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REACTIONS OF ETHYLENE AND BENZENES CATALYZED BY RHODIUM CARBONYLS UNDER CARBON MONOXIDE. THE FORMATION OF STYRENES AND 3-PENTANONE

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The reaction of ethylene with benzene catalyzed by rhodium carbonyls under carbon monoxide gives styrene and 3-pentanone in good yields, together with small amounts of propiophenone, 1-phenyl-1-penten-3-one, and 1-phenyl-3-pentanone.

As a part of our investigation of the rhodium carbonyl-catalyzed activation of aromatic carbon-hydrogen bonds and its application to organic synthesis, we have recently reported that the reaction of diphenylacetylene and benzene in the presence of a catalytic amount of $Rh_4(CO)_{12}$ and under pressure of carbon monoxide ($>20Kg/cm^2$) gives triphenylethylene and 2,3-diphenylindenone.1) Since the aromatic substitution of olefins by palladium salts has been well known,2) we studied the interaction of ethylene with benzenes in our catalytic system. We now wish to report that the reaction also leads to the direct formation of styrenes, together with the formation of 3-pentanone.

In a typical experiment, ethylene ($30Kg/cm^2$) and carbon monoxide ($25Kg/cm^2$) were introduced into a 200ml stainless steel autoclave containing $Rh_4(CO)_{12}$ (0.025 mmol) and benzene (50ml). The reaction was carried out at 220°C for 7hr. The reaction mixture was analyzed by GLC, observing the formation of styrene (0.954g) and 3-pentanone (1.162g), together with propiophenone (0.114g), 1-phenyl-1-penten-3-one (0.030g), and 1-phenyl-3-pentanone (0.030g). The products were identified by their IR, NMR, and mass spectra. The yield of styrene based on a rhodium atom was 9170%. As the catalyst, $Rh_6(CO)_{16}$ could be used and its activity was almost the same as that of $Rh_4(CO)_{12}$. On the other hand, the activity of $Rh_2(CO)_4Cl_2$ was very low (a 630% yield of styrene). These results are shown in Table 1.

$$C_6H_6 \quad + \quad 3\ CH_2{=}CH_2 \quad + \quad CO \xrightarrow{Rh_4(CO)_{12}} C_6H_5CH{=}CH_2 \quad + \quad CH_3CH_2COCH_2CH_3$$

It has been known that the reaction of ethylene with carbon monoxide in proton donating solvents by rhodium carbonyl catalysts gives 3-pentanone.3) In spite of the absence of a proton donating solvent, the pentanone is formed in our case. Direct formation of styrene from ethylene and benzene liberates necessarily one hydrogen molecule, which can be used in the formation of the pentanone. As Table 1 shows, the molar amount of the pentanone formed is larger than that of the styrene in all cases. This is due to side reaction such as the polymerization of

Table 1. The Reaction of Ethylene with Benzene under Carbon Monoxide[a)]

Run	C_2H_4 Kg/cm^2	CO Kg/cm^2	Temp. °C	Product, g (mmol)[b)] Styrene	3-Pentanone
1	30	25	200	0.405 (3.89)	0.500 (5.81)
2	30	25	220	0.954 (9.17)	1.162 (13.51)
3	30	25	250	1.227 (11.80)	1.739 (20.22)
4	10	20	250	0.555 (5.34)	0.521 (6.06)
5	20	20	250	0.727 (6.99)	0.838 (9.74)
6	40	20	250	0.793 (7.63)	1.097 (12.76)

a) 50ml of benzene and 0.025mmol of $Rh_4(CO)_{12}$ were used.

b) The yields of the products were estimated by GLC (condition: 25% DNP on Shimalite; 150°C)

styrene, but the possibility of the participation of concomitant water in the gases or the solvent employed for the formation of the pentanone may not be excluded.

Propiophenone, 1-phenyl-1-penten-3-one, and 1-phenyl-3-pentanone are also formed in small amounts as a result of the cleavage of a carbon-hydrogen bond of benzene. In the present reaction the formation of ethylbenzene could not be observed, and only a trace amount of trans-stilbene, which is known to form considerably in the phenylation of ethylene with palladium salts,2) was detected.

Similar to the case of the addition of benzene to heterocumulenes4) or acetylenes,1) this reaction also required the presence of carbon monoxide, without which styrene was not formed entirely.

Monosubstituted styrenes are obtained by similar reactions with monosubstituted benzenes. The reaction of anisole with ethylene gave a mixture of three positional isomers of vinylanisole (ortho:meta:para=67:23:10) in a 10830% yield based on a rhodium atom. Similarly, vinylfluorobenzene (78:17:5) and vinyltoluene (14:57:29) were obtained from fluorobenzene and toluene in 8320 and 6280% yields, respectively. The distributions of the isomers show similar tendencies to results in previous works1,4) and are different from those in palladium-catalyzed arylation of olefins.2) On the other hand, the reaction with aniline gave no vinylaniline, but gave propionanilide (1300%) and 1-anilino-3-pentanone (350%).

References

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