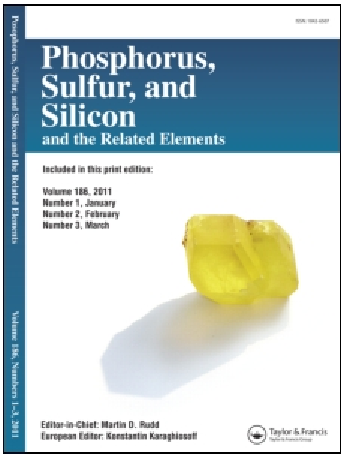

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Ylide Analogues of Fulvalenes. A Stevens Rearrangement of a Phosphonium Ylide

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YLIDE ANALOGUES OF FULVALENES. A STEVENS REARRANGEMENT OF A PHOSPHONIUM YLIDE.

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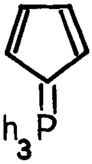
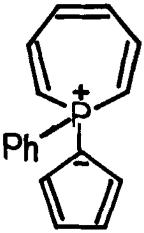
Abstract Fulvalene-ylides have been synthesised. The pentafulvalene ylide analogue (8) provides the first Stevens rearrangement of a phosphonium ylide and, through reaction with DMAD, a novel 1-phosphabicyclo[4.2.1]octatriene ylide.

INTRODUCTION

Phosphonium ylide analogues (e.g. 1) of fulvenes have been prepared.[1] However, in spite of the possibility of aromatic (e.g. 2) and, unlike fulvalenes, anti-aromatic (e.g. 3) contributions, and the intrinsic interest of extended π-systems involving d-orbitals, the analogous fulvalene-ylides are almost unknown.[2]



(1)



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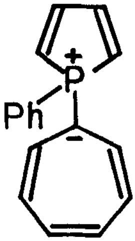
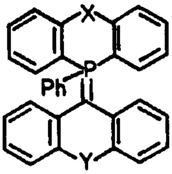


(3)

RESULTS

Relatively simple routes to the highly-coloured phenyl-substituted derivatives (4), (5), (6), (7) and (8) have been developed from the corresponding cyclic phosphines via quarternisation and base-treatment of the resulting phosphonium salt. Compounds (4-6)

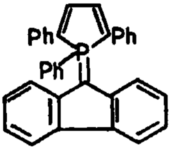


(4) X = CH_2CH_2, Y = Bond

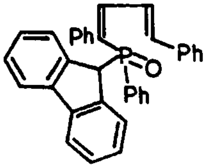
(5) X = CH=CH, Y = Bond

(6) X = Y = Bond

(7) X = Bond, Y = CH=CH



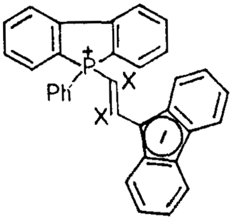
(8)



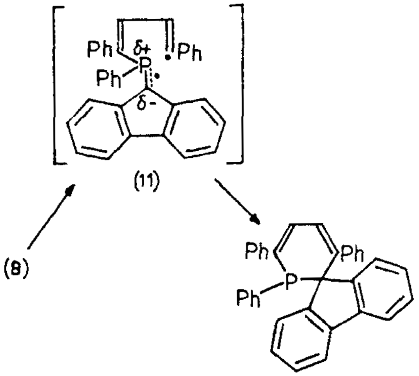
(9)

undergo normal Wittig reactions and alkaline hydrolysis to give the ring-retained phosphine oxide. However, ylide (8) shows anomalous behaviour in this and other reactions. Formation of (8), by aqueous base treatment of its phosphonium salt at 10°, was always accompanied by moderate amounts of the ring-opened phosphine oxide (9). In spite of the accepted common mechanism of hydrolysis,[3] the ylide (8) did not hydrolyse under similar conditions. However, after refluxing for several days with 2 M aqueous sodium hydroxide,(8) gave 1,2,5-triphenylphosphole oxide and fluorene.

The reaction with dimethyl acetylene dicarboxylate (DMAD) was of interest since it offered a potential route to compounds with extended conjugation. Indeed, reactions with (4-6) provided highly coloured 1:1 adducts which were shown to be isomeric mixtures by n.m.r; which of the two possibilities (e.g. 10) for restricted rotation is the source of these isomers is not yet clear.[4]



(10)



(12)

A further example of the anomalous behaviour of (8) was provided by its thermal instability. Refluxing in toluene gives a virtually quantitative yield of an isomeric phosphine (12); m/z 476(100); ^{31}P [^{1}H] δ_{CDCl_3} +27.6; λ_{max} (CH_3CN) = 353 nm (log Σ = 4.2). The u.v. spectrum and low intensity of m/z 165 (fluorenyl) for (12) suggest a spiro-1,2-dihydrophosphorin structure and this was confirmed by an X-ray structural analysis

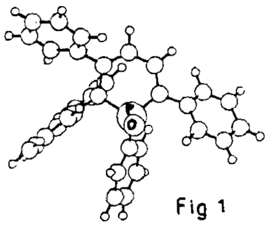
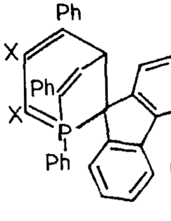


Fig 1



(13)

of the corresponding phosphine oxide (Figure 1). The thermolysis of (8) provides the first authenticated[5] example of an uncatalysed Stevens rearrangement of a phosphonium ylide, presumably *via* the intermediate (11),[6] although we have been unable to observe CIDNP effects (^{1}H or ^{31}P).

The reaction of (8) with DMAD gave a 1:1 adduct analogous to (10) and an isomeric product (13). The latter product was derived from the Stevens rearrangement product (12) as shown by a reaction of (12) with DMAD to give (13) [m/z 618(28), 346(15) and 272(100)]; in excellent yield. The mass spectrum suggests that (13) is a simple Diels-Alder adduct; however, X-ray structural analysis established a novel 1-phosphabicyclo[4.2.1]octatriene structure for (13) and the failure of the phosphine oxide derived from (12) to react with DMAD suggests that (13) is derived from initial nucleophilic attack of phosphorus on DMAD, presumably followed by cyclisation and rearrangement.

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