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Benzothiadiphosphole as Phosphorus Donating Reagent for a New Route to 2H-1,2,3-Diazaphosphole Derivatives

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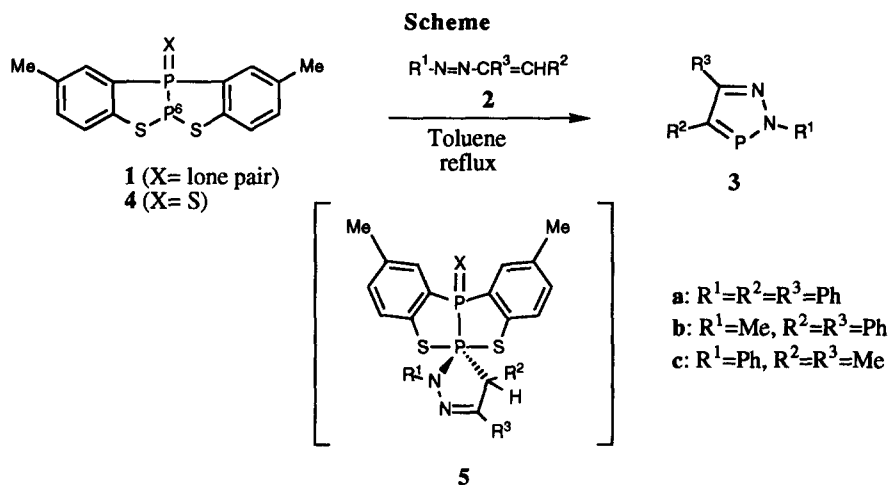
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Abstract: Conjugated azoalkenes **2** react at reflux toluene with fused benzothiadiphosphole **1** (or **4**) to give the diazaphosphole **3** in 25-52% yields. With this route it is possible to isolate the so far unknown **3a** which is difficult to obtain in other reported conditions. The P atom involved in this cycloaddition is the one between the two S atoms.

2H-1,2,3-Diazaphospholes are well known¹ and were intensively studied by many chemists². Generally these compounds are prepared by reaction of hydrazones³ or azoalkanes⁴ with PCl_3 , but in these reaction conditions is very difficult or impossible to obtain the 2-phenyl derivatives of 2H-1,2,3-diazaphosphole. In fact, during attempts to prepare phosphonium salts of 2,3,4,5-tetraphenyl-3,4-dihydro-2H-1,2,3-diazaphosphole⁵ or to obtain 2,4,5-triphenyl-2H-1,2,3-diazaphosphole⁶ (**3a**), the formation of 2,3-diphenylindole, as prevalent product, was noted. Owing to this unexpected result we realized⁷ that the difficulty to obtain **3a** from the above reaction between the corresponding ketone arylhydrazone and PCl_3 could be explained reasonably as a fastly occurring conversion, in these reaction conditions, of diazaphosphole **3a** or its precursors to 2,3-diphenylindole. As a matter of fact, we found⁸ a general procedure to obtain 2,3-disubstituted indoles in very good yields, by reaction at room temperature between ketone arylhydrazones and PCl_3 .

Recently we devised⁹ the facile and highly stereoselective one-pot synthesis of *cis*-2,10-dimethyl-[1,2,3]-benzothiadiphospholo[2,3-*b*][1,2,3]benzothiadiphosphole (**1**), a new fused heterocyclic system containing a P-P(S)₂ unit, by treating *p*-methylthioanisole with AlCl_3 and PCl_3 . It is an air insensitive solid which can be produced in 20-40 g scale and stored for some years without particular precaution. However it presents an unusual and high reactivity¹⁰, presumably due to the phosphorus atom in the 6-position, in most cases giving unexpected and/or unidentifiable products.

In order to explore more thoroughly the peculiar reactivity of compound **1**, we thought to investigate its behaviour in the reaction with conjugated azoalkenes, which from our early studies are known to react with phosphorus halides¹¹ and phosphites¹², but not with trisubstituted phosphines. Unexpectedly, all the isomers of phenylazostilbene (**2a**) react with **1** to afford the so far unknown diazaphosphole **3a**, and this procedure represents a new route to obtain diazaphosphole derivatives (see Scheme).



The reaction of **1** with the requisite azoalkene¹³ **2** was carried out at reflux toluene under argon, for about 3 h. The course of the reaction was followed by the vanishing of the colour of the azoalkene (red or orange-yellow) and it was monitored by t.l.c. and g.c.-m.s.. After evaporation of the solvent, products were separated from the reaction mixture by flash chromatography on Florisil or by distillation obtaining **3** in 25-52% yields. It should be observed that small amounts of **3** were also noted when the reaction was carried out at room temperature but with longer reaction times. Compound **3a** was isolated as an high air sensitive white solid and its low isolated yield (25%) is due to its partial decomposition during the work-up or on Florisil column to give mainly 2,3-diphenylindole. Compound **3b** was isolated (52% yield) by bulb to bulb distillation as a glassy oil (b.p. 165-167°C, 0.01mmHg). The structures of **3a,b** were assigned on the basis of analytical and spectroscopic data¹⁴. The structure of **3c** (50% yield) was assigned by comparison with authentic sample obtained with an other procedure^{3,7}.

