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# BASE PROMOTED ISOMERIZATION OF THE OXAZIRIDINE RING SYSTEM

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Emmons has observed that oxaziridines containing a 2-methyl or 2-methinyl substituent react rapidly with alkaline solutions to produce ammonia(1)(2).

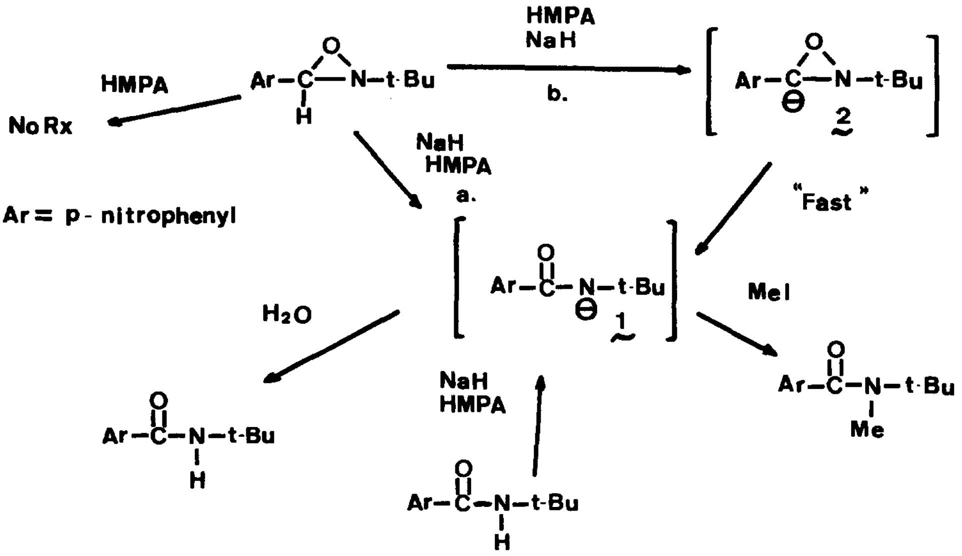
In contrast to these results, oxaziridines having no such active protons were found to be inert towards strong base(1)(2).

We have found that 2-t-butyl-3-p-nitrophenyloxaziridine when treated with one equivalent of sodium hydride in hexamethylphosphoramide (HMPA) does indeed react readily to produce a blood red solution of the anion 1. When a solution of the anion was quenched with water and products isolated by ether extraction, an 82.5% yield of N-t-butyl-p-nitrobenzamide was obtained. The physical properties of the amide isolated were in complete agreement with a sample of N-t-butyl-p-nitrobenzamide prepared from p-nitrobenzoyl chloride and t-butyl amine(3)(4).

In a like manner, a 72.0% yield of N-t-butyl-N-methyl-p-nitrobenzamide was obtained when anion 1 was quenched with methyl iodide. A comparison sample of N-t-butyl-N-methyl-p-nitrobenzamide was obtained in 87.0% yield from the reaction of N-t-butyl-p-nitrobenzamide with sodium hydride in HMPA followed by treatment of the resultant anion with methyl iodide(5).

To be sure that the rearrangement was not caused by the solvent a sample of 2-t-butyl-3-p-nitrophenyloxaziridine was stirred for 10 hrs in HMPA. Normal workup gave 97% recovery of starting material unchanged. The results are summarized in Chart I.

CHART I



Two possible mechanistic paths to account for the observed results are also shown in Chart I. First, loss of the oxaziridine proton with concerted ring opening would give anion 1 and hence the observed products (mechanism a). A second possibility (mechanism b) would be a stepwise loss of proton resulting in anion 2 followed by rearrangement to the aforementioned anion 1. Anion 2 is of considerable interest in that it contains $6\pi$ electrons and could be considered formally aromatic.

An attempt to trap anion 2 by reacting 2-t-butyl-3-p-nitrophenyloxaziridine with sodium hydride in the presence of one equivalent of methyl iodide resulted in the isolation of only starting oxaziridine and N-t-butyl-N-methyl-p-nitrobenzamide. Furthermore, when the oxaziridine was treated with sodium hydride in HMPA, and the reaction mixture was examined with NMR at room temperature, loss of the signal at $4.75\ \delta$ (oxaziridine ring proton) was seen to be complete after ca 5 min. Quenching with $D_2O$ at this juncture gave a 78.0% of deuterated benzamide with no sign of any deuterated oxaziridine(6).

The two aforementioned experiments indicate that if anion 2 is forming at all, it undergoes rapid rearrangement to anion 1 prior to reaction with electrophiles. In this light, the concerted mechanism is a very distinct possibility.

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4. The I.R., N.M.R., and T.L.C. behavior of N-t-butyl-p-nitrobenzamide obtained from both procedures was identical, and both samples melted at 161-136°(3) with no depression when mixed.

5. The I.R., N.M.R., and T.L.C. behavior of N-t-butyl-N-methyl-p-nitrobenzamide from both procedures was identical, and both samples melted at 120-122° with no depression when mixed. A sample crystallized from petroleum ether/ether, m.p. 126-127° gave correct analysis.

6. N.M.R. and I.R. analysis.