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OXIDATION OF CYCLOPROPYLAMINES AND 2-PHENYLAZIRIDINE WITH LEAD TETRAACETATE

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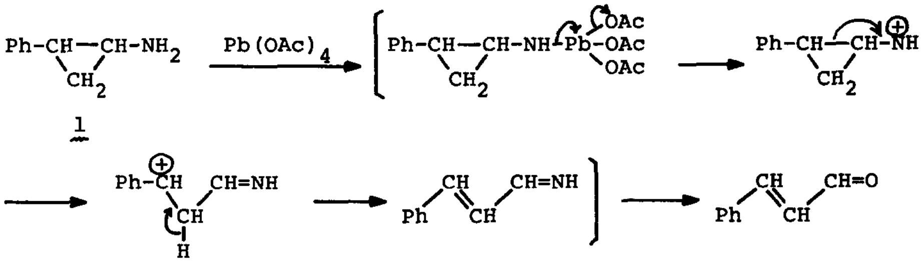
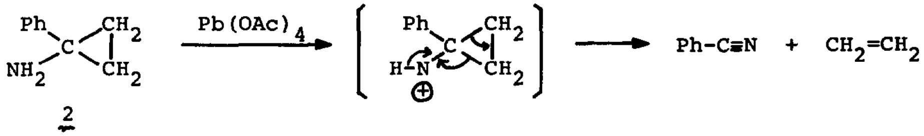
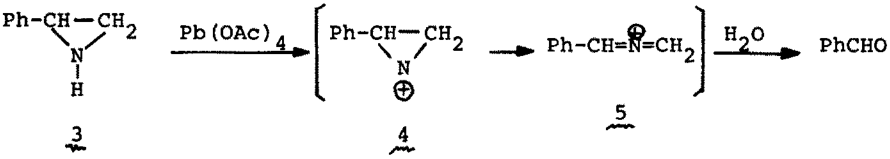
Attention has been focused on the oxidation of amines with metals in higher valency[1] in order to obtain information on reactive species such as nitrenium ions, nitrogen radicals, and nitrenes.[2] This communication deals with the lead tetraacetate oxidation of cyclopropylamines and 2-phenylaziridine.

The trans isomer of 2-phenylcyclopropylamine (1) in dichloromethane was treated with one equivalent of lead tetraacetate at -78°. Filtration of the precipitated salt and the subsequent work-up gave trans-cinnamaldehyde in 79% yield. The oxidation of the cis isomer of 1 also gave trans-cinnamaldehyde in 84% yield. Oxidation of 1-phenylcyclopropylamine (2) resulted in the formation of benzonitrile (69% yield), the accompanying ethylene being identified as 1,2-dibromoethane. The cleavage represents a new type of fragmentation. The pathway of both reactions can be explained by assuming nitrenium ions as reactive species.[3] In order to confirm this,[4] the amines trans-1 and 2 were treated successively with sodium hypochlorite and with silver perchlorate or simply with activated alumina. The products obtained under such nitrenium ion producing conditions were the same as in the above oxidation (34% yield of trans-cinnamaldehyde and 21% of benzonitrile respectively).[5]





Oxidation of 2-phenylaziridine (3) gave benzaldehyde as a sole product (42% yield), possibly via the nitrenium ion intermediate (4) and the 2-aza-allenyl cation (5)[6] successively. Hydrolysis of 5 affords benzaldehyde.[7] Since aziridines are easily obtained from olefins,[8] the present ring cleavage may find its application in the conversion of olefins to dicarbonyl compounds. Studies on this line are now progressing.



References and Footnotes

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