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C=C Double Bond Insertion in Catalytic C-H Activation. Dehydrogenative Cross Coupling of Arenes with Olefins

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The reaction of benzene with methyl acrylate and ethylene catalyzed by $RhCl(CO)(PMe_3)_2$ under irradiation gave methyl cinnamate and styrene, respectively. The reaction of toluene afforded meta-substituted isomers as major products.

Alkyl or arylhydrido complexes, which are formed through oxidative addition of hydrocarbons to coordinatively unsaturated transition metal complexes, are useful intermediates for versatile transformations of hydrocarbons. We have recently reported various functionalizations of hydrocarbons catalyzed by $RhCl(CO)(PMe_3)_2$ under irradiation which are presumed to proceed through alkyl or arylhydridorhodium complexes; carbonylation,[1)] isocyanide insertion,[2)] dehydrogenative homo-coupling,[3)] silylation,[4)] and dehydrogenation to give olefins.[5)] As a useful variation along this line, the formation of substituted olefins was anticipated to be realized through the olefin insertion of the same intermediate as above followed by β-hydride elimination. Indeed, we could obtain methyl cinnamate by the reaction of benzene with methyl acrylate (Eq. 1).

$$PhH \ + \ CH_2{=}CHCO_2Me \ \xrightarrow[\text{cat. Rh}\\ \text{room temp}]{h\nu} \ PhCH{=}CHCO_2Me \ \ (+ \ PhCH_2CH_2CO_2Me \ ) \qquad (1)$$

Similar reactions have been reported by Yamazaki et al. using $Rh_4(CO)_{12}$ as the catalyst.[7)] However, they requires severe conditions (220 °C, 20 atm of carbon monoxide to stabilize the catalyst) as compared with our new procedure which will be reported in this communication.

A 0.7 mM solution of $RhCl(CO)(PMe_3)_2$ in the mixture of benzene and methyl acrylate (v/v = 29/1) was irradiated by a high pressure mercury lamp through a Pyrex flask at room temperature. The results are summarized in Table 1. Main product was methyl cinnamate accompanied by methyl 3-phenylpropionate formed as a minor one. The reaction solution was homogeneous even after 20 h.[7)] As was the case of the carbonylation, trimethylphosphine was the best ligand for high catalytic activity. Unlike the carbonylation, however, the catalytic activity was not reduced by cutting off the short wavelength below 325 nm. Trans/cis ratio of methyl cinnamate decreased as the irradiation wavelength was shortened. A tentative mechanism is illustrated in Scheme 1 which involves i) oxidative addition of benzene to the coordinatively unsaturated rhodium species resulting in the phenylhydridorhodium complex, ii) acrylate insertion into the phenyl-rhodium bond, iii) β-hydride elimination to give methyl cinnamate and the dihydrido complex, and iv) hydrogen transfer from the latter to methyl acrylate

Table 1. The reaction of benzene with methyl acrylate catalyzed by $RhCl(CO)(PMe_3)_2$[a)]

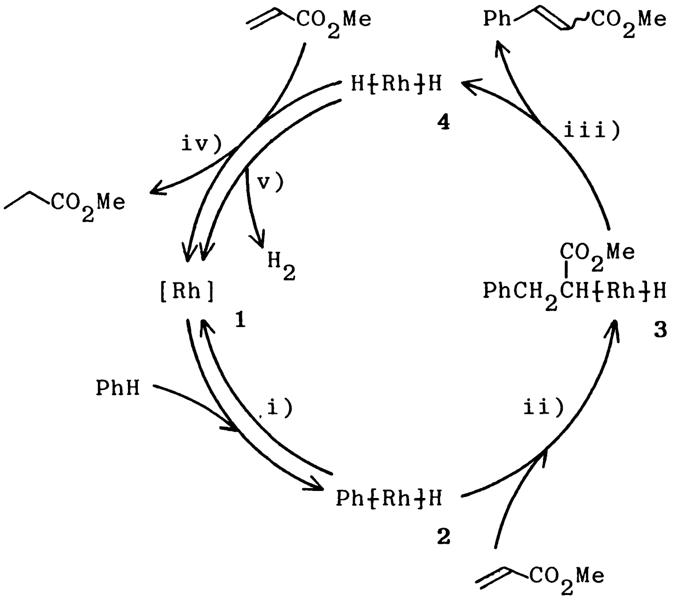
Run	Filter (wavelength)	Time / h	Yield/(%/Rh)		
			$PhCH{=}CH_2CO_2Me$ (trans/cis)	$PhCH_2CH_2CO_2Me$	Ph-Ph
1	none	4.5	636 (1.8)	346	20
		12.5	1817 (1.9)	814	52
		19.5	2412 (1.5)	1008	86
2[b)]	none	19.5	434 (1.1)	22	86
3	none	6	1460 (7.1)	445	167
4	UV-D35 (295-420 nm)[c)]	6	1361 (16.1)	442	24
5	UV-35 (> 325 nm)[c)]	6	1586 (15.6)	525	46
6	L-39 (> 375 nm)[c)]	6	633 (62.5)	217	12

