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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Catalytic Oxidative Acetoxylation of Octa-1,3-dienylbenzene

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Abstract—Acetoxylation of octa-1,3-dienylbenzene in glacial acetic acid in the presence of catalysts with intermetallic phases based on Pd and Rh and Group IIIA–VIA elements was studied. The relationship between the total selectivity of the reaction with respect to diacetoxy derivatives and the Aller–Rochow electronegativity of second modifying elements was examined. The most efficient catalytic systems were determined.

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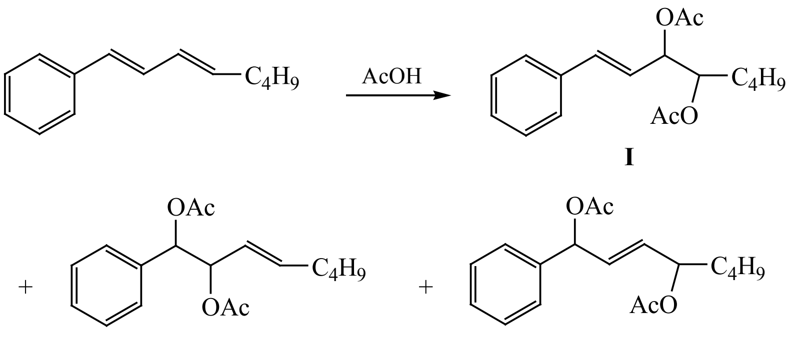
Acetoxylation of octa-1,3-dienylbenzene, the product of cross-combination of styrene and 1-hexene, is of practical interest because the diacetoxy derivatives formed can be converted into other functional derivatives that can be used in manufacture of some kinds of thermally stable and frost-resistant elastomers and in syntheses of biologically active preparations. This reaction has not been studied as applied to alkylidene-aromatic compounds primarily because of the poor selectivity of the process in the presence of homogeneous catalysts limited to palladium complexes [1]:



I

II

III

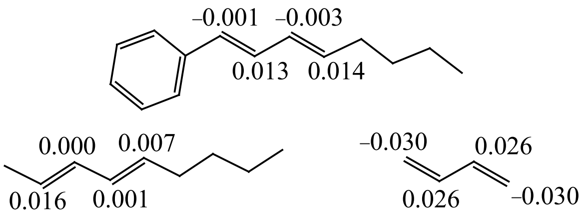
As can be seen in the above scheme, the main reaction products are 1,2- (**I**) and (**II**) and, to a lesser extent, 1,4-substituted (**III**) derivatives (irrespective of the chosen type of a catalyst) [2]. In addition, *Z*- and *E*-isomers are present in the reaction zone. The relative amounts of these configurational isomers are determined by the nature of a platinum-group atom in the catalytic formulation: Pd (Pt) directs the reaction toward formation of mostly the *E*-isomer, and Rh (Ir), mostly the *Z*-isomer (Table 1).

To explain the formation of nearly equimolar amounts of isomers **I** and **II**, we used the CNDO/2 method to perform a quantum-mechanical calculation of the charge distribution in the molecules of octa-1,3-dienylbenzene and, for comparison, 2,4-nonadiene (an analog of octa-1,3-dienylbenzene in which the phenyl group is substituted with a methyl group) and 1,3-butadiene:

Table 1. Acetoxylation of octa-1,3-dienylbenzene in the presence of various platinum-group catalysts 150°C, 9.1 MPa

M–Te/C catalyst[a]	Selectivity of formation of isomers, %						Total selectivity, %	Total yield, wt %
	Z-(**I**)	*E*-(**I**)	*Z*-(**II**)	*E*-(**II**)	*Z*-(**III**)	*E*-(**III**)		
M:								
Pd	8.1	18.8	7.8	18.1	0.7	6.5	60.0	59.9
Pt	7.6	25.6	7.4	25.8	4.3	2.0	72.7	17.8
Rh	30.1	5.4	29.8	5.6	6.2	3.0	80.1	80.0
Ir	35.9	3.4	36.1	3.3	Traces	Traces	78.7	10.1

