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SYNTHESIS OF γ,δ-UNSATURATED KETONES BY THE INTRAMOLECULAR DECARBOXYLATIVE ALLYLATION OF ALLYL β-KETO CARBOXYLATES AND ALKENYL ALLYL CARBONATES CATALYZED BY MOLYBDENUM, NICKEL, AND RHODIUM COMPLEXES

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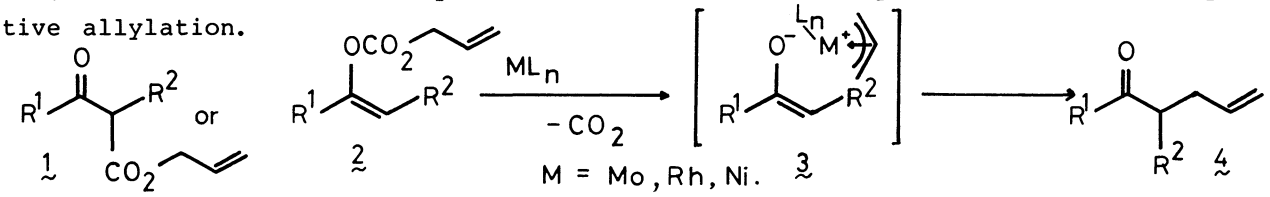
Allyl β-keto carboxylates and alkenyl allyl carbonates were converted to γ,δ-unsaturated ketones by the intramolecular decarboxylative allylation catalyzed by molybdenum, nickel, and rhodium complexes.

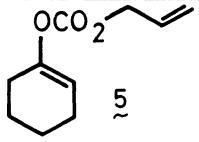
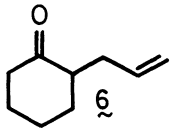
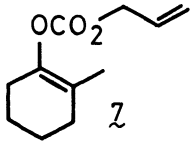
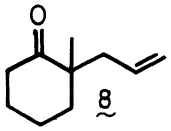
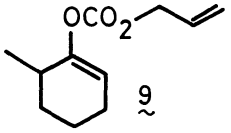
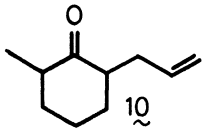
Thermal rearrangement of allyl β-keto carboxylates **1** to γ,δ-unsaturated ketones is known as the Carroll rearrangement and synthetically important reaction, which proceeds by heating to 170-200 °C.[1] Also the rearrangement is promoted by bases at lower temperatures.[2] We have previously reported that this decarboxylative allylation can be carried out under mild conditions by using palladium-phosphine complexes as a catalyst.[3,4] Furthermore, we have reported that alkenyl allyl carbonates **2** undergo the decarboxylative allylation even at 0°C by using the palladium-phosphine catalyst.[5] Now we found that certain molybdenum, nickel and rhodium complexes are also active catalysts for the decarboxylative allylation.



At first, we examined the reaction of alkenyl allyl carbonates **2** using various transition metal complexes as catalysts. The decarboxylative allylation scarcely proceeds by $Mo(CO)_6$ catalyst and addition of phosphine ligand is necessary. Dppe (diphenylphosphinoethane) is better ligand than PPh_3. $Ni[P(OEt)_3]_4$ itself is active in refluxing THF, but it showed the higher catalytic activity by the addition of PPh_3. Well-known $RhCl(PPh_3)_3$ is inactive, but $RhH(PPh_3)_4$ complex catalyzed the reaction by the addition of P^nBu_3 at 65 °C in THF. The molybdenum catalyst required higher temperature and longer reaction time than nickel and rhodium catalysts. Also turnover of molybdenum catalyst is inferior to those of nickel and rhodium catalysts. Roughly, the catalytic activity for the decarboxylative allylation is the following order, Ni > Rh > Mo.

Regioselectivity of the allylation was studied by the reaction of **7** and **9**. The thermodynamically stable enolate equivalent **7** and kinetically generated enolate equivalent **9** prepared from 2-methylcyclohexanone, were converted to **8** and **10** respectively without forming a mixture of the regioisomers. The complete regioselectivity was observed with all catalysts (Table 1).

Table 1. Reaction of Alkenyl Allyl Carbonates[a)]

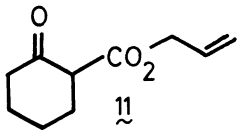
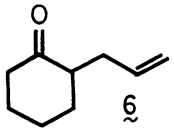
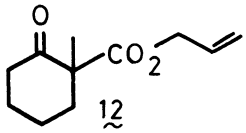
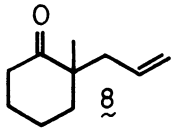
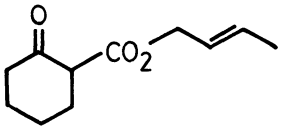
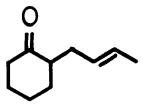
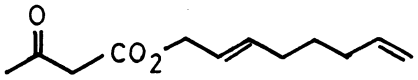
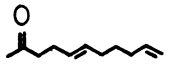
Run	Alkenyl allyl carbonate	Catalyst	Time/h	Product	Yield/%
1	 5	$Mo(CO)_6$-dppe	40	 6	81
2	5	$Ni[P(OEt)_3]_4$-PPh_3	1	6	98
3	5	$RhH(PPh_3)_4$-P^nBu_3	1	6	88
4	 7	$Mo(CO)_6$-dppe	8	 8	69
5	7	$RhH(PPh_3)_4$-P^nBu_3	2	8	67
6	 9	$Mo(CO)_6$-dppe	10	 10	81
7	9	$Ni[P(OEt)_3]_4$-PPh_3	2	10	83
8	9	$RhH(PPh_3)_4$-P^nBu_3	2	10	79

a) Molybdenum catalyzed reactions; substrate (1 mmol), $Mo(CO)_6$ (0.1 mmol), dppe (0.2 mmol), PhMe (5 cm^3) at 110 °C under argon. Nickel catalyzed reactions; substrate (1 mmol), $Ni[P(OEt)_3)]_4$ (0.05 mmol), PPh_3 (0.2 mmol), THF (5 cm^3) at 65 °C under argon. Rhodium catalyzed reactions; substrate (1 mmol), $RhH(PPh_3)_4$ (0.05 mmol), P^nBu_3 (0.2 mmol) in THF (5 cm^3) at 65 °C under argon.

