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Catalytic Codimerization of Styrene with Lower Olefins by Rhodium and Ruthenium Catalysts

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We have investigated the codimerization reaction of styrene with lower olefins such as ethylene, propylene or 1-butene in the presence of rhodium(III) or ruthenium(III) compounds as a catalyst.

Results and Discussion

The results are summarized in Tables 1 and 2. We see that the reaction of styrene with ethylene gives 3-phenyl-1-butene (**1**), 2-phenyl-2-butene (**2**) and 2-phenyl-1-butene (**3**) in high yields.[1]

In order to determine the initial product of codimerization, the relative yields of three phenylbutenes **1**, **2** and **3** were examined as a function of the length of the reaction time. It was possible to monitor the yields as shown in Fig. 1. The rate of formation of **1** is initially high. That of **2** becomes greater after about 3 hr, indicating that the initially formed product from the reaction of styrene and ethylene by rhodium (III) chloride is **1** which is then isomerized to its isomers **2** and **3**.[2]

We see from Tables 1 and 2 that the codimerization reaction of styrene with lower olefins has the following characteristics: (1) Rhodium(III) and ruthenium(III) catalysts give *internally* phenyl-substituted codimers while palladium(II) catalyst gives *terminally* phenyl-substituted products.[3] (2) Although accurate comparison is not practical owing to the lack

TABLE 1. CODIMERIZATION OF STYRENE WITH ETHYLENE

Catalyst	Solvent	Codimer yield, %[a]		
		1	2	3
$RhCl_3 \cdot 3H_2O$	Methanol	932	584	84
$RhCl_3 \cdot 3H_2O$	None	482	47	trace
$RhCl_3 \cdot 3H_2O$	Acetic acid	37	121	trace
$RhCl_3 \cdot 3H_2O$	Furfural	37	—	—
$RhCl_3 \cdot 3H_2O$	Benzene+phenol (1 : 1)	21	—	—
$[Rh(C_2H_4)_2Cl]_2$	Methanol	—	21	48
$[Rh(C_2H_4)_2Cl]_2$	None	—	trace	—
$RhCl(PPh_3)_3$	Benzene	—	—	—
$RuCl_3 \cdot H_2O$	Methanol	3	3	1
$RuCl_3 \cdot H_2O$[b]	Acetic acid	14	36	14
$RuCl_3 \cdot H_2O$	Acetonitrile	trace	trace	trace
$[PdCl_2 \cdot styrene]_2$[c]	None	*trans*-1-phenyl-1-butene, *cis*-1-phenyl-1-butene, *trans*-1-phenyl-2-butene,		1278 57 170

a) Yields are based on the catalyst used. b) α-phenylethyl acetate was also formed in 293% yield. c) Reference. 3.

TABLE 2. CODIMERIZATION OF STYRENE WITH PROPYLENE AND 1-BUTENE

Olefin (5 atm)	Catalyst (1.9 mmol)	Solvent (30 ml)	Product and yield, %[a]
Propylene[b]	$RhCl_3 \cdot 3H_2O$	Methanol	CH_3-PhCH-CH=CH-CH_3, 20
Propylene	$RuCl_3 \cdot H_2O$	Methanol	—
Propylene	$[PdCl_2 \cdot styrene]_2$[c]	None	Ph-CH=CH-C_3H_7, 72
1-Butene	$RhCl_3 \cdot 3H_2O$	Methanol	—
1-Butene	$RuCl_3 \cdot H_2O$	Methanol	—
1-Butene	$[PdCl_2 \cdot styrene]_2$	None	Ph-CH=CH-C_4H_9, trace

a) Reactions were performed at 50°C for 6 hr and yields are based on the catalyst used. b) Acetophenone was also formed in 33% yield. c) Styrene dimers were also obtained in 56% yield.

