

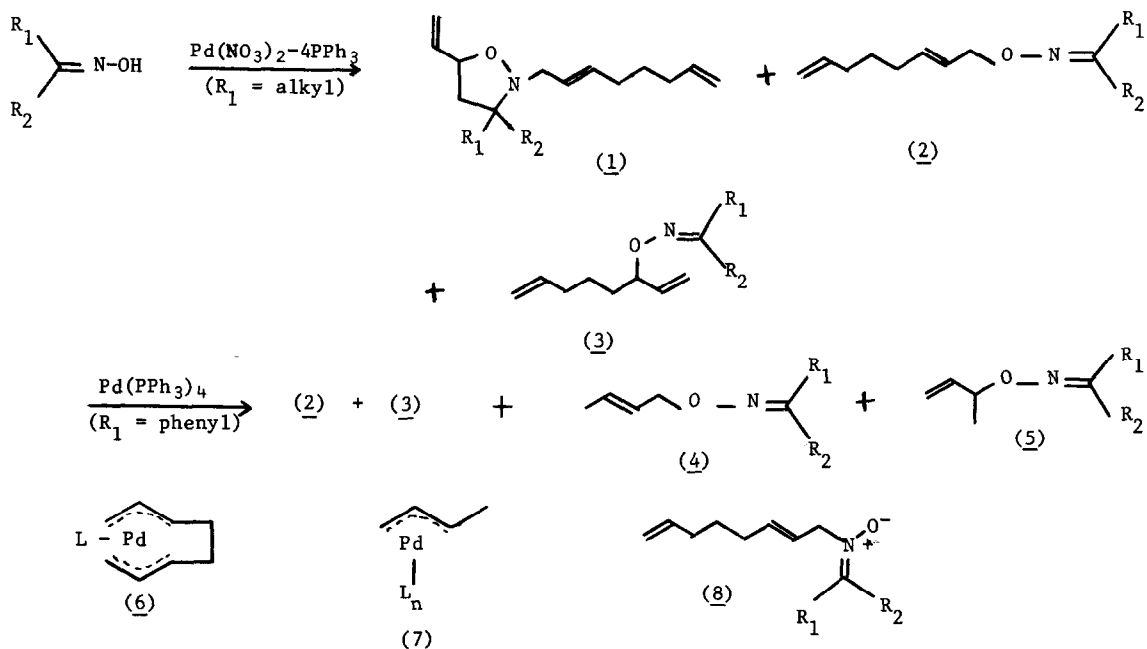
PALLADIUM CATALYSED REACTION OF OXIMES WITH BUTADIENE

Raymond Baker* and Malcolm S. Nobbs

Department of Chemistry, The University, Southampton, SO9 5NH.

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The palladium complex catalysed reactions of butadiene with electrophiles and nucleophiles have been studied extensively, and the reactions with amines, alcohols, active methylenes, Schiff bases, phenyl isocyanate and aldehydes are well reviewed¹. We have previously reported the formation of azo-compounds from the reaction of phenylhydrazones with butadiene in the presence of nickel and palladium complexes, although for the latter catalyst some N-alkylation was also observed². Furthermore, the product ratio was shown to be dependent on the palladium salt and organophosphorus ligand employed; exclusive N-alkylation was observed with Pd(NO₃)₂ and PdCl₂. We have now shown that in the reaction of oximes with butadiene, alkylation proceeds at either oxygen or nitrogen to yield a series of oxime ethers and nitrones, the latter reacting thermally with excess butadiene to yield N-alkylated isoxazolidines.



Typically, a tetrahydrofuran (10ml) solution of the oxime (30mmol), and butadiene (15ml, 180mmol) was allowed to react at 110°C for 4-12h in the presence of either tetrakis (triphenylphosphine) palladium (0.3mmol) or palladium nitrate (0.3mmol) and triphenylphosphine (1.2mmol).

The aromatic oxime adducts were isolated by column chromatography (alumina - grade 2) on elution with petroleum ether, and separated by preparative GLC (15ft 10% SE30 150°C) whilst the aliphatic oxime adducts were isolated by distillation and preparative GLC (10ft 15% Carbowax 150°C)[†].

TABLE

R ₁ R ₂ C=NOH		Yield (%)	Product Ratio (%)				
R ₁	R ₂		(1)	(2)	(3)	(4)	(5)
Me	H	63	100	-	-	-	-
Et	H	16 ^a	100	-	-	-	-
Me	Me	81	24	28	48	-	-
Et	Me	58	-	10	90 ^b	-	-
Ph	H	92	-	14	10	20	56
Ph	Me	87	-	24	16	14	46

^aPd(acac)₂-4P(OPh)₃ catalyst. ^b1:1 mixture of terminal and internal double bond.

The formation of the 2:1 (2 and 3) and 1:1 (4 and 5) oxime ether products arise by reaction of the aromatic oximes with the bis- π -allyl- (6) and π -allyl-palladium (7) intermediates derived from butadiene. The π -allylpalladium complex is considered to arise from addition of one mole of butadiene to a "Pd-H" species, derived by oxidative addition of the oxime to the complex. In contrast, the reaction of the aliphatic oximes with butadiene proceeds by either oxygen or nitrogen alkylation of the oxime by the bis- π -allylpalladium intermediate, the latter being the exclusive route for aldehyde oximes. We suggest that the nitron obtained by the N-alkylation of the oximes then undergoes a 1,3-dipolar addition reaction with excess butadiene to yield a novel route to substituted isoxazolidines (1). Evidence for the reaction mechanism was obtained from an experiment in which ethylene was added to the reaction mixture and a small amount of a product was obtained which resulted from interception of the intermediate nitron (8) by ethylene.

This reaction may be compared to the palladium (II) induced cyclisations of unsaturated ketoximes to yield either isoxazole or pyridine derivatives by attack of the oxygen or nitrogen at the activated olefin^{3,4}. The pyridine derivatives may be considered to arise by attack of the nitrogen at the co-ordinated olefin, followed by "Pd-H" elimination to yield the corresponding pyridine N-oxides.

[†]All products are fully consistent with spectral data, including CMR for the isoxazolidines. Disubstituted double bonds were assigned as mainly trans on the basis of IR and NMR data.

1. R. Baker, Chem. Rev., 1973, 73, 487.
2. R. Baker, M.S. Nobbs and D.T. Robinson, J.C.S. (Chem. Comm.), 1976, 723.
3. K. Maeda, T. Hosokawa, S.I. Murahashi and I. Moritani, Tetrahedron Letters, 1973, 5075.
4. T. Hosokawa, N. Shimo, K. Maeda, A. Sonoda and S.I. Murahashi, Tetrahedron Letters, 1976, 383.