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ALLYATION OF CARBONUCLEOPHILES WITH ALLYLIC CARBONATES UNDER NEUTRAL CONDITIONS CATALYZED BY RHODIUM COMPLEXES

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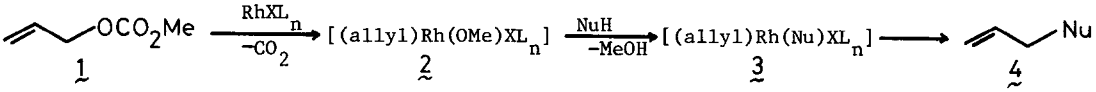
Summary: Rhodium-phosphine complexes catalyze the allylation of carbonucleophiles with allylic carbonates under neutral conditions. In addition, we found unusual regioselectivity in the rhodium catalyzed allylation.

Palladium catalyzed allylation of carbonucleophiles is a useful method for carbon-carbon bond formation.[1)] We have reported that the allylation can be carried out under neutral conditions by using allylic carbonates.[2)] In our continuing effort to study the scope of the reaction of allylic carbonates, we examined the catalytic activity of various transition metal complexes, and we found that certain rhodium-phosphine complexes catalyze the allylation of carbonucleophiles under neutral conditions. So far rhodium catalyzed conversion of allyl phenyl carbonate to allyl phenyl ether has been reported recently,[3)] but there has been no report on the rhodium catalyzed allylation reaction.[4)] We now wish to report the first example of the efficient rhodium catalyzed allylation of carbonucleophiles.



X = H, OAc, Cl.
L = P^nBu_3, PPh_3

At first, we examined the catalytic activity of various rhodium complexes and ligands for the allylation of β-keto ester **5** with **1**. Well-known $RhCl(PPh_3)_3$ itself showed almost no activity (20°C, 3 h, 4%).[4)] Interestingly, the complex showed high activity at 65°C by the addition of P^nBu_3 (1 h, 95%). $P(OEt)_3$ is also an acceptable ligand (65°C, 3 h, 90%), but it is inferior to P^nBu_3. PPh_3 (65°C, 1 h, 15%) and dppe (65°C, 3 h, 12%) are ineffective. Rhodium hydride complex, $RhH(PPh_3)_4$ gave better results.[3)] $RhH(PPh_3)_4$ itself showed considerable catalytic activity, and the reaction proceeded slowly at 20°C (2 h, 34%; 5 h, 60%; 10 h, 75%; 22 h, 96%; 25 h, 97%). The catalytic activity of $RhH(PPh_3)_4$ complex was enhanced markedly by the addition of phosphine ligands, and P^nBu_3 seems to be the best choice (20°C, 1 h, 93%). Commercially available $Rh_2(OAc)_4$ combined with PPh_3 or P^nBu_3 showed no activity at 20°C. But very high catalytic activity was observed at 65°C particularly by the addition of P^nBu_3 (3 h, 98%). In any cases, marked ligand effect was observed and P^nBu_3 seems to be the best ligand for the allylation. Contrary to Rh(I) or Rh(II) complexes, Rh(III) species such as $RhCl_3$ were completely inactive.

As for the solvent, THF, dioxane, benzene, toluene, ^{t}BuOH, acetone, MeCN, and DMSO are all acceptable. Among these solvents, no remarkable difference was observed and hence THF or dioxane was used throughout this study. Results of the allylation of various carbonucleophiles using $RhH(PPh_3)_4$-P^nBu_3 catalyst are shown in Table 1. In addition to β-keto esters, allylation of malonate, cyanoacetate, β-diketone and silyl enol ether[5] proceeded smoothly.

Similar to the palladium catalyzed allylation with allylic carbonates,[2] the rhodium catalyzed reaction can be explained by the following mechanism. The first step is the oxidative addition of allyl carbonate **1** to rhodium complex, followed by decarboxylation to form allylrhodium alkoxide complex **2**. The abstraction of an active proton from nucleophile by the alkoxide complex **2** takes place to give **3**. Finally, reductive elimination gives **4** and regenerates the rhodium catalyst. However the high regioselectivity observed in rhodium catalyzed reactions suggests some defferences in mechanisms.

As shown in Table 1, very high regioselectivity was observed with **10** and **13**. Only single isomers formed by a S_N type reaction were obtained by the reaction of **10** and **13** with acetylacetone (runs 7-9). Other isomers were not detected by GLC and NMR analyses. The regioselectivity was not complete in the reaction of **10** and **6** with β-keto esters (runs 4-6). But in these cases too, regioisomers resulted from the net S_N type reaction (**9** in run 4, **8** in run 5, and **11** in run 6) are predominant over the isomers formed by net S_N' type reaction. These results can not be explained by the formation of π-allylrhodium complexes as intermediates. σ-Allylrhodium complexes may be formed as intermediates. If the reaction proceeds via π-allylrhdium complex, the same regioselectivity should be observed from **6** and **10**. On the contrary, palladium catalyzed allylation which is widely accepted to take place via π-allylpalladium intermediates[1,6] usually gives **9** as a major product when **7** was allylated with **6** or **10**. In fact, palladium catalyzed reaction of **6** with **7** gave **8** and **9** in a ratio of 29:71, and the reaction of **10** with **7** gave **8** and **9** in a ratio of 27:73 respectively.