a) Runs 1 and 2: irradiated by UVL-100HA (Riko), 30 cm^3 scale. Runs 3 to 6: irradiated by USH-500D (Ushio), 3 cm^3 scale.

b) $RhCl(CO)(PBu_3)_2$ was used as catalyst.

c) Ranges where transmittance is over 10%.

or v) dihydrogen elimination regenerating the coordinatively unsaturated complex. As for the step iv), methyl propionate of 20-50% to cinnamate was detected after the reaction. The formation of methyl 3-phenylpropionate is explainable by the reductive elimination from **3** or methyl acrylate insertion to the rhodium-hydrogen bond of **2** followed by reductive elimination. The hydrogenation of cinnamate once formed is also feasible.



$[Rh] = RhCl(PMe_3)_2$

Scheme 1.

The regioselectivity in the reaction of toluene was very similar to those in the carbonylation[1)] and the silylation[4)] by the same system, indicating the same intermediate involved (Eq. 2). It is interesting to note that this regioselectivity is also similar to that of Yamazaki's reaction,[6)] but entirely different from that in Fujiwara's alkenylation[8)] which proceeds through elecrophilic aromatic substitution by Pd(II).

$$CH_3C_6H_5 + CH_2{=}CHCO_2Me \xrightarrow[\text{cat. Rh, room temp}]{h\nu,\ 8\ h}$$

$$\underset{\substack{973\%/Rh\ (trans/cis = 0.85) \\ (o : m : p = \mathit{ca.}0 : 64 : 34)}}{CH_3C_6H_4\text{-}CH{=}CHCO_2Me} + \underset{\substack{525\%/Rh \\ (o : m : p = \mathit{ca.}0 : 68 : 32)}}{CH_3C_6H_4\text{-}CH_2CH_2CO_2Me} \qquad (2)$$

The present reaction was applicable to olefins other than acrylate. The reaction of benzene with methyl methacrylate under the same conditions as Run 1 in Table 1 gave methyl 2-methyl-3-phenylpropenoate (trans/cis = 0.91) and methyl

2-methyl-3-phenylpropionate in 1091 and 252%/Rh, respectively after 12 h. Ethylene could also be used in place of methyl acrylate to yield styrene (Eq. 3), although the yield was poor under an atmospheric pressure.

$$\underset{}{\mathrm{PhH}} + \underset{(1\ \mathrm{atm})}{\mathrm{CH_2{=}CH_2}} \xrightarrow[\text{cat. Rh, room temp}]{h\nu,\ 36\ \mathrm{h}} \underset{299\%/\mathrm{Rh}}{\mathrm{PhCH{=}CH_2}} + \underset{168\%/\mathrm{Rh}}{\mathrm{PhCH_2CH_3}} + \underset{349\%/\mathrm{Rh}}{\mathrm{Ph{-}Ph}} \qquad (3)$$

On the other hand, the new procedure was not applicable well to alkanes, because the polymerization of methyl acrylate and the decomposition of the catalyst were rapid. In the reaction of hexane with methyl acrylate, the yield of the coupling product (methyl nonanoate) was only 3%/Rh after 3 h. The easy occurence of β-hydride elimination of the hexylhydridorhodium intermediate could be another reason for the poor yield.5) However, hexenes were detected only in 10%/Rh in this reaction.

In summary, the present paper has revealed arylation of olefins, another versatile class of C-H activation reactions photocatalyzed by $\mathrm{RhCl(CO)(PMe_3)_2}$. Further extensions of the reaction to various substrates are now under investigation.

References

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