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REARRANGEMENT OF ALLYLIC N-PHENYLFORMIMIDATES TO N-ALLYL-N-PHENYL-FORMAMIDES CATALYZED BY PALLADIUM COMPLEXES

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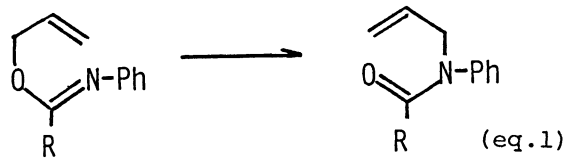
The palladium complexes such as $Pd(PPh_3)_4$ and $Pd(PhCN)_2Cl_2$ catalyzed the rearrangement of allylic N-phenylformimidates to give N-allyl-N-phenylformamides under a mild condition. The reaction courses are strongly influenced by the oxidation state of palladium complexes used.

The Claisen rearrangement and related rearrangements have been an attractive objective in synthetic organic chemistry.[1] These rearrangements usually require the elevated temperature and are accompanied by formation of a few by-products. Recently a few reports concerning these types of rearrangements catalyzed by palladium complexes have been found and their synthetic utility was enhanced so as to perform the carbon-carbon bond formation under mild conditions.[2),3)] Interestingly, in these catalytic reactions the kind of palladium complex, especially the oxidation state of palladium metal remarkably affects the reaction feature. For example, Pd(II) complexes are effective catalyst for Cope rearrangement of acyclic 1,5-dienes[2a)] and poly hetro-Claisen rearrangement,[2b)] while Pd(0) complexes are not. Moreover Pd(0) complexes catalyze Claisen rearrangement,[3a), 3b)], while Pd (II) complexes do not. In this paper we wish to report the rearrangement of allylic N-phenylformimidates catalyzed by both Pd(II) and Pd(0) complexes to give N-allyl--N-phenylformamides, (eq. 1) where there exists a change in mechanism of rearrange-



(eq.1)

R	Cata	t(h)	T(°)	Conv.(%)
H	$Pd(PhCN)_2Cl_2$	20	r.t.	100
	"	2	"	5
	$Pd(PPh_3)_4$	2	"	80
Ph	$Pd(PhCN)_2Cl_2$	2	"	23
	$Pd(PPh_3)_4$	2	"	100

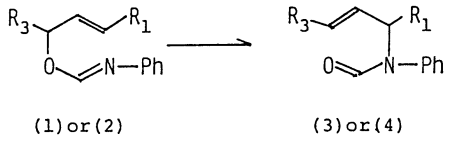
Table 1

ment attributed to the catalyst used.

Experimentally, the treatment of allylic N-phenylformimidates derived from the reaction of allyl alchohol and iminoethers with a catalytic amount of palladium complex(1.0-10 mol% of substrate) in refluxing THF gave N-allyl-N-phenylformamides. After the catalyst was removed, the reaction products were isolated by preparative GC (85-90 % isolated yields) and identified by IR and NMR spectra. Table 1 shows the results obtained from the reaction of unsubstituted allylic N-formimidates catalyzed by Pd(II) and Pd(0) complexes at room temperature. It can be seen that the catalytic activity of Pd(0) complex is much higher than that of Pd(II) complex. Slight acceleration of the rearrangement by electron withdrawing substituent at the 2-position of imidate was observed. Refluxing of THF solution of imidates in the presence of Pd(II) or Pd(0) complex provided the correspsonding amides quantitatively.

To examine the regioselectivity of the rearrangement, methyl substituted allylic N-phenylformimidates were treated with 10 mol% of $PdCl_2(PhCN)_2$ and $Pd(PPh_3)_4$ in refluxing THF. As can be seen in Table 2, Pd(II) complex catalyzed rearrangements of (1) and (2) proceeded highly regioselectively to give (3) and (4), respectively, while Pd(0) complex catalyzed rearrangements of (1) and (2) afforded a mixture of (3) and (4) in about 2:1 ratio.[4] On the other hand, thermal rearrangements of (1) and (2) in decaline at 190° only gave (3) and (4), respectively in a similar regioselectivity to that of Pd(II) promoted rearrangement.

With regard to the mechanism of the rearrangement of imidates by Pd(II) and Pd (0) complexes, the fact that the rearrangements of (1) and (2) catalyzed by Pd(0) yield a mixture of (3) and (4) in a similar ratio regardless of the position of



(1)or(2) (3)or(4)