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[1] Lindsey *et al.*[2] reported that the rhodium(III) chloride catalyzed codimerization reaction of ethylene with styrene under high pressure (1000 atm) gives only **2** in 40% conversion. The three isomers **1**, **2** and **3** we obtained presumably result from the difference in reaction pressure.

[2] T. Alderson, E. L. Jenner, and R. V. Lindsey, *J. Amer. Chem. Soc.*, **87**, 5638 (1965).

[3] K. Kawamoto, T. Imanaka, and S. Teranishi, This Bulletin, **43**, 2512 (1970) and the literature therein.

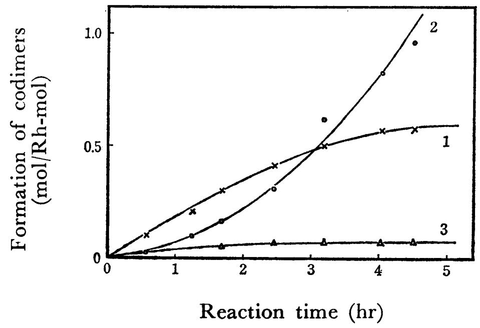


Fig. 1. Formation of 3-Phenyl-1-butene(×), 2-pheny-2-butene (○) and 2-phenyl-1-butene (△) during the reaction of styrene and ethylene with $RhCl_3$-MeOH.

of a solvent which dissolves all of these catalysts, the catalytic activity appears to decrease in the order Pd(II)>Rh(III)>Ru(III) (3) The reactivity of the gaseous olefins decreases in the order ethylene>propylene>1-butene. (4) **1** is the initial codimerization product in the case of the reaction of styrene with ethylene by rhodium(III) chloride.

In the rhodium(III) chloride catalyzed dimerization of olefins, the reaction proceeds through a rhodium hydride from a protonic solvent.[4] Thus, the present codimerization by rhodium(III) chloride seems to proceed also *via* a rhodium hydride as shown in Fig. 2. For the sake of clarity, the case with styrene, ethylene and methanol-d_1 is shown.

A rhodium hydride complex (**4**) would be formed first and then styrene coordinates with **4** giving a styrene-rhodium hydride π complex (**5**).[5] Complex **5** is transformed into a σ, π complex (**6**) through the addition of Rh-D to styrene, followed by the coordination of ethylene. In this insertion step, there are two modes of addition giving **A** or **B**, the former being favoured because of an electronic effect shown below in **C**.

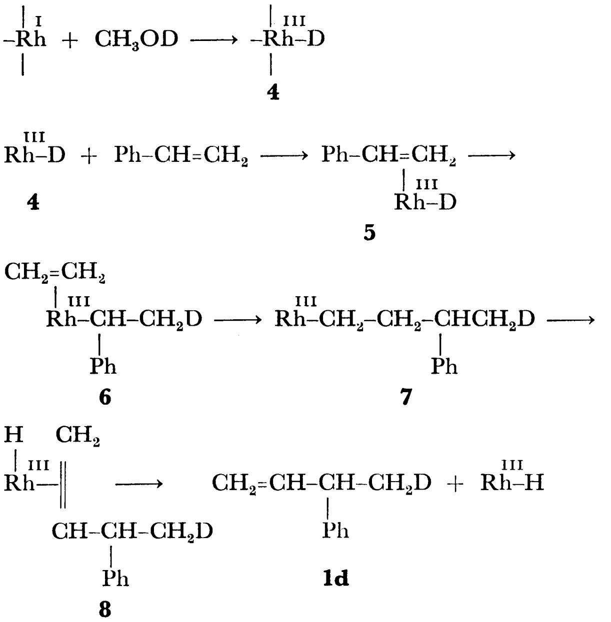
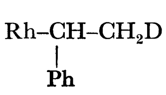
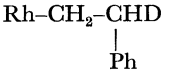


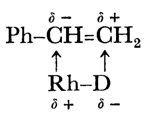
Fig. 2. Mechanism of Codimerization by Rhodium Compound.



