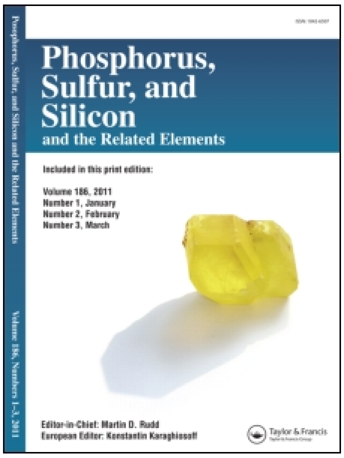

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Condensed Heterocycles VIA *a*-Heterosubstituted Phosphonate Carbanions

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In a series of papers we showed that α-heterosubstituted phosphonate carbanions in a modified Horner-Emmons reaction are useful for the preparation of a variety of classes of compounds such as enamines, desoxybenzoines, trisubstituted vinyl chlorides, enynes, and acetylenes. We found that strategically substituted diphenyl α-(aminoaryl)-α-[4-nitrophenyl] methanephosphonates react with phenylpropynal to the expected enamines. Without isolation they could be cyclized to the corresponding condensed N-heterocycles. For the reported syntheses the following arylamines were used: 4-amino-2-methylquinoline, 5-aminoquinoline, 8-aminoquinoline, 1-amino-4-nitronaphthalene, 5-amino-2,3-dihydro-1H-indene, 1, 5-diaminonaphthalene, and 1-aminoanthracene. These aminoarylsubstituted diphenyl methanephosphonates yielded the following 4-nitrophenyl substituted heterocycles: benzo[h][1,6]naphthyridine, [1,7]phenanthroline, [1,10]phenanthroline, benzo[h]quinoline, quino[8,7,h]quinoline, and naphtho[2,3,h]quinoline. The structures of these heterocycles were assigned on the basis of 1H-NMR-spectra, mass spectra, and X-ray structure analyses.

INTRODUCTION

In a series of papers from this laboratory it was demonstrated that α-heterosubstituted methanephosphonates and their anions are useful tools for the synthesis of enamines,(1) amidines,(2) substituted vinyl chlorides,(3) acetylenes,(4,5) substituted ferrocenes(6) and some heterocycles.(7,8) In the present paper the synthesis of indoles, quinolines and benzo[b]furans is briefly mentioned, however, it is also shown that anions derived of α-heterosubstituted methanephosphonates can be used for the synthesis of rather complex condensed N-heterocycles.(9)

RESULTS AND DISCUSSION.

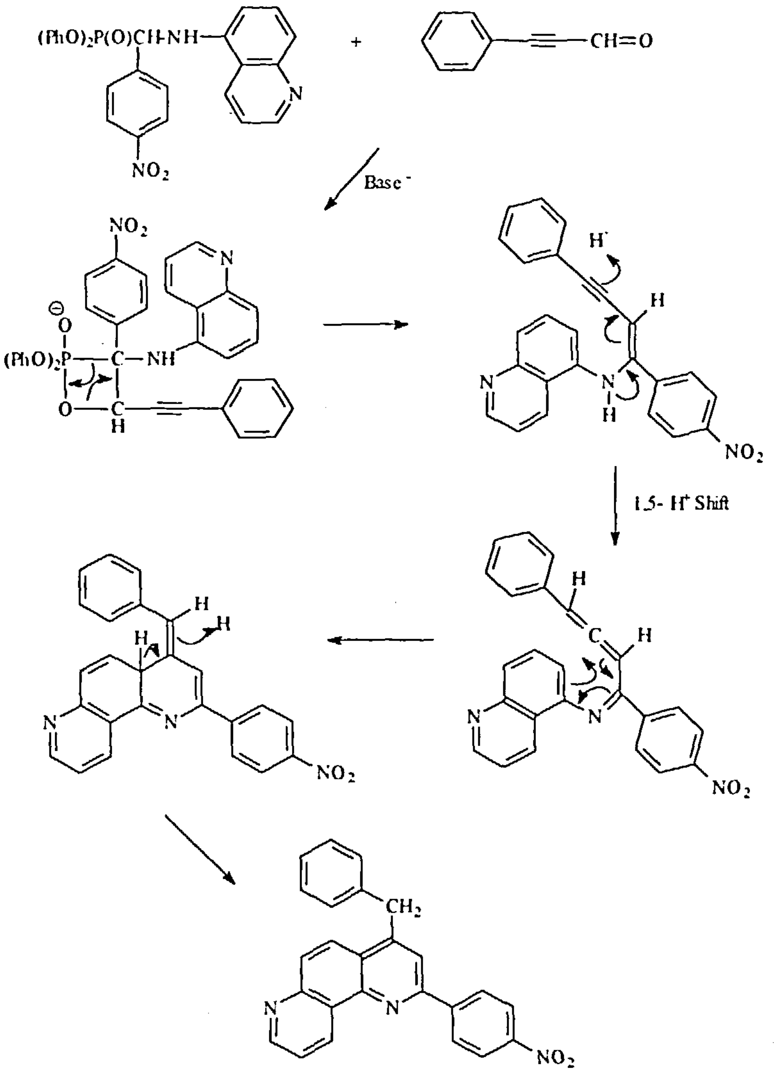
Indoles and Benzo[b]furans.

