

LIGAND EFFECT ON THE STEREOSELECTIVITY AND CATALYST ACTIVITY IN A RHODIUM-CATALYZED SYNTHESIS OF 1,4-HEXADIENE FROM ETHYLENE AND BUTADIENE

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Summary

Two types of donor ligands are differentiated in their effect on the rhodium-catalyzed codimerization of ethylene and butadiene to form *trans*-1,4-hexadiene. Weak oxygen donors, with pK_a of -5 to -2 , such as ethers, ketones, and esters, will increase the rate of reaction but have no effect on the ratio of *trans* to *cis* isomers. Stronger donors, with pK_a of -2 to 0 such as alcohol, water, DMF and phosphorus oxides increase the reaction rate and also give increased stereoselectivity in formation of the *trans* isomer; these donors all inhibit catalyst activity at high donor/Rh ratio.

Introduction

Catalytic codimerization of ethylene and butadiene by a rhodium catalyst to form predominantly 1,4-hexadiene was first carried out by Alderson [1]. Cramer [2] investigated the kinetics and mechanism of the reaction and the nature of the active catalyst species. This elegant work was carried out in alcohol, a medium in which the rhodium is solvated. Such solvation is well known to influence the path of transition metal-catalyzed reactions. It was therefore of interest to investigate this reaction in a nonpolar medium so as to determine the effect of added coordinating ligands on catalyst activity and stereoselectivity. The latter aspect is of special interest because the formation of 1,4-hexadiene is the simplest reaction which provides insight into the coupling reaction of *syn*- and *anti*- π -crotyls with olefins.

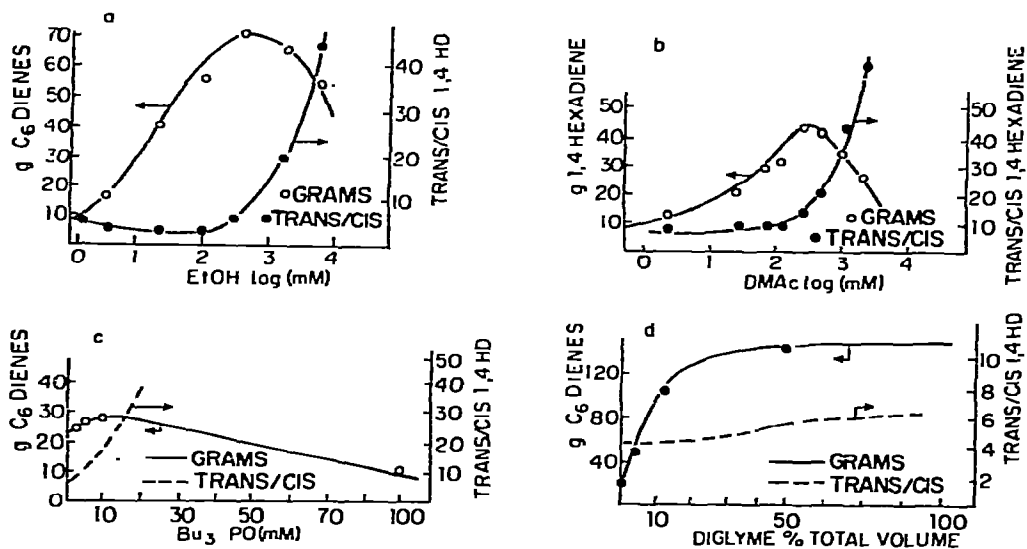
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Results and discussion

Donor effect on catalyst activity

Cramer [2] showed that π -crotylrhodium chloride (I) was a key precursor to the active catalyst species which forms 1,4-hexadiene. We found that I is relatively inactive as a catalyst in a nonpolar medium such as toluene even in the presence of HCl*. However, it becomes very active in the presence of certain donors. It therefore provides an ideal system to determine the effect of added donor ligands.

Figure 1 shows in detail how the catalyst activity changes with concentration using four donors: ethanol, dimethylacetamide, tri-*n*-butyl phosphine oxide (Bu₃PO) and diglyme. With a donor such as diglyme, the catalytic activity increases with increasing concentration and then levels off. With donors such as alcohol and DMAC, the catalytic activity reaches a maximum and then decreases with further increase in the donor concentration. With a donor such as Bu₃PO, the activity increases slightly and then drops off rapidly with donor concentration. Each donor has a particular concentration at which maximum catalyst activity is reached. The results are summarized in Table 1 showing, for a variety of donors, the donor/Rh ratio required for maximum rate and the relative maximum rate attainable.



a ETHANOL 1mm Rh, 2mm HCl, REACTION TIME, 15 min

b $\text{CH}_3\text{C}(=\text{O})\text{N}(\text{CH}_3)_2$ 1mm Rh, REACTION TIME, 15 min

c $(\text{C}_4\text{H}_9)_3\text{PO}$ 1mm Rh, 2mm HCl, REACTION TIME, 60 min

d DIGLYME 1mm Rh, REACTION TIME, 60 min

Fig. 1. Effect of donor concentration on the reaction rate and ratio of *trans/cis*-hexadiene.