$$\mathrm{Rh\text{-}\underset{\displaystyle Ph}{CH}\text{-}CH_2D}$$



$$\mathrm{Rh\text{-}CH_2\text{-}\underset{\displaystyle Ph}{CHD}}$$



$$\mathrm{Ph\text{-}\overset{\delta-}{C}H\text{=}\overset{\delta+}{C}H_2},\quad \uparrow\ \uparrow,\quad \mathrm{\underset{\delta+}{Rh}\text{-}\underset{\delta-}{D}}$$

A **B** **C**

Complex **6** undergoes rearrangement to a butylrhodium compound (**7**). Finally the elimination of β hydrogen gives **1d** and Rh-H *via* a complex **8**. The reformed rhodium hydride would serve as an active catalyst for codimerization.

Experimental[*1]

Di-μ-chlorotetrakis(ethylene)dirhodium(I) was prepared according to the method of Cramer.[6]

General Procedure for the Codimerization of Styrene with Lower Olefins by Rhodium Chloride. A glass autoclave was charged with rhodium(III) chloride (1.9 mmol), styrene (27 g, 0.26 mol) and the solvent (30 ml). The autoclave was flushed with ethylene and the pressure was elevated to 5 atm., the mixture being stirred at 50°C for 6 hr. The resulting mixture was distilled under reduced pressure to remove styrene, and then diluted with petroleum ether. The mixture was filtered to remove rhodium(III) chloride, and the filtrate was evaporated. The residue was analyzed and purified by glpc. The products were identified by IR and NMR. 3-phenyl-1-butene (**1**): IR (direct): 990, 910 ($-HC=CH_2$), 755 and 695 cm^{-1} (-Ph). NMR (CCl_4): 8.66 (d, 3H), 6.58 (m, 1H), 5.04 (m, 2H), 3.77—4.32 (m, 1H) and 2.87 τ (m, 5H). 2-Phenyl-2-butene (**2**): IR (direct): 935 (C=CH-), 752 and 697 cm^{-1} (-Ph). NMR (CCl_4): 8.24 (d, 3H), 8.02 (s, 3H), 4.29 (q, 1H) and 2.02 τ (s, 5H). 2-Phenyl-1-butene (**3**): IR (direct): 893 ($CH_2=C<$), 780 and 700 cm^{-1} (-Ph). NMR (CCl_4): 8.95 (t, 3H), 7.53 (q, 2H), 5.04 (d, 1H), 4.83 (d, 1H) and 2.76 τ (m, 5H).

Codimerization reactions of styrene with propylene and 1-butene were similarly carried out with use of the same autoclave and reaction conditions as above. *trans*-4-Phenyl-2-pentene; IR (direct): 966 (*trans* HC=CH), 762 and 700 cm^{-1} (-Ph). NMR (CCl_4): 8.72 (d, 3H), 8.36 (d, 3H), 6.68 (m, 1H), 4.55 (m, 2H) and 2.92 τ (m, 5H). *trans*-1-Phenyl-1-pentene: IR (direct): 960 (*trans* HC=CH), 740 and 695 cm^{-1} (-Ph). NMR (CCl_4): 9.03 (t, 3H), 8.51 (m, 2H), 7.82 (q, 2H), 3.78 (m, 2H) and 2.83 τ (m, 5H).

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[4] R. Cramer, *ibid.*, **87**, 4717 (1965).

[5] Since the rhodium-ethylene complex has low catalytic activity (Table 1), styrene could be considered to coordinate first with rhodium.

[*1] IR spectra were taken on a JASCO Model IR-E spectrometer. NMR spectra were obtained using JNM-4H-100 or JNM-C60HL spectrometers. Rhodium(III) and ruthenium(III) chlorides were of commercial grade.

[6] R. Cramer, *J. Inorg. Chem.*, **1**, 722 (1962).