Synthesis and Reactions of β-Enamino Phosphonium Salts. Preparation of 2-Vinyl-1-aza-1,3-dienes and Penta-1,4-dien-3-ones

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Reaction of *N,P,P,P*-tetraphenyl-λ⁵-phosphazene **1** and prop-2-ynyltriphenylphosphonium bromide **2** followed by addition of aliphatic, heteroaromatic and aromatic aldehydes leads to β-enamino phosphonium salts **7**, while substituted tetrahydropyridines **9** are obtained when α,β-unsaturated aldehydes are used. Functionalized phosphonium salts **7** are precursors of Wittig reagents and act as intermediates in the synthesis of 2-vinyl-1-aza-1,3-dienes **11** and penta-1,4-dien-3-ones **12**.

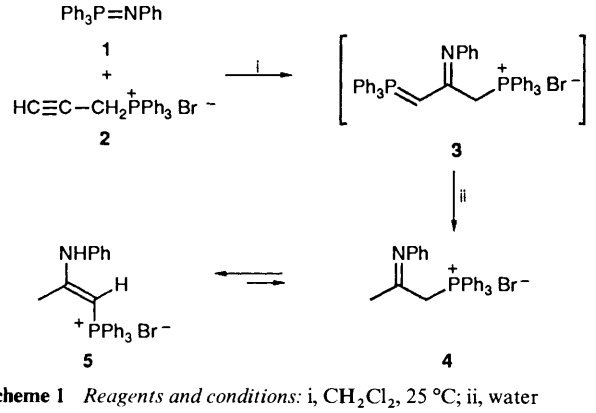
The chemistry of λ⁵-phosphazenes has received much attention in recent years because of their broad range of applications. Thus, these species have found use as starting materials in the preparation of simple organic derivatives such as amines,[1] aziridines,[2] amides,[3] nitro compounds[4] and iminic derivatives.[5,6] Moreover, their utility as key intermediates in natural-product synthesis[7] as well as in the preparation of heterocyclic compounds[8] has also been demonstrated.

In this context, we have reported the *C*-alkylation of alkyldiphenyl-λ⁵-phosphazenes and the application of these functionalized derivatives in the synthesis of acyclic[9,10] and heterocyclic[11] compounds as well as the [2 + 2]cycloaddition reaction of acetylene acid esters with λ⁵-phosphazenes derivatives[12,13] and their ability to act as starting materials in the preparation of 2-azabuta-1,3-dienes.[6]

On the other hand, functionalized β-enamines are valuable synthetic intermediates[14] in organic synthesis and we have studied the synthesis[9] and utility of phosphorylated primary β-enamines in the preparation of phosphorus-containing heterocycles.[15] In connection with our interest in the application of λ⁵-phosphazenes as intermediates in organic synthesis and in the preparation of phosphorylated β-enamines we report here a very easy method of synthesis of β-enamino phosphonium salts as well as their application as synthetic equivalents of α,α′-acetone and -*N*-phenyliminoacetone dianions **14b** and **14a** in the preparation of 2-vinyl-1-azadienes, phosphorylated pyridine derivates and divinyl ketones.

