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PALLADIUM-CATALYZED SYNTHESIS OF 2,3-DISUBSTITUTED ALLYLAMINES BY REGIOSELECTIVE AMINOPHENYLATION OR AMINOALKENYLATION OF 1,2-DIENES

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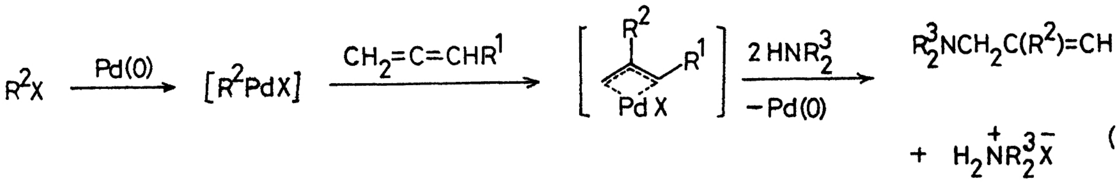
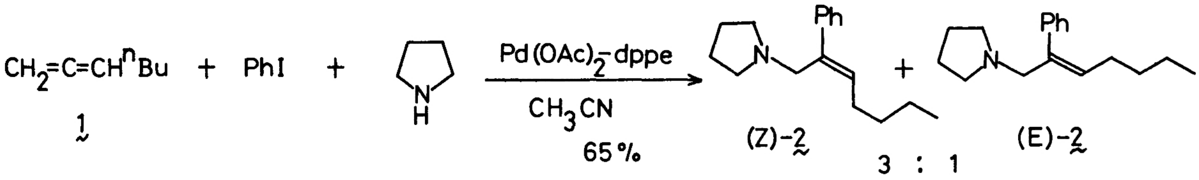
Reaction of 1,2-dienes, phenyl iodide or alkenyl bromides, and secondary amines in the presence of palladium-phosphine catalyst affords 2-phenyl or alkenyl allylic amines.

Several reactions of 1,2-dienes catalyzed or promoted by palladium compounds are known, but the selective reaction without oligomerization or polymerization is rather rare.[1] As a stoichiometric reaction, addition of phenylpalladium to 1,2-propadiene to give π-2-phenylallylpalladium has been reported.[2] π-Allylpalladium complexes are useful intermediates to prepare various allylic compounds. The catalytic reactions involving π-allylpalladium formation by insertion of 1,2-dienes to organopalladium compounds, prepared in situ from Pd(0) and organic halides are expected to occur if the π-allylpalladium complexes are decomposed by the attack of a nucleophile. We found that the palladium-catalyzed reaction of 1,2-dienes with aryl or alkenyl halides proceeded using secondary amines as nucleophiles to afford 2,3-disubstituted allyl amines (Eq. 1), and the results are reported in this paper.



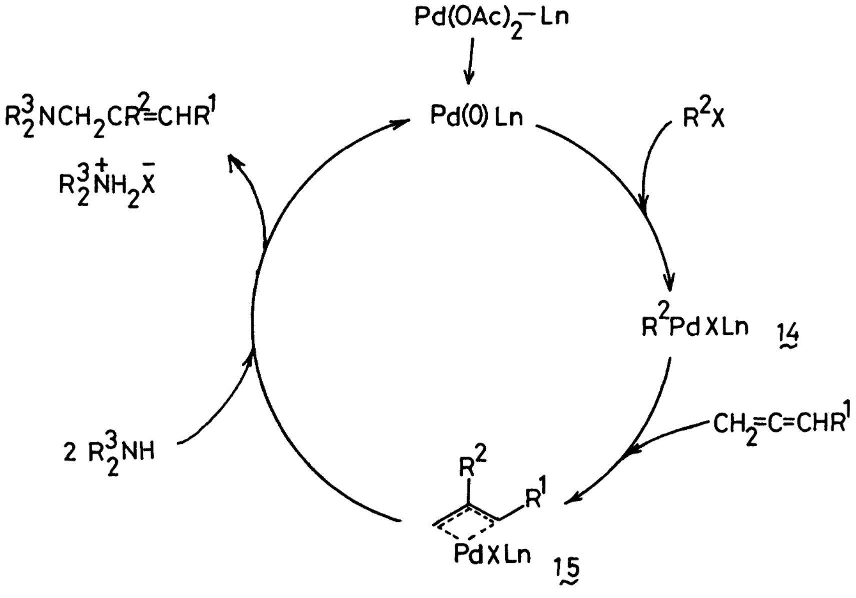
(1)