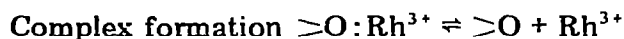
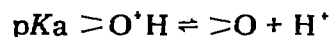
* Cramer [2] found that the rate of hexadiene formation in alcohol is first order in $[\text{H}^+]$. This is not the case in nonpolar solvents.

TABLE 1
RELATIVE EFFECT OF VARIOUS DONORS ON CATALYST ACTIVITY

Donor	pKa ^d	Optimum donor/Rh	Relative reactivity ^b
None			1
Bu ₃ PO	0	2	1.3
CH ₃ C(O)N(CH ₃) ₂	-0.5	300	5
H ₂ O ^c	-1.9	300	8
Alcohols	-2 to -1	≈500	6-8
THF	-2.1	≈500	5
Diglyme	≈-4	3000-4000	6
Ethyl acetate	-6.5	4000	6.5
Phenol ^d	-6.8	^e	1 (Donor/Rh = 200)
Acetone	-7	4000	6
			3 (Donor/Rh = 200)
Pyridine	>5.3		0

^a Ref. 3. ^b Based on amount of 1,4-hexadienes formed in first 15 min reaction time. ^c Reaction carried out in diglyme. ^d Phenol is anomalous; see discussion. ^e Not determined.

We have found that the effects of these donors on reaction rates and on stereochemistry can be correlated with the pKa of their onium salts. This measure was chosen because the complexation of Rh with a donor can be viewed as an acid-base reaction:



The higher the pKa of the onium salt, the greater will be the unprotonated donor ligand's affinity for protons and to a first approximation its affinity for complexing rhodium. Thus, diglyme (pKa -4) is a weak donor; Bu₃PO (pKa ≈ 0) is a strong donor.

The results in Table 1 show that those donors (σ -electron donors with oxygen donor sites) with pKa values between -5 and 0 increase catalyst activity when used in suitable quantity. This group can be further divided as follows: donors with a pKa value between -5 and -2 enhance the activity regardless of the quantity used. Donors whose onium salts have pKa values between -2 and 0 enhance the catalyst activity when present in limited quantity, but slow down the reactions when present in larger quantity. As outlined in the following section, this group of donors also affects the product isomer distribution.

Effect of donor ligands on stereoselectivity

Alderson [1] had observed that the amount of alcohol present strongly influences the ratio of the *trans*- to *cis*-diene formed. With little or no alcohol, the *trans/cis* ratio is less than 5; in the presence of a large excess of alcohol the *trans/cis* ratio rises to 10 or 20.

We found that oxygen donors with a pKa between -2 and 0 are capable of increasing the *trans/cis* ratio of the 1,4-hexadiene formed. The effect on the *trans/cis* ratio is proportional to the donor strength and concentration.

For example, when a relatively weak donor such as alcohol was used, a

TABLE 2
EFFECT OF VARIOUS DONORS ON THE RATIO OF *trans/cis*-HEXADIENE

Donors	pKa	Donor/Rh ^a	Relative effectiveness ^b
None			0
Acetone	-7.2	<i>d</i>	0
CH ₃ COOC ₂ H ₅	-6.5	<i>d</i>	0
Diglyme (or ethers)	(-3 to -4)	<i>d</i>	0
CH ₃ OH	-2	1000	1
H ₂ O ^c	≈ (-1.9)	250	4
CH ₃ C(O)N(CH ₃) ₂	-0.5	50	20
Bu ₃ PO	≈ 0	5	200
[(CH ₃) ₂ N] ₃ PO	≈ 0	5	200

^a Donor to Rh ratio required to bring about a *t/c* of 13-15 (>92% *trans*). ^b Relative effectiveness in forming a *t/c* ratio of >13. This equals 1000/[Donor/Rh]. ^c Reaction carried out in diglyme. ^d Did not give the high *t/c* ratio regardless of concentration.

donor to catalyst ratio of 1000 was required to bring about an appreciable increase in the *trans/cis* ratio. When a strong donor such as Bu₃PO was used, a donor to catalyst ratio of only 5 was needed to bring about the same change (Table 2). Donors with pKa of less than -2 such as ethers or ketones are too weak to cause any appreciable change in the *trans-to-cis* ratio. The extent of change in the *trans/cis* ratio with changing donor concentration can be seen in Fig. 1 and is summarized in Table 2. Water is a very effective donor for improving the *trans/cis* ratio but its effect can be realized only when it is used in a medium such as glyme in which it is soluble.