$Mo(CO)_6$ complex catalyzes the decarboxylative allylation of allyl β-keto carboxylates **1**. Contrary to the reaction of alkenyl allyl carbonates **2**, phosphine ligands such as dppe or PPh_3 poisoned the molybdenum catalyst. Similar to the palladium catalyzed reactions of allyl β-keto carboxylates [3)] and alkenyl allyl carbonates,[5)] reactivity of allyl β-keto carboxylates is somewhat lower than that of alkenyl allyl carbonates. Turnovers of these catalysts were rather limited (may be deactivated during the reaction), since longer reaction times did not increase yields markedly. In order to increase the yields, a larger quantity of the catalyst (20 mol%) was used for the molybdenum catalyzed reactions (Table 2).

Allyl carbamate **13** also undergoes the decarboxylative allylation to give N-allylmorpholine (**14**). For this reaction, nickel and molybdenum complexes are active, but rhodium complexes are not (Table 3).

Table 2. Reaction of Allyl β-Keto Carboxylates[a)]

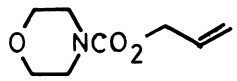
Run	Allyl β-Keto Carboxylate	Catalyst	Time/h	Product	Yield/%
1	 11	$Mo(CO)_6$	10	 6	85
2	11	$Ni[P(OEt)_3]_4$-PPh_3	3	6	58[b)]
3	11	$RhH(PPh_3)_4$-P^nBu_3	1	6	48[c)]
4	 12	$Mo(CO)_6$	15	 8	68
5	12	$RhH(PPh_3)_4$-P^nBu_3	2	8	43
6		$Mo(CO)_6$	10		67
7		$Mo(CO)_6$	7		64

a) Molybdenum catalyzed reactions; substrate (1 mmol), $Mo(CO)_6$ (0.2 mmol), PhMe (5 cm^3) at 110 °C. Nickel and rhodium catalyzed reactions; see Table 1.

b) 2,2-Diallylcyclohexanone was obtained (19%).

c) 2,2-Diallylcyclohexanone was obtained (14%).

Table 3. Reaction of Allyl Carbamate[a)]



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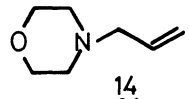

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Run	Catalyst	Time/h	Yield/%
1	$Mo(CO)_6$-dppe	11	96
2	$Ni[P(OEt)_3]_4$	3	85
3	$RhH(PPh_3)_4$-P^nBu_3	15	trace

a) Reaction conditions; see Table 1.

Similar to the palladium catalyzed reactions, these rearrangements can be explained by the formation of π-allyl complexes as intermediates, followed by decarboxylation, and intramolecular allylation of ketone enolate complexes **3**. In addition to the decarboxylative allylation, we observed the palladium-catalyzed decarboxylative dehydrogenation of **1** and **2** to give α,β-unsaturated ketones by using MeCN as a solvent.[6-8] However, we could not detect the formation of α,β-unsaturated ketones by the reactions of **1** and **2** catalyzed by nickel, rhodium, and molybdenum complexes in MeCN. Intermediate π-allyl complexes of these metals seem to be somewhat different in nature. In contrast to the extensively studied π-allylpalladium chemistry,[9,10] only few reports have been given on the π-allyl chemistry of other transition metals. As related reactions, only intermolecular allylation of carbonucleophiles with allylic compounds by nickel[11] and molybdenum[12,13] complexes is known.

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References

1) M. F. Carroll, J. Chem. Soc., 1940, 704 and 1941, 507.
2) S. R. Wilson and M. F. Price, J. Org. Chem., 49, 722 (1984).
3) I. Shimizu, T. Yamada, and J. Tsuji, Tetrahedron Lett., 21, 3199 (1980).
4) T. Tsuda, Y. Chujo, S. Nishi, K. Tawara, and T. Saegusa, J. Am. Chem. Soc., 102, 6381 (1980). Use of $Ni(PPh_3)_4$ and $RhCl(PPh_3)_3$ for the decarboxylation of allyl β-keto carboxylate **11** has been briefly described in this paper without giving experimental data.
5) J. Tsuji, I. Minami, and I. Shimizu, Tetrahedron Lett., 24, 1793 (1983).
6) I.Shimizu, and J. Tsuji, J. Am. Chem. Soc., 104 5844 (1982).
7) I. Shimizu, I. Minami, and J. Tsuji, Tetrahedron Lett., 24 1797 (1983).
8) J. Tsuji, I. Minami, I. Shimizu, and H. Kataoka, Chem. Lett., 1984 1133.
9) J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer-Verlag (1980), Heidelberg.
10) B. M. Trost, Tetrahedron, 33, 2615 (1977).
11) T. Cuvigny and M. Julia, J. Organomet. Chem., 250, C 21 (1983).
12) B. M. Trost and M. Lautens, J. Am. Chem. Soc., 105, 3343 (1983) and 104, 5543 (1982).
13) T. Tatsumi, K. Hashimoto, H. Tominaga, Y. Mizuta, K. Hata, M. Hidai, and Y. Uchida, J. Organometal. Chem., 252, 105 (1983).

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