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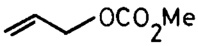
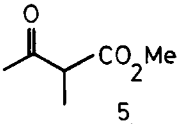
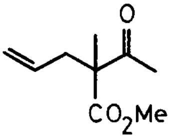
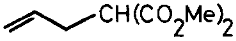
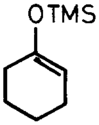
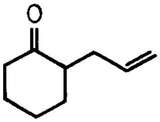
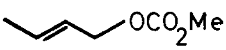
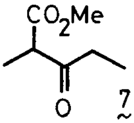
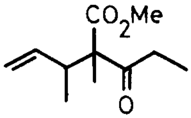
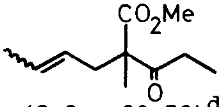
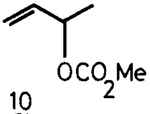
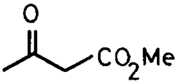
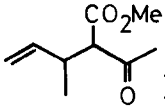
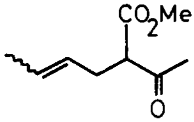
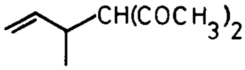
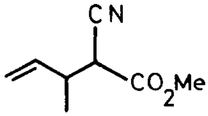
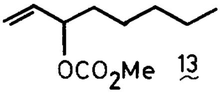
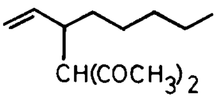
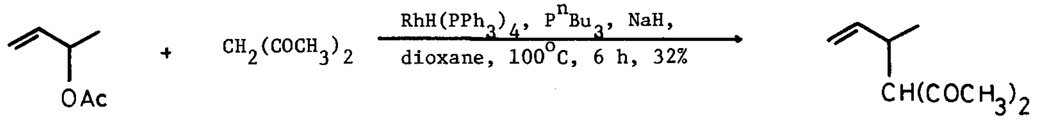
a) Unless otherwise stated, the reactions were carried out using allylic carbonate (2 mmol), carbonucleophile (1 mmol), $RhH(PPh_3)_4$ (0.05 mmol), and P^nBu_3 (0.1 mmol) in THF (5 mL) at 20°C or in dioxane (5 mL) at 100°C under argon. b) Isolated yield. c) Diallylated product was also obtained (19%). d) Ratios of regioisomers were calculated by GLC analysis. e) To avoid diallylation, the reaction was carried out using 1 mmol of carbonate and 2 mmol of nucleophile. f) Regioisomers were not detected by GLC and NMR analyses.

Table 1 ALLYLATION CATALYZED BY $RhH(PPh_3)_4$-P^nBu_3.[a)]

RUN	ALLYLIC CARBONATE	NUCLEOPHILE	TEMP. (°C)	TIME (h)	PRODUCT	YIELD (%)[b)]
1	 1	 5	20	1		93
2	1	$CH_2(CO_2Me)_2$	20	1		67[c)]
3	1		100	2		56
4	 6	 7	100	2	 8  9 (8:9 = 28:72)[d)]	97
5	 10	7	100	2	8, 9 (8:9 = 86:14)[d)]	81
6[e)]	10		100	2	 11  12 (11:12 = 90:10)[d)]	74
7[e)]	10	$CH_2(COCH_3)_2$	100	2		86[f)]
8[e)]	10	$CH_2(CN)(CO_2Me)$	100	2		69[f)]
9[e)]	 13	$CH_2(COCH_3)_2$	100	4		71[f)]

Allylic acetates can be used for the allylation by the addition of a stoichiometric amount of NaH. But acetates are less reactive than carbonates,[2] and poor results were obtained under similar conditions as shown below (compare with run 7).



Successful rhodium catalyzed allylation, particularly with interesting regioselectivity, reported in this communication may offer a new aspect in π-allyl or σ-allyl chemistry of transition metal complexes. Further studies on its application are in progress.

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References and notes

1) For reviews on the palladium catalyzed allylation,
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b) B. M. Trost, **Tetrahedron, 33,** 2615 (1977).
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3) Y. Hayashi, S. Komiya, T. Yamamoto, and A. Yamamoto, **Chem. Lett., 1984,** 977.
4) It has been reported that, compared with palladium complexes, $RhCl(PPh_3)_3$ is a poor catalyst for the allylation of carbonucleophiles, see;
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5) J. Tsuji, I. Minami, and I. Shimizu, **Chem. Lett., 1983,** 1325.
6) Recently, studies on regioselectivity in the nucleophilic substitution of π-allylpalladium intermediates have been reported, see;
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