No correlation was observed between the dipole moment of the additive and its effect on the stereoselectivity. Thus the dielectric constant of CH₃CN ($\epsilon = 35$) lies between that of CH₃OH ($\epsilon = 53$) and C₂H₅OH ($\epsilon = 24$); but CH₃CN has no effect on the (*t/c*) ratio of the product.

Effect of ethylene concentration

Cramer [2] has shown that the rate of formation of 1,4-hexadiene is first order in ethylene at low concentrations. We have found that the product ratio is also affected.

At constant donor/Rh (enough ethanol was present to give adequate reaction rate but not to influence isomer distribution), the *t/c* ratio of the pro-

TABLE 3
EFFECT OF CHANGE OF ETHYLENE PRESSURE ON THE RATIO OF *trans/cis*-HEXADIENE AND REACTION RATE^a

E (psi) ^b	<i>trans/cis</i>	Rate (g of 1,4-hexadiene/15 min)
10	22	2-3
20	17	
30	11	8
100	3	41

^a The reaction was carried out in the presence of small amount of alcohol, not enough to enhance the *t/c* ratio. ^b Derived from the difference in reactor pressure before and after the introduction of ethylene.

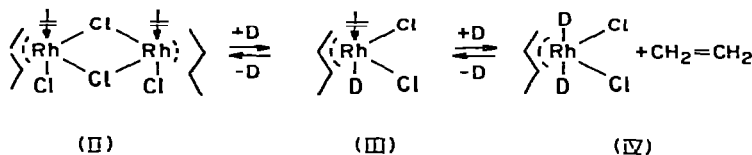
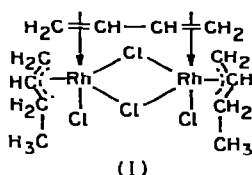
duct drops from 22/1 to 3/1 as the ethylene partial pressure is increased from 10 to 100 psi. (Table 3).

Discussion of mechanism

Donor effect on catalyst activity

In the absence of donor species complex I is relatively inactive in codimerizing ethylene and butadiene to form C-6 dienes. Cramer has shown that the active catalyst is a monomeric Rh complex. This low activity of I can be attributed to its dimeric structure (I or II) under the reaction conditions [2,8]. Addition of suitable electron donors converts the dimer first into the monomeric form III and then into IV (Scheme 1).

SCHEME 1



The effect of donors on the catalyst activity can be explained if we assume that III with ethylene coordinated to one site and a donor to the other is the active catalyst and that IV, with both coordination sites occupied by donors, is catalytically inactive.

With weak donors such as ketones or ethers (Fig. 1d), the reaction rate increases slowly, reaches a maximum and levels off at the maximum as the concentration of the donor is increased. These donors break up dimer II to form III but do not compete with ethylene for a second coordination site. Phenol with an aromatic substituted oxygen is anomalous; although it has a pK_a comparable to acetone, it has no effect on catalyst activity.

With donors such as alcohol or DMAC ($pK_a -2$ to 0), the reaction rate increases very rapidly, reaches a maximum and then decreases with additions of more donor. This indicates that these compounds not only will break up dimer II but also will coordinate with III to form inactive IV. The point of maximum activity will be a function of the ability of the donor to compete with ethylene for the coordination site on III.

With Bu_3PO (a strong donor, pK_a 0), the reaction rate increases only slightly before suggesting preferential formation IV.

With very basic donors, such as pyridines, arsines, or phosphines, the catalyst is inactive, presumably due to irreversible dicoordination.

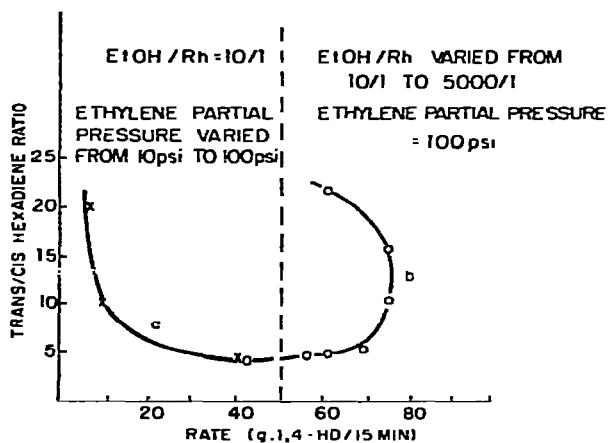
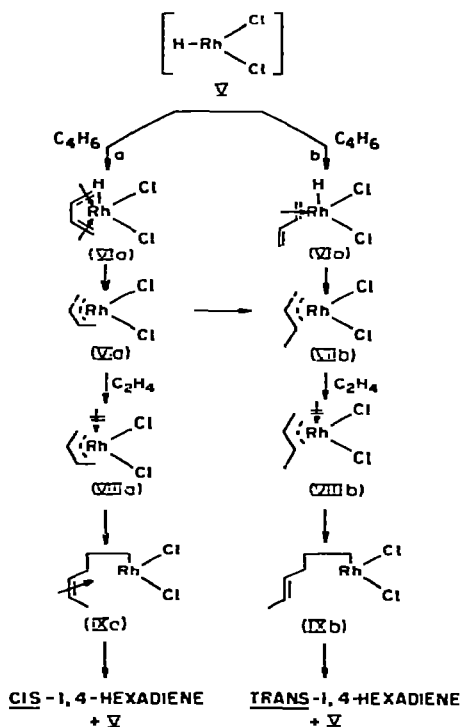