In a typical experiment, 1,2-heptadiene (**1**) (2 mmol) in CH_3CN (2 cm^3 was added to a boiling solution of PhI (2.5 mmol), $Pd(OAc)_2$ (0.05 mmol), 1,2-bis(diphenylphosphino)ethane (dppe) (0.1 mmol), and pyrrolidine (1 cm^3) in CH_3CN (5 cm^3). The mixture was refluxed for 1 h. After evaporation of the solvent, the residue was distilled (bulb-to-bulb distillation, 130-140 °C / 1 Torr) to give N-(2-phenyl-2-heptenyl) pyrrolidines (**2**) in 65% yield. The product was found to be a 3 : 1 mixture of the Z and E isomers.[3,4]



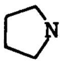
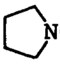
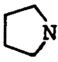
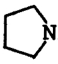
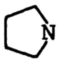
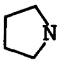
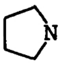
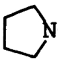
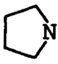
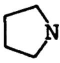
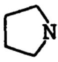
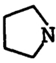
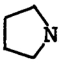
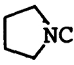
The results of the reactions using various 1,2-dienes, halides, amines, and phosphines are summarized in the Table 1. Tri(o-tolyl)phosphine was also a good ligand for allylic amine synthesis, but allylic amines were not obtanied with triphenylphosphine. Pyrrolidine is the suitable secondary amine for this reaction. However, when diethylamine was used, the allylic amine **8** was obtained in only 8% yield, and no allylic amine was obtained with N-methylaniline. Alkenyl bromides also react to give 2-aminomethyl-1,3-dienes. 1,2-Dienes with acetoxy, hydroxy, or methoxy group were converted to the corresponding allylic amines in good yields (runs 8-11).

The reaction is explained by the following mechanism (Scheme 1). Oxidative addition of the halides to Pd(0) species, formed in situ from $Pd(OAc)_2$, affords phenyl- or alkenylpalladium halides **14**. Regioselective insertion of 1,2-diene to **14** at the sp carbon gives π-allylpalladium complex **15**, which is decomposed by the nucleophilic attack of secondary amines to produce the allylic amines along with regeneration of Pd(0).



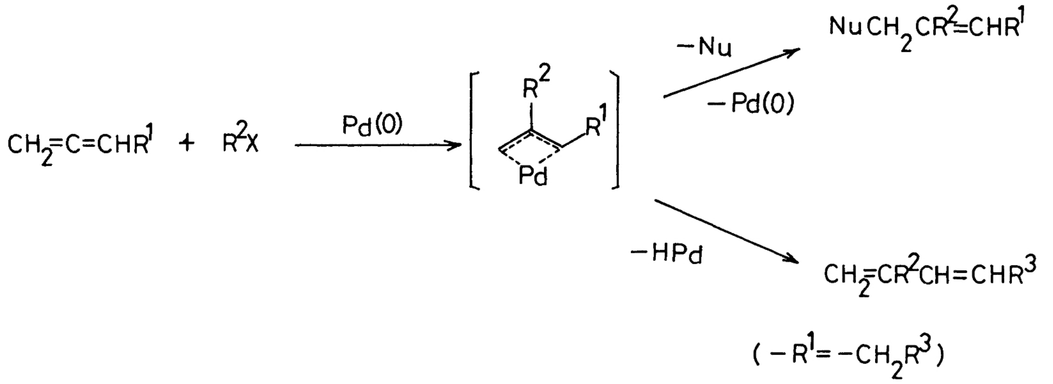
Scheme 1.

