

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

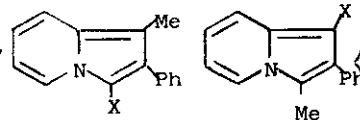
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Electron rich N-heterocyclic compounds with a low oxidation potential ($E_{1/2}$) can promote radicalisation of electrophiles R-Y having weak bonds ($R=-NO, -NO_2, -N_2Ar, -O-COPh, \dots$) and Y being an organic residue having some electron affinity (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 (cripto-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 Wheeler intermediate and final products.

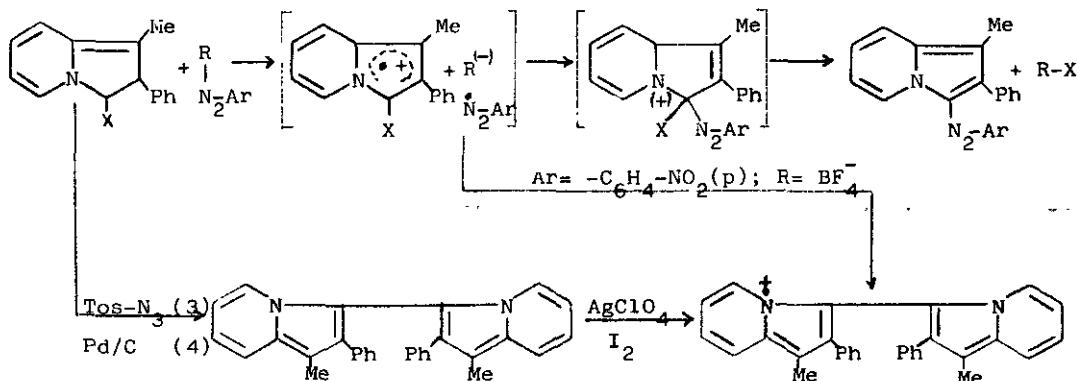
Reagents : $Ar-\overset{(+)}{N}_2\overset{(-)}{Y}, Ph_2N-N=N-Ph, Ar-SO_2-N=N-Ph,$

a : X = -H ($E_{1/2}=0.20$ V)
b : X = -SPh ($E_{1/2}=0.38$ V)
c : X = $-\overset{|}{C}H_2$ ($E_{1/2}=0.18$ 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 = $-\overset{|}{C}H_2$ ($E_{1/2}=0.08$ 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.Takehi, S.Ito, A.Hamaguchi and T.Okano, Bull. Chem. Soc. Jp. 54, 2833(1981)