphosphine catalyst is less active in the hydrogenation of the studied substrates than the triphenylphosphine catalyst.

According to [6], the treatment of a solution of the Wilkinson complex with molecular H_2 results in the absorption of 1 mole of H_2 per mole of complex to give the dihydride complex

$$(Ph_3P)_3RhCl \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} (Ph_3P)_2RhClH_2 + Ph_3P$$

Here the color of the solution changes from red to pale yellow. If after this an inert gas is passed through the solution, then the reverse reaction occurs and the color changes to the original red color. When the thienyl analog was studied the color changed from yellow to red in an H_2 atmosphere, but the color of the solution did not change on subsequent treatment with an inert gas. This retention of the color, and also the slower H_2 absorption rate, are apparently related to the greater stability of the thienyl hydride complex when compared with the Wilkinson hydride complex.

CONCLUSIONS

1. The thiophene analog of the Wilkinson complex was synthesized and it was shown that the concept of isosterism can serve as one of the criteria for seeking new homogeneous hydrogenation catalysts.

2. The catalytic properties of the thienyl analog of the Wilkinson complex were studied in the homogeneous hydrogenation of allyl alcohol, allylbenzene, and α-acetamidocinnamic acid.

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