

Selective Isomerization of 2-Allylphenol to (Z)-2-Propenylphenol Catalyzed by Ru(cod)(cot)/PEt₃

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Ru(cod)(cot) (cod = cycloocta-1,5-diene, cot = cycloocta-1,3,5-triene) catalyzes selective isomerization of 2-allylphenol to (Z)-2-propenylphenol in the presence of triethylphosphine with high yield (94%) and (Z)-selectivity (97%).

Although catalytic isomerization of olefins by transition metal complexes has been well documented and applied in some commercial processes,¹ the stereoselectivity and activity control is still a crucial subject in the processes. 2-Allylphenols and their isomerized derivatives are potentially important precursors for biologically active heterocycles, and considerable attention has been paid on the isomerization of 2-allylphenols to 2-methylbenzo[*b*]furans, 2,3-dihydro-2-methylbenzo[*b*]furans, (*E*)-2-propenylphenols, etc.²⁻⁶ In the course of our study on successive O-H and *sp*³-C-H bond activation of 2-allylphenol by Ru complex,⁷ we found highly (*Z*)-selective isomerization of 2-allylphenol to 2-propenylphenol catalyzed by Ru(cod)(cot) (cod = cycloocta-1,5-diene, cot = cycloocta-1,3,5-triene) in the presence of PEt₃ under ambient conditions.

Table 1 summarizes the results of catalytic isomerization of 2-allylphenol promoted by Ru(cod)(cot) under various reaction conditions. 2-Allylphenol was isomerized to thermodynamically unfavorable (Z)-2-propenylphenol in 94% yield with 97% (*Z*)-

selectivity in the presence of Ru(cod)(cot) (1 mol%) with 10 equiv. of PEt₃ at 20 °C.⁸ The present result is in sharp contrast to the known isomerization catalysts such as PdCl₂(PhCN)₂,⁹ RuH₂(PPh₃)₄¹⁰ and RuH₂(CO)(PPh₃)₃,¹¹ which gave 80, 92 and 93% (*E*)-selectivity, respectively. Although Ru(cod)(cot) itself can also catalyze the isomerization with low (*Z*)-selectivity, addition of 3 equiv. of PEt₃ significantly enhanced the rate and the (*Z*)-selectivity. Under these conditions, (Z)-2-propenylphenol was slowly isomerized to the (*E*)-isomer. However, this unfavorable isomerization process was completely eliminated by adding 10 equiv. of PEt₃, although the reaction became slightly slower.

This isomerization of C=C double bond showed large solvent effect. Nonpolar solvents such as hexane and benzene gave reasonably high yield and (*Z*)-selectivity, while low activity and/or selectivity were observed in THF, ether and DMSO. It is interesting to note that protic solvent such as methanol also gave a good result. Selection of tertiary phosphine ligand is also an important factor for the reactivity and selectivity. When PEt₂Ph as supporting ligand was used, the catalytic activity increased with high (*Z*)-selectivity. However, use of PMe₃ and PPr₃ as supporting ligand significantly diminished the activity of the catalyst without loss of (*Z*)-selectivity. Employment of PPh₃ decreased both activity and selectivity of the isomerization reaction.

In order to clarify the reaction mechanism, isomerization of various 2-allylphenol derivatives were carried out. 1-Allyl-2-methoxybenzene was not isomerized at all, indicating importance of the hydroxyl group in the substrate. Isomerization of allylbenzene was sluggish to give only a small amount of mixture of (*E*)- and (*Z*)-2-propenylbenzene (6% yield, 83% (*Z*)-selectivity). 2-Cinnamylphenol and 2-prenylphenol were not isomerized by this catalyst, suggesting the involvement of pre-coordination of the allyl group to Ru, that is prevented by the steric congestion on the allyl moiety.

