Reaction of Butadiene with Schiff Bases Catalysed by a Palladium Complex. Formation of a Derivative of Piperidine

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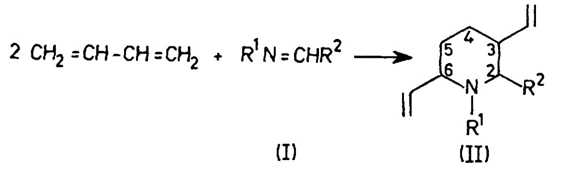
Summary Reaction of butadiene with Schiff bases is catalysed by $Pd(NO_3)_2$–Ph_3P to give 2,3,6-trisubstituted piperidines.

Bis-π-allyl complexes are active intermediates in synthetic reactions,[1] *e.g.* reaction of butadiene with olefins, acetylenes, and carbonyl compounds. All these reactions involve insertion of a multiple bond into a carbon–metal bond. The carbon–nitrogen double bonds of isocyanates[2] and Schiff bases[3] are also reactive toward some carbon–metal bonds.

We now report that palladium nitrate catalyses the reaction of butadiene with Schiff bases in the presence of triphenylphosphine ($Pd:PPh_3 = 1:3$) to give substituted piperidines (Scheme).† Liquified butadiene (24 mmol) was allowed to react with MeN:CHPh (8 mmol) in the presence of $Pd(NO_3)_2$ (0·1 mmol) and Ph_3P (0·3 mmol) in DMF (1 ml) at 80°C. After 10 h (II; R^1 = Me, R^2 = Ph) was formed (73%). G.l.c. showed the presence of four stereoisomers, the distribution of which depends upon the reaction time (see



(I) (II)

Scheme

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† Identification is based on n.m.r., i.r., and mass spectral evidence.

Table). We assigned the stereochemistry of the substituents on the 2-, 3-, and 6-carbon atoms as shown in the Table.‡

Table

Stereochemistry of the substituents and the distribution of the stereoisomers (R^1 = Me, R^2 = Ph)

	Stereochemistry[a]			Distribution[b] %	
Isomer	6-	3-vinyl	2-phenyl	10 h	40 h
IIa	e	e	e	37	45
IIb	e	a	e	11	40
IIc	a	e	e	17	9
IId	a	a	e	34	6

[a] e = equatorial; a = axial. [b] Total yields of (II): 10 h, 73%; 40 h, 91%.

For this reaction palladium nitrate was the best catalyst. Palladium chloride or acetylacetonate were ineffective. We have carried out reactions with *N*-benzilidene-methyl-, ethyl- and allyl-amine and *N*-benzilidene-aniline and obtained the corresponding products in moderate to high yields. It is likely that this reaction can be applied to Schiff bases having aromatic substituents (R^2) on the carbon atom and alkyl, allyl, and aromatic substituents (R^1) on the nitrogen atom of (I).

Treatment of an isomeric mixture of (II) with a catalytic amount of $Pd(NO_3)_2$–Ph_3P (1:3) in propan-2-ol at 80 °C gave only isomers (IIa) and (IIb). It is likely that this isomerization of (IIc) and (IId) into (IIa) and (IIb) proceeds through a π-allyl intermediate formed by the fission of the C-6–nitrogen bond,[4] because the relation of the stereochemistry between R^2 and vinyl group on the C-3 atom remains unaltered during the isomerization. A similar intermediate is proposed in the reaction of isocyanate with metal complexes.[2]

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‡ Assignment of the structure of the isomers was made by examination of the n.m.r. spectra of g.l.c.-separated samples. The assignment is based on the chemical shifts and coupling constants of well-resolved signals due to the protons on the C-2, C-3, and C-6 atoms.

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[4] T. Takahashi, A. Miyake, and G. Hata, *Bull. Chem. Soc. Japan*, **1972**, **45**, **1183**.