[a] As the second element of the catalytic formulation was chosen Te, which exhibits good performance in acetoxylation of 1,3-butadiene



The results obtained demonstrate that the distributions of effective charges on carbon atoms at double bonds are fundamentally different in the molecules under consideration. For example, in octa-1,3-dienylbenzene, the electron densities on the first and third, second and fourth carbon atoms nearly coincide. In addition, a certain difference in signs is observed for the first and second, third and fourth atoms. All the described features are also characteristic of 1,3-butadiene, only being more pronounced. By contrast, a different situation was observed for 2,4-nonadiene, in which the electron density on the respective carbon atoms is lowered. The data obtained suggest that 1,3-butadiene is more active in complexation with the catalyst (in chemisorption of reagents), and then follows octa-1,3-dienylbenzene and, further, 2,4-nonadiene. This suggestion is in agreement with the data previously obtained for 1,3-buta- and 2,4-octadienes [3], with the yield of diacetoxy derivatives and the rate of the chemical reaction being very low in the last case. By contrast, 1,3-butadiene was found to be the most reactive among conjugated alkadienes. Presumably, steric factors exert a considerably weaker influence in the given cases, compared with the electronic characteristics of the molecules.

It became possible to understand the substantially lower yields of diacetoxy derivatives in the presence of Pt and Ir catalysts on measuring IR spectra of catalyst–substrate chemisorbates. For example, the band appearing in IR spectra of octa-1,3-dienylbenzene–Pt–Sb and octa-1,3-dienylbenzene–Ir–Bi sorbates in the spectral range 2800–3700 cm^{-1} at 3015 cm^{-1} has low intensity, compared with the spectrum of the substrate or with similar spectra for Pd and Rh, which may be indicative of the presence of both π- and σ-adsorbed forms. It is known [4] that the σ-binding leads to a firmer adsorption of the substrate on active catalytic centers, which impairs the activity of the catalysts.

In the next stage of the study, it was necessary to choose the most efficient acetoxylation catalyst among the known set of catalysts previously synthesized for similar purposes. Of stronger interest were binary heterogeneous intermetallic catalysts based on palladium and rhodium, which contained As, Te, Ge, Sb, Ga, Sn, Bi, In, or Tl as a second element (Table 2).

As can be seen in Table 2, the formation selectivity of isomers **I** and **II** varies rather widely, from 50 to 70%, and that of isomer **III**, from 5 to 12%. It can be clearly seen that this is due to the nature of the second atom in the platinum-group component of the catalyst, with the highest selectivity with respect to isomers **I** and **II** observed in the presence of Pd–Sb and Rh–Bi systems; the yield of isomer **III** is the lowest for palladium and rhodium catalysts.

The phase compositions were reported in [5] for some systems of this kind and it was demonstrated that just these phases are active in acetoxylation. To these belong Pd_3Sb, Pd_4Te, PdSn ($PdSn_3$), $RhBi_4$, Rh_2Te ($Rh_{10}Te$).

It was of indubitable interest to relate the efficient operation of catalysts to a physical parameter of the second component of the catalytic systems. Previously,

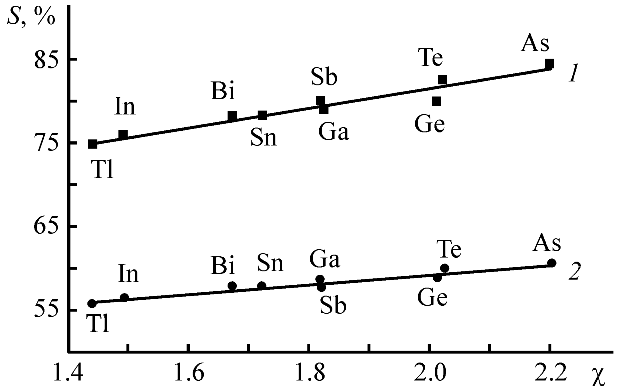


Fig. 1. Sum of the selectivities *S* of formation of diacetoxy derivatives of octa-1,3-dienylbenzene vs. the electronegativity of the second elements of catalytic formulations (*1*) Rh–M and (2) Pd–M. (χ) Allred–Rochow electronegativity.