Together with compound **3** we also obtain the corresponding hydrazone ($R^1NH-N=CR^3-CH_2R^2$) in about 10% yield, small amounts of 2,3-disubstitued indole (in the cases **a** and **c**) and other unidentifiable products. It should be noted that the use of a little excess of azoalkene reduces the reaction time. This might be due to the different reactivity of the possible isomers of **2**. In fact in the case **2c** four isomers were detected by g.c.-m.s. analysis and we observed the progressive disappearance of the different isomers during the reaction. In particular, we noted a different vanishing rate, although all isomers reacted. Unfortunately, all attempts to obtain or to characterize an intermediate adduct were unsuccessful. However, it is possible to hypothesise a spirocyclic adduct (**5**) with pentacoordinate P6 atom, in probable equilibrium with different ionic forms. Its decomposition gives **3** presumably by reductive elimination¹⁶ mechanism. Unfortunately, it was impossible to identify other by-products, in order to confirm the above hypothesis.

It should be noted that the use of **4**¹⁷ instead of **1** gives practically identical results. This finding confirms that the P6 should be the adduct spiro atom and consequently the P atom of diazaphosphole system.

We also tested P_4S_3 as other source of phosphorus in place of benzothiadiphosphole **1**, obtaining **3** in very small amounts together with several by-products. However, this result is interesting because it supports that the $P-P(S)_2$ unit has a fundamental role in this kind of reaction.

Finally, we have tested the relative stability of **3a,b,c** in a protic solution; when **3a** and **3c** were allowed at room temperature in CH_2Cl_2 or CHCl_3 solution a slow formation of 2,3-diphenylindole and 2,3-dimethylindole respectively was observed. Bubbling HCl in these solutions, the conversion to indoles is accelerated. In the same conditions no decomposition products were obtained with **3b**. These results support clearly the mechanism reported for our indolization reaction⁷ in which an acid promoted cleavage of P-N bond of diazaphosphole or preferentially of an its precursor, giving indoles by a very fast 3,3-sigmatropic rearrangement in which the N-Ph group is involved. Obviously this type of rearrangement does not occur for **3b**, which have a N-Me group, and then it is more stable in the same conditions .

In conclusion, we report a novel method to produce 2H-1,2,3-diazaphosphole derivatives which have made available the hitherto unisolated **3a**, and the proved easy mobility of the P6 atom in **1** probably might be useful to obtain new phosphorus compounds using other substrates. Moreover, we have found a clear evidence that 3-phenyl-2H-1,2,3-diazaphosphole derivatives undergoes a facile transformation to the corresponding indole.

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13. For **2a** see: Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Rosini, G.; Foresti, G. *J. Chem. Soc., Perkin Transaction I*, **1981**, 2322-2327; Similar procedure was used to obtain a mixture of isomers of **2b**. Methylhydrazine was added to a solution of acetoxybenzoin in benzene solution and the mixture was allowed at room temperature for 15 days. The yellow solution was washed with saturated aqueous Na₂CO₃. The residue was chromatographed on a silica gel column (diethyl ether as eluent) obtaining a mixture of isomers of **2b** as yellow oil which was immediately used in our reaction. **2c** was obtained as a mixture of isomers and as yellow oil from reaction of 3-Cl-2-butanone and phenylhydrazine; similar procedure was used to isolated **2c**.
14. The mass spectrum of **3a** exhibits peaks at *m/z* 314 (base peak, M⁺), 122, 89, 77. Exact mass calcd. for C₂₀H₁₅PN₂: (M⁺) 314.0973, found 314.0986. The mass spectrum of **3b** exhibits peaks at *m/z* 252 (base peak, M⁺), 236, 207, 165, 89, 77. Exact mass calcd. for C₁₅H₁₃PN₂: (M⁺) 252.0816, found 252.0813. The ³¹P NMR spectrum (CDCl₃) of **3a** and **3b** show signals at δ = 220.0 and 227.8 respectively in a characteristic region of diazaphosphole¹⁵.
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17. Compound **4** was obtained by reaction of **1** with a suspension of sulfur in benzene and the mixture was refluxed for two hours. **4** was isolated as pale yellow solid (m.p. 179-180°C) by crystallization or by fast chromatography on a short florisil column.

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