Results and Discussion

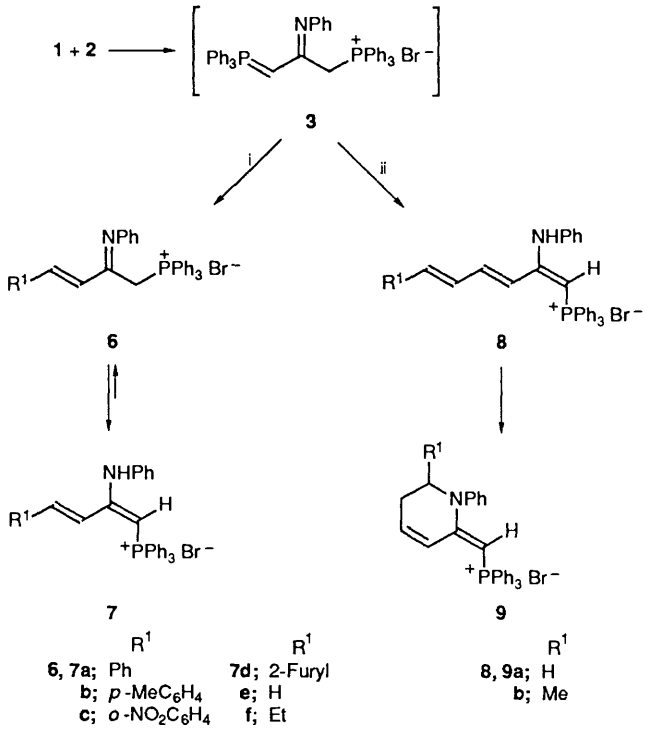
Synthesis of β-Enamino Phosphonium Salts **7** *and Substituted Tetrahydropyridines* **9**.—Reaction of *N,P,P,P*-tetraphenyl-λ⁵-phosphazene **1** and triphenyl(prop-2-ynyl)phosphonium bromide **2** in methylene dichloride at room temperature[16] followed by hydrolysis afforded a mixture of two isomeric derivatives such as the imine and the β-enamino phosphonium salts **4** and **5** in excellent yield (Scheme 1). Compounds **4** and **5** were characterized on the basis of their spectroscopic and mass spectrometry data. Thus, the ^{31}P NMR spectrum showed two different absorptions, at δ_P 17.0 and 20.0, in an approximate tautomer ratio 80:20 as evidenced by the relative peak areas for each salt, in which the high-field chemical shift corresponds to the enamino derivative **5**. Further examination of the ^{1}H and ^{13}C NMR spectra is consistent with the enamine and imine structures of the phosphonium salts **5** and **4**. Thus, in the ^{1}H NMR spectrum, vinylic and amine protons of the enamine **5** resonate at δ_H 4.75 and 10.6 as well resolved doublets with couplings constants of $^{2}J_{PH}$ 14.5 and $^{4}J_{PH}$ 3.6 Hz, respectively, and the methyl group gives a singlet at δ_H 2.10, while the ^{13}C NMR spectrum shows an absorption at δ_C 57.8 ($^{1}J_{PC}$ 117.0 Hz) assignable to the carbon bonded to phosphorus. These values are similar to those previously reported for primary β-enamino λ⁵-phosphazenes.[9] Conversely, the imine phosphonium salt **4** showed clearly different absorptions, namely a doublet at δ_H 5.92 (*J* 11.4 Hz) for the methylene protons as well as a high-field signal for the methyl group at δ_H 2.60, while in the ^{13}C NMR spectrum the absorption of the methylene carbon is shifted to higher field (δ_C 34.5) with a lower value of the phosphorus–carbon coupling constant ($^{1}J_{PC}$ 60.5 Hz) relative to those of the phosphonium salt **5** and supporting the proposed structure of the tautomer **4**. On the other hand, the vicinal ^{13}C–^{31}P coupling constant ($^{3}J_{PC}$ 7.0 Hz) in derivative **5** evidenced that the methyl group and phosphorus atom in the β-enamino derivative **5** are relatively *cis*.[9,17] Formation of compounds **4** and **5** can be assumed to proceed *via* hydrolysis, under the reaction conditions, of the phosphonium ylide **3** obtained by [2 + 2]cycloaddition of derivatives **1** and **2**, followed by electrocyclic ring opening in a similar way to that described for other acetylenic compounds.[12]



Scheme 1 *Reagents and conditions:* i, CH_2Cl_2, 25 °C; ii, water

This reaction can be used for the one-pot synthesis of the not readily available functionalized phosphonium salts **7** when hygroscopic intermediate **3**, without isolation, undergoes Wittig reaction with aldehydes. Thus, treatment of λ⁵-phosphazene **1** with acetylenic compound **2** followed by addition of aromatic, heteroaromatic and aliphatic aldehydes gave β-enamino phosphonium salts **7** in excellent yields. Spectroscopic data were in agreement with the assigned structure. Thus, mass spectrometry showed the loss of HBr and the ^{31}P NMR spectrum of compounds **7** showed two different absorptions: δ_P ~16 (major product) and ~24 (minor product), from which it can be inferred that crude compounds **7** contain in solution a small proportion of the corresponding imine tautomer **6** (10–19%) due to imine–enamine equilibrium. For example, a tautomer ratio of (83:17) for **7a**/**6a**, was observed from ^{31}P

NMR chemical shifts (δ_P 16.5 and 24.1), while in the ^1H NMR spectrum the enaminic proton of **7a** appears at δ_H 4.31 as a well resolved doublet with a phosphorus–hydrogen coupling constant of 14.1 Hz, and the ^{13}C NMR spectrum shows an absorption at δ_C 61.4 ($^1J_{PC}$ 117.9 Hz) assignable to the carbon bonded to phosphorus, supporting the same hybridization for this carbon atom as that observed in enamine **5**. The stereochemistry of the carbon–carbon double bonds was elucidated from the coupling-constant values. Thus, ^{13}C–^{31}P coupling constants ($^3J_{PC}$ 7.0 Hz) showed that the amino and the phosphonium salt groups are in a *trans* (*E*) relationship,[9,17] and the vicinal coupling constant for coupling between the vinylic protons ($^3J_{HH}$ 15.8 Hz) also reveals the *E*-configuration.



