

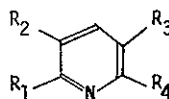
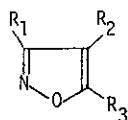
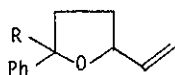
SYNTHESES OF HETEROCYCLIC COMPOUNDS BY INTRAMOLECULAR OXYPALLADATION

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Novel syntheses of heterocyclic compounds by intramolecular oxypalladation of 1-phenyl-4-hexene-1-ol (**1**) derivatives and unsaturated ketoximes are reported. Thus, treatment of **1** with a catalytic amount of $\text{Pd}(\text{OAc})_2$ in the presence of $\text{Cu}(\text{OAc})_2$ at r.t. under an oxygen atmosphere gave 2-phenyl-5-vinyltetrahydrofuran (**2a**) in 32% yield. Similarly, introduction of substituents (Me, Et, and Ph) into 1-position of the compound **1** led to the formation of corresponding vinyltetrahydrofurans **2b-d** in 15-38% yield. Formation of isoxazoles **3a-f** from α,β -unsaturated ketoximes can be accomplished in relatively high yield by either treatment with $\text{PdCl}_2(\text{PPh}_3)_2$ in the presence of PhONa in benzene at reflux for 8 hr (Method A) or with PdCl_2 in the presence of Na_2CO_3 in CH_2Cl_2 at r.t. for 20 hr (Method B). Isoxazole **3g** or **3h** were also obtained by the treatment of oximes of 4-hexene-2-one (β,γ -unsaturated ketoxime) or 1-phenyl-4-pentene-1-one (γ,δ -unsaturated ketoxime) with Method B, respectively, while the treatments of these oximes with Method A gave pyridine derivatives (**4b** or **4c**). 4-Methyl-1-phenyl-3-pentene-1-one oxime (β,δ -unsaturated ketoxime) gave also 3-methyl-6-phenylpyridine (**4a**) in 43% yield. Pyridine derivatives **4c-f** were quite generally produced by the treatment of γ,δ -unsaturated ketoximes, but in poor yields. However, utilization of conjugated ketoximes gave rise to an improvement of pyridine synthesis (**4g-k**).



2	R
a	H
b	Me
c	Et
d	Ph

3	R ₁	R ₂	R ₃
a	t-Bu	H	Ph
b	i-Pr	H	Ph
c	Me	H	Ph
d	Ph	H	Et
e	Ph	H	Ph
f	Ph	Me	i-Pr
g	Me	H	Et
h	Ph	H	n-Pr

4	R ₁	R ₂	R ₃	R ₄
a	Ph	H	Me	H
b	Me	H	H	H
c	Ph	H	H	H
d	Me	H	Me	H
e	Ph	H	H	Me
f	$-(\text{CH}_2)_4-$		H	H
g	Me	H	H	Me
h	Me	H	Me	Ph
i	Me	Me	H	Ph
j	t-Bu	H	H	Ph
k	Et	H	H	Ph