Fig. 2. Relationship of *trans/cis* ratio and reaction rate.

The *trans/cis* ratio

The catalytic cycle for formation of 1,4-hexadiene can be represented as shown in Scheme 2 [2,4-6].

SCHEME 2



The key intermediates in the formation of both *cis*- and *trans*-1,4-hexadienes are the *anti*- π -crotylrhodium (VIIa) and the *syn*-isomer (VIIb). The ratio of *trans/cis* products is determined by (a) the ratio of VIIb/VIIa ini-

tially formed in the reaction of butadiene with the rhodium hydride V and (b) the extent of isomerization of VIIa to the more stable VIIb prior to reaction with ethylene.

A measure of the initial *anti/syn* ratio and of the rate of conversion of the *anti*- to the *syn*- π -crotyl can be obtained by raising the ethylene concentration; this should increase the rate of the forward reactions of VIIa and VIIb with ethylene independent of isomerization. Table 3 shows that the *t/c* ratio drops from 22 to 3 as the ethylene concentration is raised at constant EtOH/Rh ratio. This suggests that the isomerization of VIIa to VIIb is occurring at a rate competitive with the insertion reaction to form IXa and IXb; furthermore, the initial ratio of VIIa/VIIb reaches 3/1. This is quite different from the nickel-catalyzed formation of 1,4-hexadiene where the *t/c* ratio is independent of ethylene concentration [4].

Donors can intervene in this catalyst cycle to change the *trans/cis* ratio in either one of the two critical steps. Donors could change the initial ratio of VIIa/VIIb, possibly by affecting the mode of butadiene coordination with the hydride (VIa vs. VIb). They could also change the reactivity of VIIa either by increasing the rate of isomerization of VIIa to VIIb or slowing the forward reaction with ethylene so that VIIa had more time to convert to VIIb. The present data are insufficient to resolve the relative importance of these two factors. It is important to note that the only donors which affect the isomer distribution also reduce the reaction rate at higher donor concentrations. This might suggest that the donors merely reduce the rate of the insertion reaction (VIIa \rightarrow IXa). There is, however, no simple correlation between reaction rate and *t/c* ratio as would be required by such a mechanism. The complex relationship between rate and *t/c* is shown in Fig. 2. Curve a represents runs carried out at constant but low ethanol concentration and increasing ethylene pressure; the drop in *t/c* with increasing rate has been discussed above. Curve b is from reactions carried out at constant ethylene pressure and increasing donor concentration. The *t/c* is at first unchanged while reaction rate almost doubles; then the *t/c* abruptly rises while reaction rate stays constant and finally continues to rise as reaction rate falls.

Unless there is a rather fortuitous balancing of rates, the results suggest that the donors increase the rate of isomerization of VIIa to VIIb. They may also affect the initial ratios of these two compounds but the relative importance of this factor cannot be determined.

Experimental

Equipment. The reactor system, the analytical methods and other controlling devices are described in refs. 4 and 9. Details on general reaction procedure are described in ref. 9.

Standard reaction conditions. The reaction was carried out at 70° at 140 psi. The reaction mixture consisted of 1 l toluene, 1 mmol rhodium catalyst, the required amount of electron donor, 180 g butadiene and enough ethylene to give a total pressure of 140 psi (equal to 100 psi in ethylene partial pressure), unless otherwise noted.

Standard catalyst. This was crotylrhodium chloride, $(C_4H_7)_2Rh_2Cl_4 \cdot C_4H_6$,

as prepared according to the procedure given in ref. 8. The catalyst was first dissolved in a small amount of inert solvent such as methylene chloride or *o*-dichlorobenzene and then injected into the reaction system [9].

Electron donors. These were reagent grade liquids or solids further purified by distillation or recrystallization. Tributylphosphine oxide (Carlisle Chemical Company) was used without further purification.

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