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On the Catalytic Addition of Alcohols to 1,3-Butadiene with Rhodium Trichloride Hydrates

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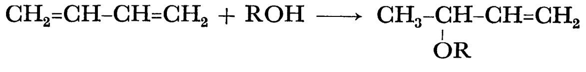
Recently, it was disclosed by Dewhirst[1] that ethanol added to 1,3-dienes in the presence of $RhCl_3 \cdot 3H_2O$ to give allylic ethers, but the mechanism of formation of the ethers was left uncertain.

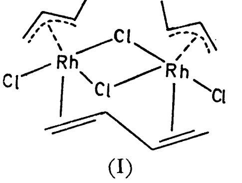
We wish to report some facts which may shed light on the mechanisms of this new addition reaction.

Table 1 summarizes the results of the addition reactions of various alcohols to 1,3-butadiene. The reaction proceeds at room temperature under nitrogen in the presence of catalytic amount of $RhCl_3 \cdot nH_2O$ (n=2 or 3) to give an addition product which is found to be a single component from glc analysis. The addition product of EtOH separated by preparative glc, a colorless liquid of bp 76°C, was confirmed to be 3-ethoxybut-1-ene by comparison of the IR and NMR spectra with those of an authentic sample.[2] Similarly, the addition products of the other alcohols were identified as 3-alkoxybut-1-ene.

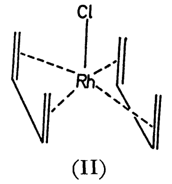


$$CH_2{=}CH{-}CH{=}CH_2 + ROH \longrightarrow CH_3{-}\underset{\displaystyle OR}{\underset{|}{CH}}{-}CH{=}CH_2$$

The known binuclear rhodium complex (I)[3] was



(I)



(II)

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[1] K. C. Dewhirst, *J. Org. Chem.*, **32**, 1297 (1967).

[2] J. D. Roberts, Wm. G. Young, and S. Winstein, *J. Amer. Chem. Soc.*, **61**, 2157 (1942).

[3] J. Powell and B. L. Shaw, *J. Chem. Soc.*, *A*, **1968**, 597.

Table 1. Addition reaction of alcohols to 1,3-butadiene

Alcohol) (100 m*l*	Butadiene (mmol)	$RhCl_2 \cdot 3H_2O$ (mmol)	Time (hr)	Addition (mmol)	Product %[c]	Intensity of ν_{OH}[d] (l. mol^{-1} cm^{-1}) 10^{-4}
Me-	240	0.95	63	12.4	5.2	0.53
Et-[a]	600	3.05[b]	20	33.0	5.5	0.62
Pr^n-	144	2.05	60	15.8	11.0	—
Bu^n-	180	0.95	96	32.8	18.2	0.72
Bu^i-	180	0.95	96	21.1	11.8	—
Bu^s-	180	0.95	96	21.1	11.8	0.58
Bu^t-	180	0.95	96	6.3	3.5	0.42
Allyl-	240	0.95	48	9.8	4.1	—

a) EtOH 30 m*l*.
b) Dihydrate was used.
c) On the basis of butadiene fed.
d) Cited from Ref. 7).

isolated from the reaction mixture as brown crystals, and this was found to be able to catalyze the selective addition of *n*-PrOH to butadiene to give 3-*n*-propoxybut-1-ene. Therefore it is likely that I is an intermediate of the reaction, although other nascent π-allylic complex which might be convertible to I is not necessarily excluded.

The mononuclear rhodium complex (II)[3,4] which may be formed at lower temperature in the reaction mixture would not be a true intermediate, since the yield of 3-*n*-propoxybut-1-ene decreased drastically at lower temperature as shown in the Table 2.

Table 2. Temperature dependence of the addition reaction of *n*-PrOH to 1,3-butadiene[a]

Reaction Temp (°C)	Time (hr)	Yield of 3-*n*-propoxybut-1-ene (mmol)	Yield of 3-*n*-propoxybut-1-ene %[b]
70	40	1.9	0.5
50	40	24.3	6.1
20	42	7.8	2.0
10	42	1.1	0.3

a) $RhCl_3 \cdot 3H_2O$ 1 mmol, *n*-PrOH 800 mmol, and 1,3-Butadiene 400 mmol.
b) On the basis of butadiene fed.

It should be noted that the Pd complex catalyzes dimerization of butadiene in alcohols[5,6] producing predominantly 1-alkoxy derivatives of butadiene dimer in contrast to the present rhodium catalyst.

The yields of the addition products seem to have linear correlations with intensities of the OH stretching vibrations of the alcohols which are considered to be a measure of ionization degree of the OH bonds.[7] This indicates a predominant contribution of the ionic nature of the alcohols to the addition reaction, while the steric influence of the alkyl group should not be overlooked since the butanol family shows somewhat different correlation.

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[4] L. Porri, A. Lionetti, G. Allegra, and A. Immirzi, *Chem. Commun.*, **1965**, 336.

[5] S. Takahashi, H. Yamazaki, and N. Hagihara, This Bulletin, **41**, 254 (1968).

[6] E. J. Smutny, *J. Amer. Chem. Soc.*, **89**, 6793 (1967).

[7] G. M. Barrow, *J. Phys. Chem.*, **59**, 1129 (1955).