Reactions of *o*-Phenylenediamine and Some Iminophosphorane Derivatives with Dimethyl Acetylenedicarboxylate

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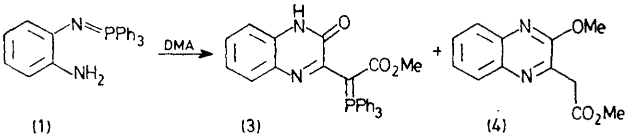
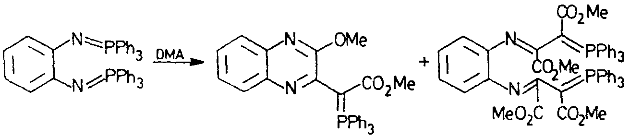
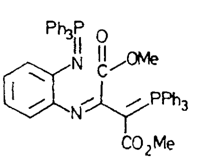
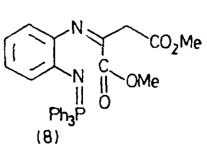
Summary Reactions of certain iminotriphenylphosphoranes derived from *o*-phenylenediamine with dimethyl acetylenedicarboxylate (DMA) involve Wittig-like elimination of triphenylphosphine oxide from an ester carbonyl group; *o*-phenylenediamine reacts with DMA in ether to give a mixture of tautomers.

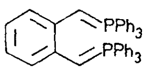
IN continuing our studies of iminophosphoranes[1] we have investigated the reactions of DMA with the mono- and bis-iminotriphenylphosphoranes (**1**) and (**2**) derived, by methods similar to that of Horner and Oediger,[2] from *o*-phenylenediamine.

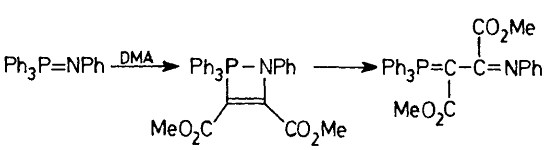

(1) (3) (4)


(2) (5) (6)


(7)

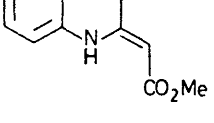

(8)

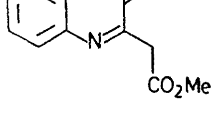

(9)


SCHEME

The products, which gave satisfactory spectral and microanalytical results, were found to be the ylide (**3**), m.p. 195—196 °C, and the quinoxaline (**4**), m.p. 67—68 °C, from (**1**); and the mono- and bis-ylides (**5**), m.p. 195—196 °C and (**6**), m.p. 290—291 °C, from (**2**). Simple iminophosphoranes are known to react with the acetylene through an intermediate phosphazacyclobutene (Scheme). A similar mechanism explains the formation of the bis-ylide (**6**) and the mono-ylide (**3**), the latter involving subsequent amide formation between the primary amine and an ester group.

Compound (**5**) probably arises from an intramolecular Wittig reaction on an initially formed mono-adduct (**7**), and


(A)


(B)

compound (**4**) from a similar elimination of triphenylphosphine oxide from the intermediate (**8**), the product of the addition of the amino group to the acetylenic ester.†

The reactions forming compounds (**4**) and (**5**) are remarkable in that they involve iminophosphoranes in Wittig reactions with ester carbonyl groups, a previously unrecognised pathway. Methylenephosphoranes containing ester substituents are frequently used (without intramolecular side-reactions of this sort) in the synthesis of unsaturated esters,[6] and the formation of aryl ethers in the present work is probably caused by the aromatic stability of the products and the close proximity of the appropriate groups in the intermediates. The bis-ylide (**9**) undergoes a similar reaction[7] and stabilised methylenephosphoranes react with strongly electrophilic esters to give vinyl ethers,[8] but no comparable reaction of iminophosphoranes has been reported to date.

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† *o*-Phenylenediamine itself reacts with DMA[4,5] in refluxing ether to give a mixture of the tautomers (A) and (B), which can be readily distinguished by their i.r. spectra [ν (C=O) 1695 (A) and 1740 cm^{-1} (B)] and n.m.r. spectra in $(CD_3)_2SO$ [τ 4·5 (s, CH) (A) and 6·1 (s, CH_2) (B)]. In CF_3CO_2D solution the tautomers rapidly equilibrate [τ 2—3 (m, 4H, Ar) and 6·01 (lit.[4] 4·1) (s, OMe)]. The ν (C=O) frequency reported for compound (A)[4] (1740 cm^{-1}) may have been determined on a mixture of the tautomers.

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