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PREPARATION AND REACTIONS OF SOME ANHYDRO-5-HYDROXY-1-ALKYL-OR-ARYL-PYRIDAZINIUM HYDROXIDES

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In the course of our studies of 3(2H)-furanones and their reactions with nucleophiles (1,2), we found that the compounds (I) reacted with monosubstituted hydrazines to yield the 5-oxidopyridazinium betaines (II).

The structure of these betaines was deduced by spectroscopic methods and by the alkylation products study of preformed pyridazinones (III) and will be discussed.

Sodium borohydride reduction of compounds (II) afforded the chelated dihydrocompounds (VI). These 5-hydroxy-1,6-dihydropyridazine derivatives showed magnetic nonequivalence of the ethoxycarbonyl methylene protons in their NMR spectra.

The compounds (VI) were N-alkylated under basic conditions to afford the 1,2-disubstituted-1,2,3,4-tetrahydropyridazin-4-one derivatives (VII), whereas methylation with the diazomethane yielded the O-methyl derivatives alone or accompanied by the N-methylated compounds (VII) depending of the nature of the R substituent.

REFERENCES

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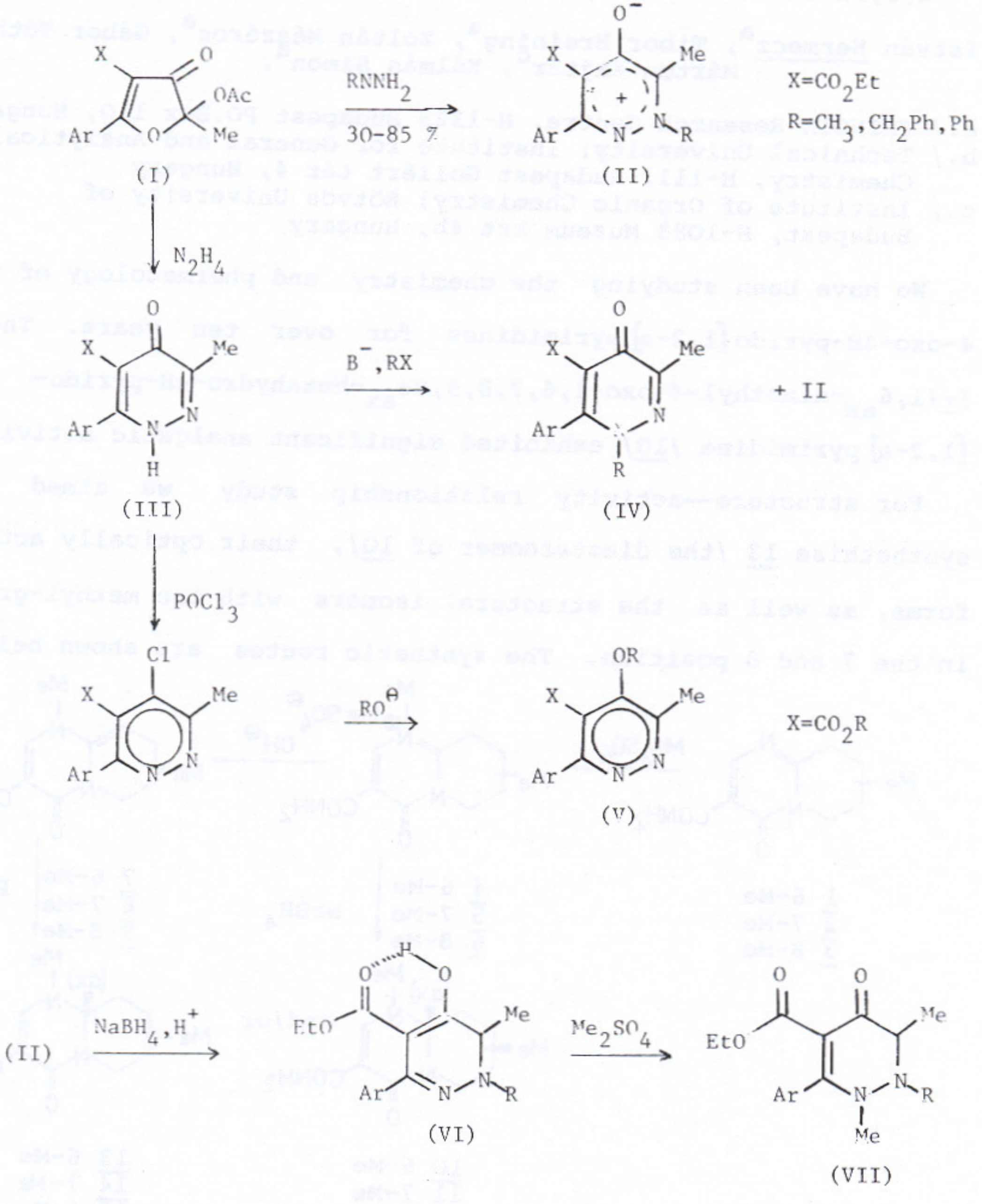
X
O
OAc
Ar
Me
(I)
RNNH$_2$
30-85 %
O$^-$
X
Me
+
Ar
N
N
R
(II)
X=CO$_2$Et
R=CH$_3$,CH$_2$Ph,Ph
N$_2$H$_4$
O
X
Me
N
Ar
N
H
(III)
B$^-$,RX
O
X
Me
N
Ar
N
R
(IV)
+ II
POCl$_3$
Cl
X
Me
N
Ar
N
RO$^\ominus$
OR
X
Me
N
Ar
N
(V)
X=CO$_2$R
(II)
NaBH$_4$,H$^+$
H
O
O
EtO
Me
Ar
N
N
R
(VI)
Me$_2$SO$_4$
O
O
EtO
Me
Ar
N
N
R
Me
(VII)