بحث رقم 4 (رسالة الدكتوراه)

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Title:	STUDIES ON OXAZIRIDINES AND 1,2,4-OXADIAZOLES (OXAZIRIDENES, OXADIAZOLES)
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The first work in this thesis discusses the preparation of N-alkyl- and N-alkoxyalkyloxaziridines and their isomeric nitrones. The products from their hydrolysis and N-substituted hydroxylamines and the parent carbonyl compounds. The site of protonation is on the oxygen of 3-aryloxaziridines leading to C-O bond cleavage to give protonated nitrones. The common intermediates (protonated nitrone) have been seen by $\sp1$H nmr and uv spectroscopy. Kinetic results showed the hydrolyses of 3-phenyl- and 3-p-nitrophenyloxaziridines to be slower than the corresponding nitrones. The 3-p-methoxyphenyloxaziridines hydrolysed faster than the nitrones. Also, hydrolyses were studied in the absence of acid. Similar studies on 3,3-diaryloxaziridines and C,C-diarylnitrones are reported. The protonated nitrones are not intermediates in the hydrolysis of these oxaziridines.

Secondly, mechanisms of reactions of some 3,5-disubstituted-1,2,4-oxadiazoles with nucleophiles are studied. The reactions of 1,2,4-oxadiazoles with Ph$\sb3$P were studied, the products (triphenylphosphine imines) were identified. From the LFE correlation with $\sigma\sp-$, a mechanism was deduced. Thermolysis of the imines produced Ph$\sb3$PO and nitriles. The stability of these imines depends on the group attached the carbonyl function. The relative rate of the thermolysis of N-aroly-N$\sp\prime$-triphenylphosphorylidine-benzamidines was studied, found to be first order and from the correlation with σ, a mechanism was deduced. The overall reaction of oxadiazoles with Ph$\sb3$P gave Ph$\sb3$PO and nitriles via the imine intermediate. Correlation between $\sp{13}$C nmr chemical shifts and substituent effects have been studied for several 1,4-disubstituted benzene systems, and their side-chains, showing that inductive effects are predominant at the α-carbon. The reverse inductive contribution observed is explained in terms of a π-polarisation mechanism.