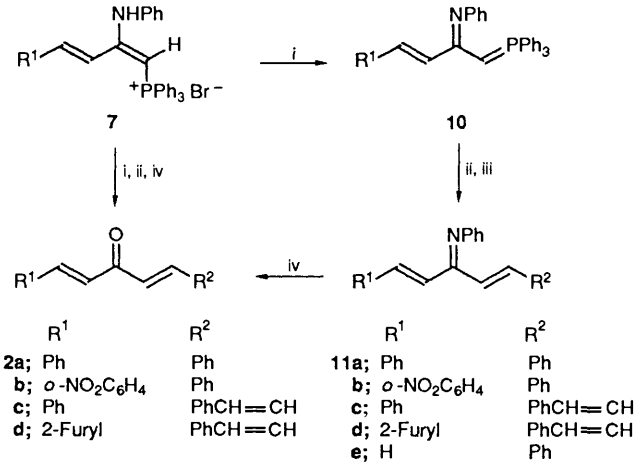
Scheme 2 *Reagents:* i, R^1CHO; ii, $R^1CH{=}CHCHO$

However, α,β-unsaturated aldehydes show different reactivity. Thus, reaction of substrate **1** with phosphonium salt **2** in acetonitrile followed by addition of acrylaldehyde and heating of the reaction mixture at reflux of acetonitrile did not give the acyclic phosphonium salt **8a**, but the tetrahydropyridine derivative **9a** was obtained instead (Scheme 2). The cyclic structure **9a** is supported by the spectroscopic data, which showed only one absorption, at δ_P 15.5, in the ^{31}P NMR spectrum. Indeed, the ^1H NMR spectrum presented absorptions at δ_H 2.60 and 3.69 for the methylene groups, while the vinylic protons appeared at δ_H 5.73 and 6.34 with $^3J_{HH}$ 10.0 Hz. Similar behaviour showed crotonaldehyde (but-2-enal) leading to heterocycle **9b**. Formation of compounds **9** could be explained through Wittig reaction of the phosphonium ylide with the aldehyde, followed by electrocyclic ring closure of the conjugated enamino phosphonium salts **8**.

This method provides an easy entry to β-enamino phosphonium salts **7** by making use of commercially available starting reagents under mild reaction conditions.

Reactions of β-Enamino Phosphonium Salts with Aldehydes. Synthesis of Divinylic Imines **11** *and Ketones* **12**.—Phosphonium salts **7** can be used as key intermediates in synthetic organic chemistry for the preparation of 1-azabuta-1,3-dienes, which are versatile starting materials for the construction of a wide range of different sized heterocycles.[18]

Taking into account our previous results in the reaction of β-enamino λ^5-phosphazenes[9] we explored the Wittig reaction of stabilized phosphonium ylides **10** generated *in situ* from β-enamino phosphonium salts **7**, and found that treatment of derivatives **7** with a base such as butyllithium followed by addition of aldehydes and aqueous work-up led to 2-vinyl-1-azabuta-1,3-dienes **11** (Scheme 3) in excellent yields. Spectroscopic data were consistent with the proposed structure, in which a vicinal coupling constant of 16.5 Hz for the vinylic protons of compound **11a** evidenced an *E* configuration for both carbon–carbon double bonds.

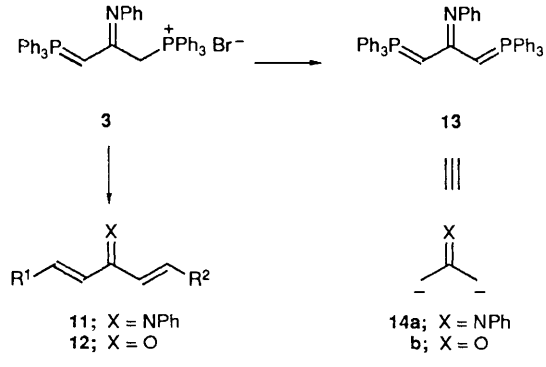


Scheme 3 *Reagents and conditions:* i, BuLi, THF, −70 °C; ii, R^2CHO; iii, water; iv, H_3O^+

Imines **11** are precursors of attractive building blocks in the synthesis of cyclopentanoid natural products[19] such as divinyl ketones. Thus, acid hydrolysis of compounds **11** with 1 mol dm^{-3} H_2SO_4 led to the corresponding carbonyl compounds **12**. These mild reaction conditions did not change the present stereochemistry in the azadiene system, and afforded the ketone with *E* configuration ($^3J_{HH}$ 15.8 Hz for **12a**).