satisfactory correlations have been obtained between the total selectivity of formation of diacetoxy derivatives of 1,3-buta- and 1,3-pentadienes and the electronegativity of modifying elements. It was found that, in the given case too, there is a correlation between similar parameters (Fig. 1), which is only characteristics of systems of the alkadiene series. Based on the data obtained, we can only state that the larger the electronegativity of Group-IIIA–VIA elements (and, accordingly, the more pronounced the contribution of ionic binding in intermetallic compounds), the higher the selectivity of acetoxylation. This relationship may be due to the nature of the substrate chemisorption on the active center of a catalyst, because, with increasing electronegativity of the second element, Pd and Rh acquire an effective positive charge to a greater extent, and this charge favors not only an increase in the adsorption coefficients, but also a better organization of reagent molecules on the catalyst surface.

Table 2. Acetoxylation of octa-1,3-dienylbenzene in the presence of various intermetallic catalysts, 150°C, 10 MPa, reaction duration 5 h

Active element of a catalyst	Selectivity of formation of isomers, %		Conversion, %
	I + II	**III**	
Pd–As	52.2	8.3	97.8
Pd–Te	52.8	7.2	99.8
Pd–Ge	53.1	5.4	99.2
Pd–Sb	54.2	3.3	99.9
Pd–Ga	52.3	6.2	99.6
Pd–Sn	51.1	6.9	98.6
Pd–Bi	52.1	5.7	99.0
Pd–In	51.7	4.6	99.2
Pd–Tl	51.8	3.7	99.8
Rh–As	72.3	12.2	98.0
Rh–Te	70.9	9.2	99.9
Rh–Ge	70.7	9.2	99.6
Rh–Sb	71.0	9.1	99.4
Rh–Ga	70.3	9.0	99.7
Rh–Sn	68.8	9.3	98.7
Rh–Bi	74.2	4.0	99.8
Rh–In	70.1	5.9	99.5
Rh–Tl	70.1	4.8	99.9

In the next stage of the study, it was necessary to stereochemically control the reaction, i.e., to affect the relative amounts of *Z*- and *E*-isomers. It seemed reasonable that this can be done by using the data in Table 1, from which follows that *E*-isomers are mostly formed on palladium, and *Z*-isomers, on rhodium. In acetoxylation of octa-1,3-dienylbenzene on a bimetallic Pd–Rh catalyst (Fig. 2), the nature of the obtained dependences of the formation selectivity of geometric isomers on the concentration of rhodium indicates that the selectivities of the identical isomer being generated change in opposite directions as the concentration of rhodium in the Pd_3Sb/C catalyst increases. As it follows from the data in Table 1 and Fig. 1, the change in the content of the isomers in the catalyzate on passing from a 100% palladium to 100% rhodium catalyst is controlled by both kinetic and thermodynamic factors. In particular, the latter means that mutual isomerization of products **I–III** occurs during the process and the reaction ends as the equilibrium state, under the given conditions, is attained.