A possible reaction mechanism has been proposed (Figure 1). At first a (aryloxo)(hydrido)ruthenium(II) complex (**A**) is generated by the O-H oxidative addition of 2-allylphenol to ruthenium(0) species. This step is reasonable, since protonation of Ru(cod)(cot) giving (hydrido)ruthenium species was reported by Tkatchenko¹² and we have recently reported the formation of hydrido(2-methylphenoxo)tris(trimethylphosphine)ruthenium(II) by the reaction of Ru(cod)(cot) with 2-methylphenol in the presence of trimethylphosphine.⁷ Therefore, the oxidative addition of the O-H bond of 2-allylphenol to ruthenium(0) species is considered to take place to give **A**. Then, the allyl moiety coordinates to the ruthenium center, that is consistent with the large steric effect of the allyl moiety (**B**). Intramolecular *cis*-Markovnikov addition of the ruthenium hydride to the allyl group takes place to give oxaruthenacycle (**C**), from which a facile β-hydrogen elimination (**C**→**D**) followed by reductive elimination takes place to give (Z)-2-propenylphenol and **A**. The crucial step

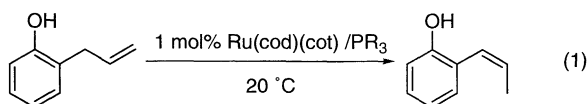


Table 1. Isomerization of 2-allylphenol to 2-propenylphenol catalyzed by Ru(cod)(cot)/PR₃

L	[L]/[Ru]	Solvent	Time /h	Yield /%	Z-Selectivity /%
None	0	Hexane	31	92	53
PEt ₃	3	Hexane	10	93	89
PEt ₃	10	Hexane	45	94	97
PEt ₃	3	Benzene	30	94	96
PEt ₃	3	THF	15	9	96
PEt ₃	3	Ether	15	10	89
PEt ₃	3	DMSO	43	13	23
PEt ₃	3	MeOH	48	95	94
PMe ₃	3	Hexane	15	2	100
PPr ₃	3	Hexane	15	19	95
PPh ₃	3	Hexane	27	41	49
PEt ₂ Ph	3	Hexane	6	92	98

for these high (*Z*)-selectivity is considered to be the diastereotopic elimination of one of the benzylic hydrogens in **C**. Thus, molecular mechanics (MM2) calculations of two possible intermediates for **C** leading (*Z*)- and (*E*)-isomers were carried out by CAChe program using a model compound $\text{Ru}(\text{OC}_6\text{H}_4\text{CH}_2\text{-CHMe})(\text{PMe}_3)_3$,¹³ assuming that the transition state structure of β -hydrogen elimination is similar to the conformation of intermediate **C**. The structure (**C_Z**) leading to (*Z*)-isomer had 5.7 kcal/mol lower total energy than the other (**C_E**). This may be understood by the effective steric repulsion between the terminal Me group and the apical PMe_3 ligand in the oxametallacyclic intermediate (**C_E**). Further the mechanistic investigations as well

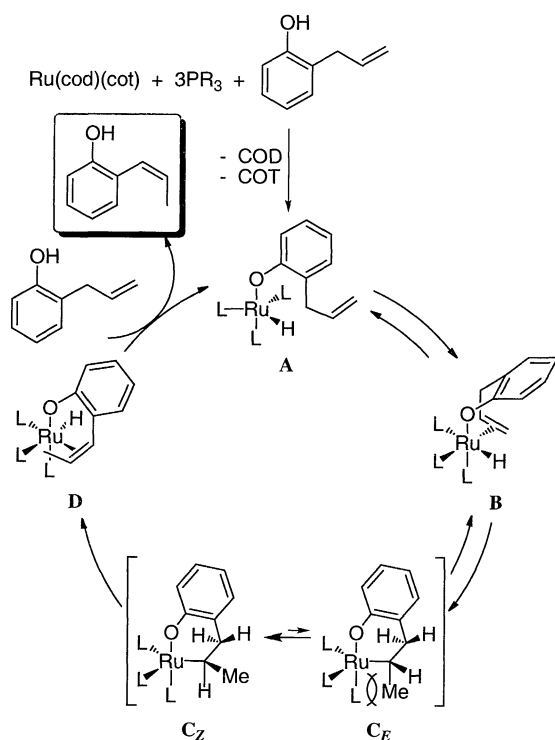


Figure 1. A proposed mechanism for the Ru-catalyzed isomerization of 2-allylphenol.

as scope and limitations of selective isomerization are now underway.

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- 13 A *tpb* geometry where the oxygen and the methine carbon occupy sites at apical and equatorial positions, respectively, and the three trimethylphosphine ligands occupy two equatorial and one apical sites, is assumed. By changing O-Ru-C-C(Ph) dihedral angles in **C**, two distinct local minima were found. Estimated total energy of the possible two structures leading to (*Z*)- and (*E*)-isomers were 8.0 and 13.7 kcal/mol, respectively.