

ELECTRON TRANSFER PROCESSES: REACTION OF INDOLIZINES WITH
DIAZONIO IONS OR CRIPTO-IONS

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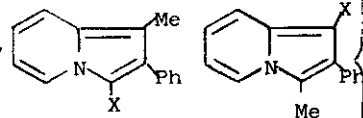
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Electron rich N-heterocyclic compounds with a low oxidation potential ($E_{1/2}$) can promote radicalisation of electrophiles R-Y having weak bonds ($R=-NO, -NO_2, -N_2Ar, -O-COPh, \dots$) and Y being an organic residue having some electron affinity (MAH=Molecule Assisted Homolysis)(1), the R-Y bond being the weaker the higher the electron affinity of the Y residue, so that R-Y behave as ionic form (crip-to-ions of Merwein)(2). In this case the radical cation can give dimerisation, followed by oxidation, or the two radicals can entereact with formation of Whe=land intermediate and final products.

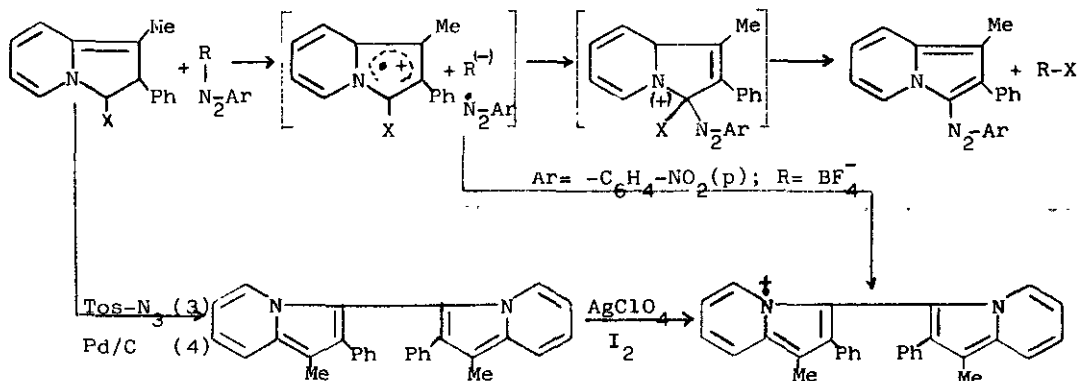
Reagents : $Ar-\overset{(+)}{N}_2\overset{(-)}{Y}, \quad Ph_2N-N=N-Ph, \quad Ar-SO_2-N=N-Ph,$

a : X = -H ($E_{1/2}=0.20$ V)
b : X = -SPh ($E_{1/2}=0.38$ V)
c : X = $-\overset{|}{CH}_2$ ($E_{1/2}=0.18$ V)
(3'-indolizil)
d : X = $-N_2Ph$ ($E_{1/2}=0.37$ V)
e : X = $-COMe$ ($E_{1/2}=0.58$ V)
f : X = $-CHO$ ($E_{1/2}=0.66$ V)



a : X = -H ($E_{1/2}=0.21$ V)
b : X = -SMe ($E_{1/2}=0.23$ V)
c : X = -SPh ($E_{1/2}=0.38$ V)
d : X = $-\overset{|}{CH}_2$ ($E_{1/2}=0.08$ V)
(1'-indolizil)
e : X = $-N_2Ph$ ($E_{1/2}=0.34$ V)
f : X = $-COMe$ ($E_{1/2}=0.55$ V)
g : X = $-CHO$ ($E_{1/2}=0.61$ V)

Mechanism :



- (1) W. Pryor, J. H. Coco and R. N. Houk, J. Am. Chem. Soc. 96, 5591 (1974)
- (2) L. Horner, Angew. Chem. 62, 359 (1950)
- (3) M. Colonna, L. Greci, P. Bruni and G. Padovano, Gazz. Chim. Ital. 101, 396 (1971)
- (4) H. Kakehi, S. Ito, A. Hamaguchi and T. Okano, Bull. Chem. Soc. Jp. 54, 2833 (1981)