The anion derived of dimethyl or diphenyl 1-phenyl-(4-nitroanilino)-methane phosphonate, **1**, when reacted with substituted o-nitrobenzaldehydes yields in a typical Horner-Emmons reaction the expected enamine which upon hydrolysis gives 2-nitrobenzyl aryl ketones. These ketones can be reduced in good yields to substituted 1-arylindoles..

Indoles and Quinolines

By employing anions derived of 1-(4-nitroaniline) 1-(2′-styryl)-phosphonates, **2**, the expected vinylogous enamines and, after hydrolysis, the corresponding vinylogous desoxybenzoins were formed. Inspecting these species it becomes evident that depending on whether they are synthesized from a phosphonate derived of o-nitrocinnamaldehyde or one obtained using o-nitrobenzaldehyde one arrives at isomeric desoxbenzoines. Also the synthesis of novel enynamines was undertaken. These species could be obtained by reacting anion **1** with phenylpropargylaldehyde. Upon hydrolysis of these novel enynamines under vacuum and reflux temperature a surprising reaction occurred. Instead of yielding the expected yne analogous desoxybenzoine, the enynamine, cyclized to yield substituted 4-benzyl-2-phenylquinolines. Going through the same sequence of reaction, but starting with a phosphonate derived of 1-amino-4-nitronaphthalene a benzoquinoline, namely 4-benzyl-6-nitro-2-(4-nitrophenyl)-benzo[h]quinoline was obtained. From a phosphonate derived of 8-aminoquinoline 4-benzyl-2-(4-nitrophenyl)-[1,10]-phenanthridine was formed. Its assigned structure was secured by an X-ray analysis. 4-Benzyl-2-(4-nitrophenyl)-[1,7]-phenanthroline and 4-benzyl-5-methyl-2-(4-nitrophenyl)-benzo[h]-1,6-naphthiridine were isolated by using phosphonates derived of 5-amino- and 4-amino-3-methylquinoline resp. Employing 1-aminoanthracene, the tetracyclic system 4-benzyl-2-(4-nitrophenyl)-naphtho[h]quinoline resulted. Still another tetracyclic system could be prepared by starting with a phosphonate derived of 1, 5-diaminonaphthaline. Using, however, a phosphonate derived from 1, 2-diaminobenzene, not the expected 4, 7-diphenyl-2, 7-di-(4-nitrophenyl)-[1,10]-phenanthroline could be isolated but instead 1-(4-nitrobenzyl)-2-(4-nitrophenyl)-benzimidazole was formed. As expected, when running the reaction sequence with a phosphonate obtained from 5-amino-2, 3-dihydro-1H-indene as expected two isomers were found in the reaction mixture, the 4-benzyl-2-(4-nitrophenyl)-5, 6-trimethylenequinoline as the major product and the 6, 7-isomer representing the minor product

The aboev described heterocycles were synthesized from the appropriate phosphonates and an arpmatic amine. In figure **1** the sequence of reactions necessary tc get the listed heterocycles is outlined. As an example the synthesis of 4-benzyl-2-(4-nitrophenyl-[1.7])phenanthroline is given.



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