SYNTHESIS OF BRIDGEHEAD NITROGEN HETEROCYCLES UTILIZING INTRAMOLECULAR RING TRANSFORMATION

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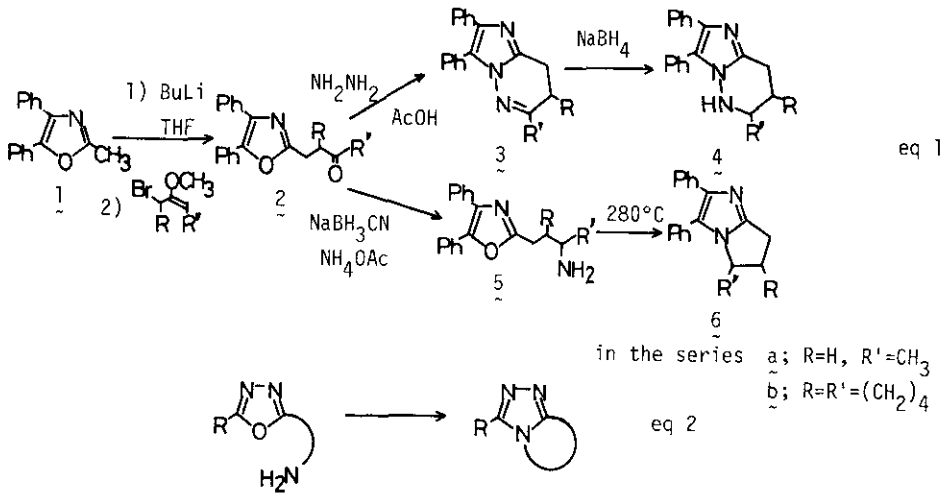
Fused imidazoles were synthesized by an intramolecular ring transformation of γ-keto-oxazoles with hydrazine and by an intramolecular dehydration of γ-amino-oxazoles. γ-Keto-oxazoles 2a and b were prepared by the reaction of lithiated 2-methyloxazole 1 with methyl enol ether of α-bromoketones followed 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 aslo discussed.



eq 1

in the series a; R=H, R'=CH_3
b; R=R'=$(CH_2)_4$

eq 2