

SYNTHESIS OF BRIDGEHEAD NITROGEN HETEROCYCLES UTILIZING INTRAMOLECULAR RING TRANSFORMATION

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Fused imidazoles were synthesized by an intramolecular ring transformation of γ -keto-oxazoles with hydrazine and by an intramolecular dehydration of γ -amino-oxazoles. γ -Keto-oxazoles **2a** and **b** were prepared by the reaction of lithiated 2-methyloxazole **1** with methyl enol ether of α -bromoketones followed by hydrolysis. γ -Keto-oxazoles **2a** and **b** gave 7,8-dihydroimidazo[1,2-*b*]pyridazine **3a** and 6,7,8,9,9a,10-hexahydroimidazo[1,2-*b*]cinnoline **3b** on treatment of **2a** and **b** with hydrazine hydrate in acetic acid at room temperature. The transformed fused imidazoles **3a** and **b** were further converted into the corresponding tetrahydroimidazo[1,2-*b*]pyridazine **4a** and octahydroimidazo[1,2-*b*]cinnoline **4b** by each reduction with NaBH_4 . γ -Amino-oxazoles **5a** and **b** were derived from **2a** and **b** with NaBH_3CN in the presence of ammonium acetate. The pyrolysis (280°C , 5 mmHg) of **5a** and **b** provided cyclodehydrated 6,7-dihydro-5H-pyrrolo-[1,2-*a*]imidazole **6a** and 4a,5,6,7,8,8a-hexahydro-9H-imidazo[1,2-*a*]indole **6b** respectively. Similar transformation of 1,3,4-oxadiazole (eq 2) will be also discussed.

