

THE REACTION OF α,β -UNSATURATED KETOXIMES INTO ISOXAZOLES WITH PALLADIUM COMPLEXES

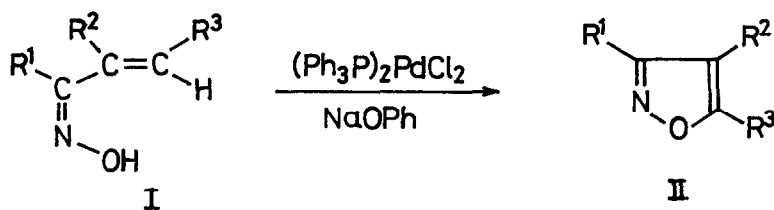
Kazuyuki Maeda, Takahiro Hosokawa, Shun-Ichi Murahashi, and Ichiro Moritani

Department of Chemistry, Faculty of Engineering Science, Osaka University
Machikaneyama, Toyonaka, Osaka, Japan

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Recently, we described the cyclization reaction of allylphenols with dichlorobis(benzonitrile)palladium to give 2-substituted benzofurans.¹ In relation to this reaction, we have found facile cyclization reaction of α,β -unsaturated ketoximes with palladium complexes leading to the corresponding isoxazoles. This is the first case of oxidative cyclization of α,β -unsaturated ketoximes by transition metal complexes, although the cyclization induced by iodine-potassium iodide in basic medium has recently reported by Büchi and Vederas.²

The general procedure of the reaction is as follows. A mixture of α,β -unsaturated ketoxime (5 mmol), sodium phenoxide (25 mmol) and dichlorobis(triphenylphosphine)palladium (5 mmol) in dry benzene (200 ml) was heated at reflux for 8 hrs under argon atmosphere. The cyclized product was isolated on distillation after removal of resulting palladium black. Thus, treatment of the oxime of 1,3-diphenyl-2-propen-1-one (Ia) afforded 3,5-diphenylisoxazole (IIa) in 92 % yield. Similarly, the oximes Ib and Ic gave the corresponding isoxazole IIb and IIc in



- a, $R^1 = \text{C}_6\text{H}_5$, $R^2 = \text{H}$, $R^3 = \text{C}_6\text{H}_5$
 b, $R^1 = \text{t-C}_4\text{H}_9$, $R^2 = \text{H}$, $R^3 = \text{C}_6\text{H}_5$
 c, $R^1 = \text{C}_6\text{H}_5$, $R^2 = \text{CH}_3$, $R^3 = \text{i-C}_3\text{H}_7$

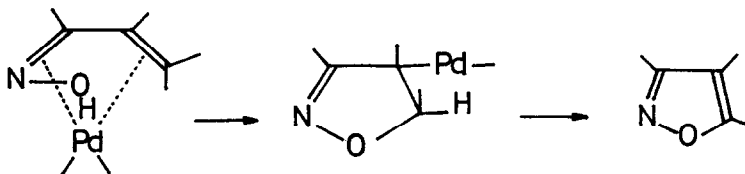
50 and 15 % yield, respectively. The structures of these isoxazoles were determined by analyses and spectral data, Iia, mp 140-141°; Iib, bp 98-103°/8 mm, mp 42.5-43°; Iic, bp 98-108°/1 mm.

The reaction can be also carried out with other palladium complexes such as Pd(acac)₂ and Pd(OAc)₂ in the presence of phosphine ligands. These results shown in Table indicate that the formation of isoxazole Iib is affected both by varieties of phosphine ligands and by the relative ratio of palladium complexes to the phosphine ligand. The combination of Pd(acac)₂ and triphenylphosphine on the ratio of 1 : 2 is most effective among various combinations. The bidentate ligand of diphenylphosphinoethane lowers the yield of Iib. Other complexes such as Ni(acac)₂-2PPh₃, RhCl(PPh₃)₃-PhONa, and RuCl₂(PPh₃)₃-PhONa are inefficient in the reaction.

TABLE
The reaction of Iib with palladium complexes

Complexes	Yield of Iib (%)
(PPh ₃) ₂ PdCl ₂ -PhONa	50
Pd(acac) ₂ - PPh ₃	26
Pd(acac) ₂ - 2PPh ₃	54
Pd(acac) ₂ - 4PPh ₃	14
Pd(acac) ₂ - (Ph ₂ PCH ₂ -) ₂	34
Pd(acac) ₂ - 2P(OPh) ₃	15
Pd(OAc) ₂ - 2PPh ₃	27

The reaction would be elucidated by intramolecular coupling of the co-ordinated carbon-carbon double bond with the oxygen atom induced by palladium metal as shown in the following scheme.



REFERENCES

- 1) T. Hosokawa, K. Maeda, K. Koga, and I. Moritani, Tetrahedron Lett., 739 (1973).
- 2) G. Büchi and J. C. Vederas, J. Amer. Chem. Soc., 94, 9128 (1972).