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Unusual Regioselectivity in the Carbonylation of Substituted Benzenes via the C-H Activation Catalyzed by $RhCl(CO)(PMe_3)_2$

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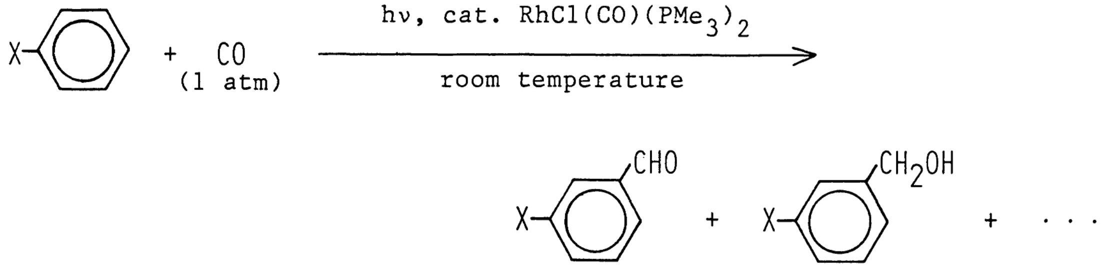
Meta-substituted benzaldehydes were obtained as the major product in the carbonylation of mono-substituted benzenes via the C-H activation catalyzed by $RhCl(CO)(PMe_3)_2$ under irradiation.

Current organic chemical industry has been largely built up on the foundation of indirect conversion technology of natural hydrocarbon resources; less reactive hydrocarbons like paraffins are first activated into more reactive chemical feedstocks like olefins which are subsequently transformed into useful end products. In this sense, direct and selective functionalizations of less reactive and plentiful hydrocarbons under mild conditions are intriguing challenges facing organic chemists. We reported the efficiently catalytic carbonylation of C-H bonds assisted by transition metal complexes to give benzaldehyde directly from benzene.1) In addition, we have recently achieved the highly regioselective C-H activation of terminal methyl groups of alkanes to give aldehydes2) and olefins,3) catalyzed by $RhCl(CO)(PMe_3)_2$ under irradiation in the presence of carbon monoxide. We now wish to report the unusual regioselectivity in the carbonylation of substituted benzenes via the rhodium catalyzed C-H activation, in which the meta-substituted benzaldehydes and benzyl alcohols were mainly formed. The meta-selectivity is quite unique in view of the ortho-, para-selectivity obtained in the conventional carbonylation of arenes with carbon monoxide via electrophilic reactions such as the Koch reaction4) and the Fujiwara reaction.5)



(1)

A typical reaction procedure was as follows; 0.7 mM solution of the catalyst ($RhCl(CO)(PMe_3)_2$ 6.7 mg (0.021 mmol) in toluene (30 cm^3)) placed in a Pyrex flask was irradiated by a 100 W high pressure mercury lamp (UVL-100H, Riko Corp.) at room temperature under an atmospheric pressure of carbon monoxide (balloon). The reaction did not proceed when either of the complex or the light was absent. The products were characterized by the GC retention time and GC-MS.

The results are summarized in Table 1. The reactivities of the substrates for the carbonylation were in the following order when evaluated from the sum of the yields of aldehydes and alcohols; toluene ≑ benzene > anisole > chlorobenzene ≑ benzonitrile. Electron-withdrawing groups of substituted aryl halides normally accelerate the oxidative addition of C-halogen bonds to transition metal complexes.6) The reactivity of substituted benzenes in the present reaction, however, was not parallel with the electron-withdrawing ability of the substituents. The low yields obtained in the reactions of chlorobenzene and benzonitrile are presumably due to their coordination to the rhodium (vide infra).7)