Table 1. Reaction of 1,2-Dienes, Halides, and Secondary Amines with $Pd(OAc)_2$-Phosphine[a)]

Run	1,2-Diene	Halide	Amine	Phosphine	Product[b)]	Yield/%[c)]
1	$CH_2=C=CH^iBu$ **3**	PhI	NH	dppe	$NCH_2C(Ph)=CH^iBu$ **7** (E : Z = 1 : 3)[d,e]	82
2	**3**	PhI	NH	P(o-Tol)$_3$	**7**	62
3	**3**	PhI	NH	PPh_3	**7**	0
4	**3**	PhI	Et_2NH	dppe	$Et_2NCH_2C(Ph)=CH^iBu$ **8** (E : Z = 1 : 2.5)[d)]	8
5	**3**	PhI	Ph(Me)NH	dppe	$Ph(Me)NCH_2C(Ph)=CH^iBu$	0
6	**3**	PhCH=CHBr	NH	dppe	$NCH_2C(CH=CHPh)=CH^iBu$ **9**	79
7	**3**	$PhC(Br)=CH_2$	NH	dppe	$NCH_2C[C(Ph)=CH_2]=CH^iBu$ **10**	9
8	$CH_2=C=CHCH(OH)Ph$ **4**	PhI	NH	dppe	$NCH_2C(Ph)=CHCH(OH)Ph$ **11** (E : Z = 1 : 9)[d)]	84
9	**4**	PhI	NH	P(o-Tol)$_3$	**11**	85
10	$CH_2=C=CHC(Me)_2CH_2OAc$ **5**	PhI	NH	dppe	$NCH_2C(Ph)=CHC(Me)_2CH_2OAc$ **12**	70[f)]
11	$CH_2=C=CHCH(OMe)^iBu$ **6**	PhI	NH	dppe	$NCH_2C(Ph)=CHCH(OMe)^iBu$ **13**	90[f)]

a) Reactions were carried out using 1,2-dienes (1 mmol), halides (1 mmol) and secondary amines (1 cm^3) with $Pd(OAc)_2$ (0.05 mmol)-phosphine (0.05-0.1 mmol) in boiling CH_3CN (3 cm^3) for 1-3 h under nitrogen. b) E and Z mixture unless otherwise stated. c) Isolated yields by column chromatography on Al_2O_3 or SiO_2 with Et_2O-hexane or AcOEt-hexane. d) NMR analysis. e) GLC analysis. f) Single isomer, but the stereochemistry was not confirmed.

The palladium-catalyzed synthesis of allylic amines described here is useful for organic synthesis, and the present method also provides a new preparative method of π-allylpalladium intermediate, which can be converted to either a variety of allylic compounds by nucleophilic reactions or 1,3-dienes by elimination of Pd(0) (Scheme 2).[6)]



Scheme 2.

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References

1) Recent works on the palladium-catalyzed reaction of 1,2-dienes; D. R. Coulson, J. Org. Chem., 37, 1253 (1972) and 38, 1483 (1973); H. Siegel, H. Hopf, and A. Germer, P. Binger, Chem. Ber., 111, 3112 (1978); H. Watanabe, M. Saito, N. Sutou, and Y. Nagai, J. Chem. Soc., Chem. Commun., 1981, 617

2) R. R. Stevens and G. D. Shier, J. Organometal. Chem., 21, 495 (1970).

3) (E)-2 NMR (CCl_4) δ 3.20 (2H, br, $NCH_2C=$), 5.58 (1H, t, J=7 Hz, C=CH), 7.20 (5H, br s, Ph).
(Z)-2 NMR (CCl_4) δ 3.40 (2H, br, $NCH_2C=$), 5.72 (1H, t, J=7 Hz, C=CH), 6.8-7.8 (5H, m, Ph).

4) The authentic (E)-2 isomer was prepared from (E)-2-phenyl-2-buten-1-ol[5)] by chlorination with CCl_4-PPh_3 followed by amination with pyrrolidine.

5) R. Mornet and L. Gouin, Bull. Soc. Chim. Fr., 1977, 737.

6) Reaction of 1,2-heptadiene (1) and PhI with N-methylpyrrolidine in the presence of $Pd(OAc)_2$-dppe catalyst gave 2-phenyl-1,3-heptadiene. I. Shimizu and J. Tsuji, Abstracts of 30th Symposium on Organometallic Chemistry Japan, 1983, 232.

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