REACTIONS OF 1,2,3-TRIAZINES WITH NUCLEOPHILIC REAGENTS

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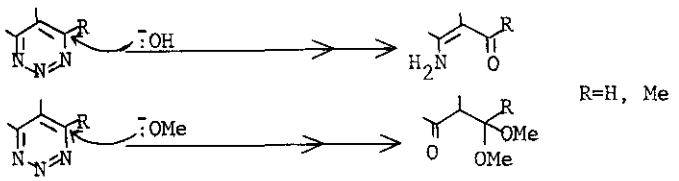
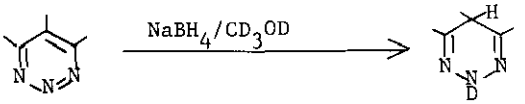
Among six-membered aromatic heterocyclic compounds, 1,2,3-triazines are regarded as highly π-deficient, and the carbons at 4- and 6-positions are expected to have less electron densities than that at 5-position, according to an SCF calculation. We now report the reactions of 1,2,3-triazines and their derivatives with nucleophiles.

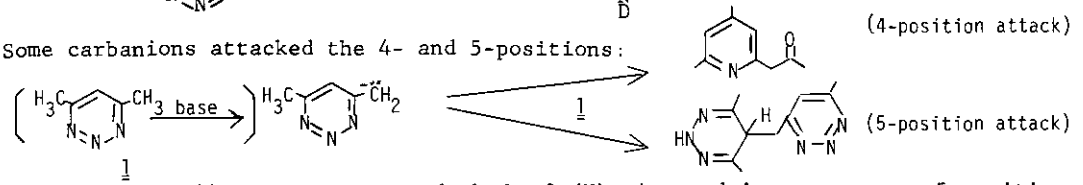
Hydroxide and methoxide ions attacked the 4- (6-)position of the triazines:



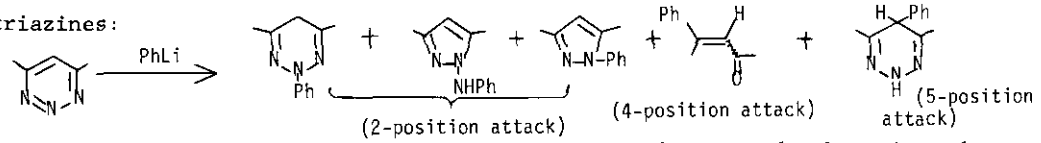
As already reported, the 5-position is the exclusively active site to $NaBH_4$ reduction:



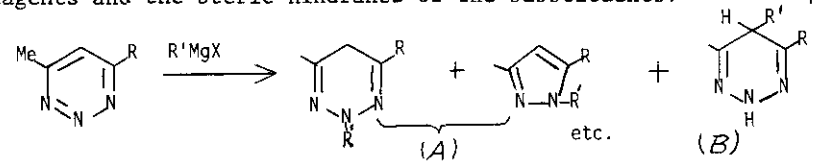
Some carbanions attacked the 4- and 5-positions:



Some organometallic reagents attacked the 2-(N), 4-, and in some cases, 5-positions of triazines:



Next case suggests the high reactivity of the 5-position towards the Grignard reagents and the steric hindrance of the substituents.



R=H, R'MgX=PhMgBr
A≪B
R=Me, R'MgX=MeMgI
A∼B
R=Me, R'MgX=PhMgBr
A>B

Reactivities of quaternary salts and N-oxides of triazines will also be discussed.