The regioselectivity in the present reaction was quite unusual when compared with the electrophilic substitution reactions of arenes. Thus, meta-substituted products were obtained as the major regioisomer regardless of the electronic nature of the substituents, except for the case of chlorobenzene. The meta-selectivity was also inconsistent with the ortho-, para-selectivity observed in the radical reactions of substituted benzenes.8) One possible explanation for this phenomena is as follows; ortho-positions were presumably sterically unfavorable to be attacked, while the small difference of the reactivity beween meta- and para-positions gave the statistical distribution of the two isomers to result in the preferential formation of meta-substituted products. In the reaction of toluene, meta- and para-tolualdehyde were formed in a 2 : 1 ratio with very small amounts of the ortho-isomer and phenylacetaldehyde. The result agrees with the regioselectivity observed in the stoichiometric reaction of $(C_5Me_5)RhH_2(PMe_3)$ with toluene under irradiation,9) where the higher reactivity of the C-H bonds on the aromatic ring than the benzylic position was ascribed to the η^2-coordination of arenes. The higher ortho-selectivity of chlorobenzene than the others may be due to the existance of the interaction between the chlorine and the rhodium resulting in the so called ortho-metallation. A substantial formation of the ortho isomers in the anisole reaction also supports the participation of the ortho-metallation through the oxygen-rhodium interaction. The ortho-metallation of benzonitrile is considered to be difficult to occur, since it coordinates to the rhodium(I) center in an end-on manner.10) As a matter of fact, the formation of the ortho-isomer was very little.

In the reactions of benzene, toluene, and anisole, the lower rhodium concentration (0.7 mM) afforded much higher turnovers than the higher concentration (7 mM). This is presumably because, when the complex was charged abundantly, the light intensity was not enough to convert all $RhCl(CO)(PMe_3)_2$ effectively into the active catalyst, $RhCl(PMe_3)_2$, which was in the equilibrium with $RhCl(CO)(PMe_3)_2$ under irradiation.1,11) In the reactions of chlorobenzene and benzonitrile, the active catalyst was likely to be deactivated by the coordination of the chlorine and the nitrogen to the vacant site. In these systems, the turnover numbers were not improved so much even if the rhodium

Table 1. Carbonylation of substituted benzenes by $RhCl(CO)(PMe_3)_2$

X in XC_6H_5	Rh/mM	Yield / %/Rh			
		XC_6H_4CHO (o:m:p)	$XC_6H_4CH_2OH$ (o:m:p)	total[a] (o:m:p)	other products
H-	7	1544	147	1691	$PhCO_2H$ 5, Ph-Ph 35, PhCOPh 54
H-	0.7	6517	738	7255	$PhCO_2H$ 108, Ph-Ph 215, PhCOPh 688
CH_3-	7	1525 (2:63:35)	200 (8:72:21)	1725 (2:64:34)	$PhCH_2CHO$ 13, $PhCH_2CH_2Ph$ 30, $(CH_3C_6H_4)_2CO$[b] 68, $CH_3C_6H_4CO_2H$ 6
CH_3-	0.7	3909 (1:53:46)	3354 (3:71:26)	7263 (1:62:37)	$PhCH_2CH_2Ph$ 2165, $CH_3C_6H_4CO_2H$[b] 59 $(CH_3C_6H_4)_2CO$[b] 650
CH_3O-	7	566 (12:54:34)	93 (26:69:5)	659 (14:56:30)	
CH_3O-	0.7	3930 (7:52:41)	993 (37:59:4)	4923 (13:54:33)	
Cl-	7	115 (41:36:23)	37 (70:20:10)	151 (48:32:20)	C_6H_5-C_6H_4Cl[b] 14
Cl-	0.7	33 (-:-:-)	4 (-:-:-)	37 (-:-:-)	C_6H_5-C_6H_4Cl[b] 666
NC-	7	82 (1:85:14)	0	82 (1:85:14)	
NC-	0.7	65 (4:82:14)	62 (-:77:23)	127 (-:-:-)	

CO 1 atm, room temperature, 16.5 h.

a) $XC_6H_4CHO + XC_6H_4CH_2OH$. b) Regioisomeric mixtures.

concentration was decreased. On the other hand, the ratios of the by-products (e.g. alcohols, biaryls, and ketones) against the aldehydes were changed by the catalyst concentration, although the regioselectivities of the carbonylation were not affected so much. This may be because the light was absorbed by the aldehydes rather than the complex when the concentration of the metal was low. The high alcohol/aldehyde ratio was observed in the reaction of toluene (Rh 0.7 mM) compared with that of benzene, possibly because of the easy hydrogen abstraction from the toluene methyl group by the photo-excited aldehyde affording stable benzyl radical and the alcohol. In fact, a large amount of dibenzyl was detected in this system.

In summary, the present method offers a novel and unusual meta-selective carbonylation of arene C-H bonds under mild conditions, which is difficult to be attained by conventional methods. Further extension of the substrates and the catalysts is now under investigation.

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