SYNTHESIS AND REACTIONS OF 1,2,3-TRIAZINES

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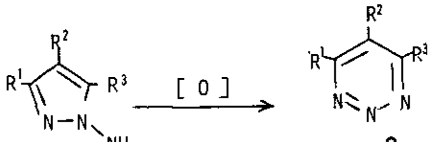
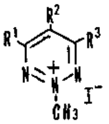
Monocyclic 1,2,3-triazines were synthesized and their properties were investigated.

Synthesis Oxidation of methyl- and/or phenyl-substituted N-aminopyrazoles(1) using $Pb(AcO)_4$ afforded 1,2,3-triazines(2) although the method afforded only a trace amount of unsubstituted one (2, $R^1=R^2=R^3=H$). *The latter was obtained by* nickel peroxide-AcOH oxidation of 1 in 18% yield. Isolated 1,2,3-triazines were moderately stable and the exact molecular structure of unsubstituted one was examined by X-ray crystallography.



Quaternization Methylation of 2 with MeI afforded 2-methylated salts(3). N-Amination with O-mesitylenesulfonylhydroxylamine gave 2-imino compounds(4) which existed in the monomeric form in a solution($CHCl_3$). Although N-oxidation of 2 with m-chloroperbenzoic acid afforded the corresponding 1-oxides(5) and 2-oxides(6) when $R^1 \neq Ph$, only 2-oxides were obtained when $R^1=R^2=Ph$. The molecular structure of 4,5,6-triphenyl-1,2,3-triazine 2-oxide was confirmed by X-ray analysis. The methylation of the oxide 6 with Me_2SO_4 afforded N-methylated product(7) although 5 decomposed under the quaternizing conditions.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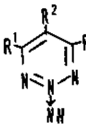
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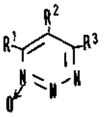
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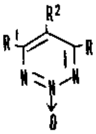
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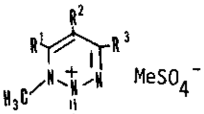
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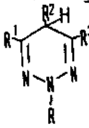
Reduction Catalytic reduction of 2, 5, and 6 gave the 2,5-dihydro compounds(8, R=H). Reduction of 2 and 3 with sodium borohydride(SBH) also yielded 8(R=H and Me). The major products of SBH reduction of the oxide 5 were 2 and 8, while the major products from 6 were 1,4,5,6-tetrahydro compounds 9 and/or 10. SBH reduction of 7 yielded the 1,6-dihydro compounds 11 as major products.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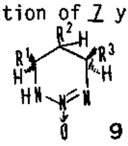
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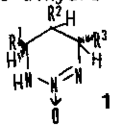
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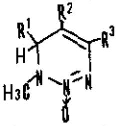
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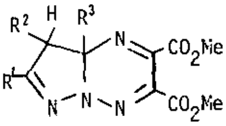
Other Reactions 1,3-Dipolar cycloaddition of 4 with dimethyl acetylenedicarboxylate yielded the rearranged adducts(12). Results of other reactions will be stated.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References: JCS Chem.Comm.,1980, 1182; JCS Chem.Comm.,1981, 1174;
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