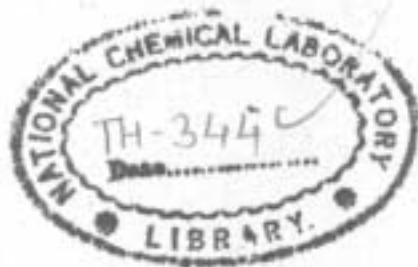


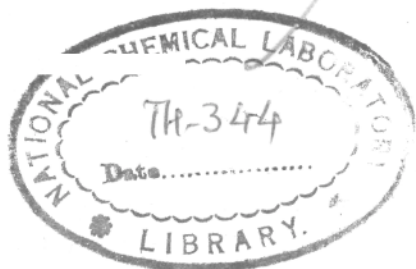
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SYNTHESIS OF HETEROCYCLIC COMPOUNDS  
CONTAINING NITROGEN, OXYGEN  
AND PHOSPHORUS  
A THESIS  
SUBMITTED TO THE  
UNIVERSITY OF POONA  
FOR THE DEGREE OF  
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S U M M A R Y  
CHAPTER I

A brief review of earlier work, relevant to that discussed in this chapter, is presented.

The synthesis of 2-chloro-3,6-diaryl-3,4-dihydro-1,3,2-Oxazaphosphorin-2-oxides, by the interaction of phosphorus oxychloride and triethylamine with aryl  $\beta$ -aryl-aminoethyl ketones obtained by the condensations of substituted anilines with Mannich base hydrochlorides of various aromatic ketones such as acetophenone, p-methoxyacetophenone, p-nitroacetophenone, 2-acetylthiophene, 2-acetylnaphthalene, is exhaustively covered along with the mechanisms involved.

CHAPTER II A

A short review of syntheses and biological properties of cyclophosphamide is presented,

The synthesis of 2 [bis(2-chloroethyl)amino]-3,6-diaryl-3,4-dihydro-1,3,2-oxazaphosphorin-2-oxides by replacement of chloro group in the corresponding dihydro-oxazaphosphorins by 2-chloroethylamino group along with other synthesis are discussed in this portion.

CHAPTER II B

1-Aryl-4-arylamino-1-propanols, obtained by the sodium borohydride reduction of the respective aryl  $\beta$ -aryl-aminoethyl ketones, treated with POCl<sub>3</sub> and Et<sub>3</sub>N yielded 2-chloro-3,6-diaryltetrahydro-1,3,2-oxazaphosphorin-2-oxides. This synthesis along with replacement reactions of chloro-substituent at 2-position of the oxazaphosphorin ring by aliphatic secondary amines is described in this part.

CHAPTER III A

Various reactions of dihydro-oxazaphosphorin ring system enlisted below are covered in this chapter.

- (a) Replacement of -Cl substituent on phosphorus by various nucleophiles viz. azide, fluoro, sec, alkylamine, ethoxy, hydroxy, etc.
- (b) Contraction of the ring to yield azetine, quinoline and tetrahydroquinoline by thermal and photo-chemical modes.
- (c) Hydrogenation of the double bond by Na/liq. NH<sub>3</sub>, Raney Ni; H<sub>2</sub>, Pd/C in a bid to obtain tetrahydrooxazaphosphorins.
- (d) Allylic bromination and oxidations along with hydride abstraction reactions.

CHAPTER III B

Mass spectral cycloreversion reactions of 2-chloro-3,6-diaryl-3,4-dihydro-1,3,2-oxazaphosphorin-2-oxides<sup>2</sup> with emphasis on the retro Diels-Alder fragmentation mode in these oxazaphosphorins is discussed in great detail along with other fragmentation modes.

REFERENCES

1. B. D. Tilak, V. N. Gogte and A.S. Modak, Ind. J. Chem. 5 20B, 414-5 (1981).
2. V. N. Gogte, F.S. Kulkarni, A. S. Modak and B. D, Tilak, Org. Mass Spectrom., (in press).