Another way to affect the relative amounts of

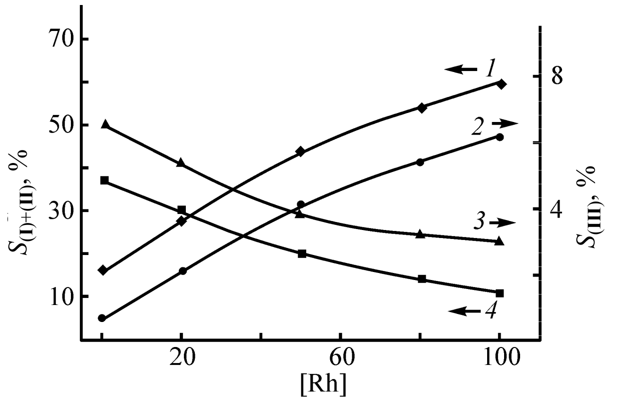


Fig. 2. Selectivities $S_{(I)+(II)}$ and $S_{(III)}$ of formation of (*1, 2*) *Z*- and (*3, 4*) *E*-isomers (**I**)–(**III**) vs. the rhodium content [Rh] of the Pd_3Sb/C catalyst.

geometric and structural isomers is based on the data in Table 1, from which follows that, in the presence of the Ir catalysts, *Z*- and E-diacetoxy derivatives **III** are formed in trace amounts. This fact stimulated tests of catalysts of new composition, additionally containing iridium. In this case, it was necessary to consider two variants: combinations of Ir with Pd and Rh. Depending on the results obtained, it would be possible to also consider more complex compositions with due consideration for the fact that the final goal to be achieved is to create a catalyst that would enable the reaction of oxidative cross-combination of styrene and 1-hexene, followed by acetoxylation of the resulting octa-1,3-dienylbenzene, on the same catalyst or system of catalysts. The data obtained are listed in Table 3.

It can be seen that introduction of iridium into the catalyst positively affects the selectivity of the catalytic system. For example, introduction into the system of no more than 10% iridium in the form of Ir_2O_3 results in that a smaller amount of isomer (III) is formed, which leads to an increase in the selectivity with respect to the main isomers; However, the yield of target products simultaneously somewhat decreases because of the incomplete conversion of the substrate (on average, by 10%). The last problem can be well tackled with by raising the reaction duration from 5 to 6 h. In this case, the total yields of the target isomers **I** and **II** reach values obtained on unmodified palladium and rhodium catalysts; however, the fraction of *Z*-isomers somewhat increases.

Thus, the data obtained suggest that, upon introduction of iridium into complex Pd–RH catalysts [5] favoring the single-reaction scheme of the process, the yield of vicinally substituted diacetoxy derivatives of isomers **I** and **II** will be only kinetically controlled. This suggestion was confirmed by introduction of 1–10% iridium in terms of the metal into a catalytic system containing Pd_3Sb–$RhBi_4$ active phases (Table 4).

Our results indicate that, in the given case too, the iridium component has a positive effect, which consists in that the selectivity of formation of isomers **I** and **II** becomes higher. According to the values of selectivity, presence of Ir has no adverse effect on the first reaction, oxidative cross-combination.

EXPERIMENTAL

We performed our quantum-mechanical calculations with HyperChem software (Version Professional Release 6.03, Hypercube Inc., by the CNDO/2 method with geometric optimization.

Table 3. Acetoxylation of octa-1,3-dienylbenzene in the presence of Pd–Ir and Rh–Ir catalytic systems. 150°C, 9 MPa, reaction duration 5 h

Catalyst	Metal ratio, at/at	Selectivity of formation of isomers, %						Conversion, %
		Z-(**I**)	*E*-(**I**)	*Z*-(**II**)	*E*-(**II**)	*Z*-(**III**)	*E*-(**III**)	
Pd–Ir	1 : 0.05	9.3	21.6	9.0	20.8	0.04	2.2	96
	1 : 0.1	9.3	21.7	9.0	20.9	0.01	1.1	91
	1 : 0.2	9.2	21.0	8.9	20.0	Traces	Traces	80
Rh–Ir	1 : 0.05	32.5	5.5	31.2	5.9	1.1	0.4	96
	1 : 0.1	33.1	5.9	32.8	6.2	0.1	Traces	94
	1 : 0.2	34.4	6.4	33.6	6.9	Traces	The same	85