(1);R_1=CH_3,R_3=H
(2);R_1=H,R_3=CH_3
(3);R_1=CH_3,R_3=H (eq.2)
(4);R_1=H,R_3=CH_3

Table 2

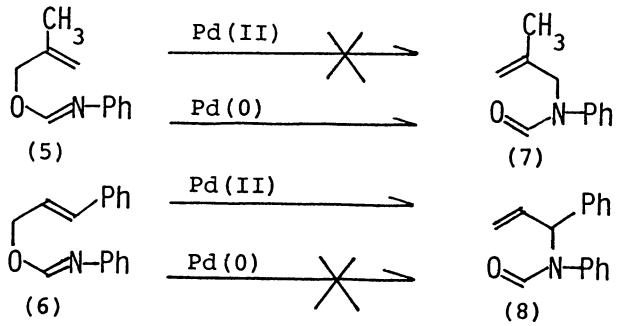
R_1	R_3	Cata.	t	Products	Conv.(%)
CH_3	H	$Pd(PPh_3)_4$	2	(3):(4)=2:1	100
		$Pd(PhCN)_2Cl_2$	2	(3)	"
		– *	15	(3)	"
H	CH_3	$Pd(PPh_3)_4$	2	(3):(4)=1.5:1	"
		$Pd(PhCN)_2Cl_2$	2	(4)	"
		– *	15	(4)	"

* In decaline

methyl substituent in an allyl group indicates that the Pd(0) complex catalyzed rearrangement involves π-allyl palladium complex as an intermediate which should be generated by oxidative addition of C-O bond of imidate to Pd(0) species. To clarify the intermediacy of π-allyl palladium, the effect of added phosphine ligands on the regioselectivity of rearrangement of (2) catalyzed by Pd(0) complex was examined. When tri-n-butylphosphine(strong σ-donor ligand) was added, the reaction became slower and hence the conversion was lower than when PPh_3 was added. The products ratio of (3) to (4) was 2.7:1. When $P(OEt)_3$ ligand (weaker σ-donor ligand) was added, the ratio became 1.3:1. These results can be explained in terms of the steric and electric effects of added phosphine ligands in the nucleophilic attack to π-allyl palladium complex as reported by Trost [5] and Åkermark [6] and are consistent with a mechanism as shown in scheme I (a).

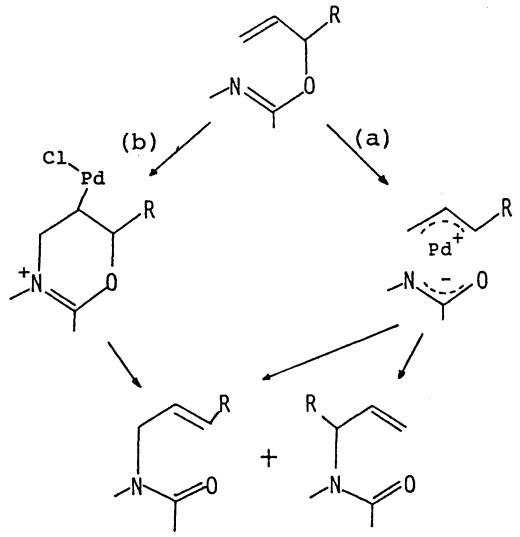
In marked contrast to the Pd(0) catalyzed reaction, Pd(II) complex promoted rearrangement which gives a single product involves the six membered ring intermediate rather than the π-allyl palladium complex as shown in scheme I (b). A similar mechanism has been proposed by Overman for the Pd(II) complex catalyzed Cope rearrangement of 1,5-dienes and for Hg(II) promoted rearrangement of allylic carbamates.[2a),2c)]

It is notable that there are structural limitations in the catalytic rearrangement of imidates. Pd(0) complex catalyzted rearrangement of (5) under these conditions proceeded slowly to give the corresponding amide (7) in ca. 50 % yield, while Pd(II) did not catalyze the reaction at all. Moreover, the rearrangement of 3-phenylallylic imidate (6) was catalyzed by Pd(II) complex to give the amide (8), while no rearrangement took place when Pd(0) complex was used (eq.3).



(eq.3)

These results also support the proposed mechanism as shown in scheme I. A methyl group at C-2 should retard the initial π-complexation by its steric hindrance.[2a] On the other hand, the effect of phenyl substituent at C-3 may be rationalized by a favorable π-allyl complexation involving phenyl group.



Scheme I

The catalytic rearrangement of allylic N-phenylformimidates is found to occur readily under these conditions and, interestingly, the path of rearrangement depends on the oxidation state of palladium complex, indicating that the coordination ability of substrate to palladium and the stability of π-allyl complex seem to be important factors to determine the reaction course.

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4) ^{1}H NMR spectrum of (3), -CHO 8.35, -CH$_3$ 1.65, -CH=CHCH$_3$ 5.55(m), -CH$_2$CH=CH$_3$ 4.30; (4),-CHO 8.15, -CH$_3$ 1.15, -CH=CH$_2$ 5.9(m) and 5.2(m), -CHCH$_3$ 5.2(m), -CHCH$_3$-CH=CH$_2$ 1.28(d) (chemical shift, ppm).
Since ^{1}H and ^{13}C NMR spectra and IR spectra of the stereoisomers of (4) produced by the rearrangement are nearly identical, the stereochemistry of the rearrangement is not clear. The identification of the stereoisomers is now under investigation.
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