Table 4. Oxidative cross-combination of styrene and 1-hexene and acetoxylation of the resulting octa-1,3-dienylbenzene on the Pd3Sb–RhBi4–Ir/C catalytic system.[a] 150°C, 9 MPa, reaction duration 6 h

Ir content of the system, at %	Selectivity of formation of diacetoxy isomers, %					
	Z-(**I**)	*E*-(**I**)	*Z*-(**II**)	*E*-(**II**)	*Z*-(**III**)	*E*-(**III**)
1	24.3	16.9	24.3	17.0	0.60	0.52
3	24.0	16.3	24.0	16.2	0.48	0.36
5	24.4	15.9	23.5	15.6	0.37	0.30
7	24.8	15.6	24.0	15.4	0.20	0.11
8	25.1	15.1	24.4	15.0	Trace amounts	Trace amounts
10	24.5	15.6	24.0	15.5	The same	The same

[a] The data are presented for the second stage.

The IR spectra were measured with a UR-20 instrument in pellets with KBr.

The individual compositions of starting materials and catalyzates were determined chromatographically on a Khrom-5 chromatograph equipped with a flame-ionization detector and a stainless steel capillary column 0.25 mm in diameter and 50 m long [XE-30 on Chromaton NAW as liquid phase, carrier gas nitrogen (30 cm^3 min^{-1}), temperature raised from 70 to 270°C at a rate of 3 deg min^{-1}, evaporator temperature 300°C].

The catalysts were prepared by preliminary treatment of a 10-g portion of AR-5 activated recuperation carbon with a 15% aqueous solution of nitric acid, with the mixture evaporated on a water bath until the liquid phase disappeared. The calculated amount of catalyst components in the form of nitrates, chlorides, or oxides was dissolved in a mixture of 30 ml of water and 45 and 25 ml of, respectively, nitric and hydrochloric acids. After that the resulting solution was poured onto the carbon and evaporated to dryness. The thus prepared catalyst was calcined in the reactor at 150°C for 1–1.5 h, the temperature was raised to 200°C, a flow of hydrogen was switched on (10–20 l h^{-1}), reduction was performed at 500–550°C for 1 h, and the reactor was cooled in the presence of the oxidizing agent.

The reactions of oxidative cross-combination and acetoxylation were commonly performed in the batch mode in a stainless steel autoclave. A 0.05-l vessel was charged with 30 ml of glacial acetic acid, 0.8–0.9 g of a powdered catalyst, and a calculated amount of the reagents. The autoclave was hermetically sealed, electric heating was switched on. After the required temperature was reached, air from a cylinder was forced into the autoclave to obtain the required pressure. The agitation was performed on an automated rocker. The reaction duration was chosen to be the longest on the basis of preliminary data obtained on a stationary autoclave installation.

CONCLUSIONS

(1) It was shown that the reactivity of octa-1,3-dienylbenzene in the primary chemical event of the acetoxylation reaction is related to the amount of positive effective charge on the central Pd and Rh atom of catalysts, which provides formation of η^2-olefin or η^3-allyl structures.

(2) It was demonstrated that the low reactivity of Pt and Ir catalysts is due to the occurrence of π–σ binding of the substrate with the platinum-group component of the catalyst. However, formation of 1,4-addition isomers is eliminated in the presence of Ir.

(3) A catalytic formulation based on Pd and Rh was found. This formulation provides formation of isomers via 1,2- and 1,4-addition of acetoxy groups to octa-1,3-dienylbenzene with a selectivity of 80% and more. Additional introduction of 10% iridium into the Pd_3Sb–$RhBi_4$/C formulation improves the selectivity of the diacetoxylation reaction and the process becomes kinetically controlled.

(4) It was found that the acetoxylation process is accompanied by mutual isomerization of *Z*- and *E*-configurantional isomers, with the structural-skeletal isomerization presumably having a steplike nature.

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