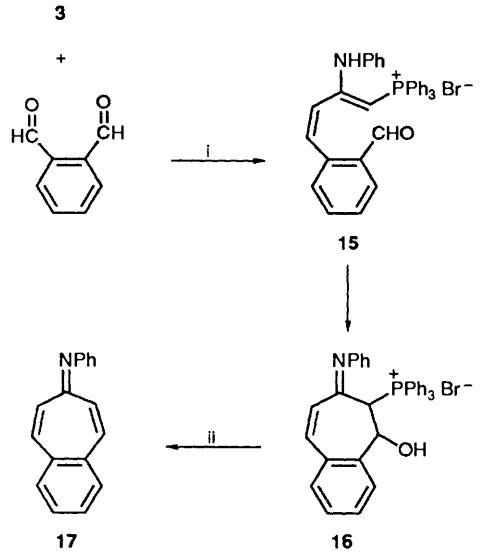
These carbonyl compounds **12** can also be prepared from β-enamino phosphonium salts **7** and aldehydes without the isolation of the imines **11**, by quenching of the reaction with 1 mol dm^{-3} H_2SO_4. These results showed that the phosphonium ylide **3** is a valuable precursor in the preparation of conjugated imines **11** and ketones **12** through formation of two carbon–carbon double bonds by double Wittig reaction of compound **3** with two aldehydes. This would correspond to using ylide **3** as the synthetic equivalent of acetone **14b** and *N*-phenylacetone imine α,α′-dianion **14a**[20] (Scheme 4).

This type of reactivity can be shown by the reaction of compound **3** with a dicarbonylic derivative. Thus, treatment of λ^5-phosphazene **1** with propargylic salt **2** in methylene dichloride, followed by addition of phthalaldehyde gave the



Scheme 4

hydroxy phosphonium salt **16** (δ_P 15.9). Formation of compound **16** could be explained through Wittig reaction of the phosphonium ylide **3** with an aldehyde group of the dicarbonylic compound, leading to the enamine **15**, whose cyclization affords the seven-membered carbocyclic compound **16**. Treatment of derivative **16** with sodium hydride in dimethylformamide (DMF) led to the formation of the *N*-phenylimine derived from benztropone, *i.e.* product **17**, whose spectral data were consistent with the proposed structure (Scheme 5).



Scheme 5 *Reagents and conditions:* i, MeCN, 60 °C; ii, NaH–DMF, water

It is noteworthy that the preparation of divinylic ketimines **11** and ketones **12** does not require the isolation and purification of the phosphonium salts **7**. Improved overall yields are obtained in a *one-pot* reaction when these salts **7**, after evaporation of the solvent, are directly metallated in tetrahydrofuran (THF) with subsequent addition of aldehydes and aqueous or acid work-up, respectively.

In conclusion, we have shown that functionalized phosphonium ylide **3**, easily obtained by reaction of λ^5-phosphazenes **1** and propargylic salt **2**, can be considered as a synthetic equivalent of acetone and *N*-phenylacetone imine α,α′-dianions and as a precursor in the preparation of β-enamino phosphonium salts **7** and substituted tetrahydropyridines **9**, as well as in the synthesis of 2-vinyl-1-azabuta-1,3-dienes **11** and penta-1,4-dien-3-ones **12**.

Experimental

General.—M.p.s were taken on samples in open capillary tubes using a Büchi melting-point apparatus and are uncorrected. NMR spectra were obtained using a Bruker AC300 spectrometer with deuteriated chloroform as solvent; chemical shifts are reported downfield from internal $SiMe_4$ for ^1H, from $CDCl_3$ for ^{13}C, and from H_3PO_4 (85%) in the case of ^{31}P NMR spectra. IR spectra were recorded on a Philips PU 9716 or a Perkin-Elmer 1720-X FT spectrophotometer. Microanalyses were performed on a Perkin-Elmer model 240 instrument, and mass spectra were obtained using a Hewlett-Packard 5987 A spectrometer. Starting materials **1** and **2** are available from Aldrich.

Reaction of N,P,P,P-*Tetraphenyl-*λ^5*-phosphazene* **1** *with Triphenyl(prop-2-ynyl)phosphonium Bromide* **2**. *Synthesis of Anilinoprop-1-enyl(triphenyl)phosphonium Bromide* **5** *and 2-Triphenyl-2-(phenylimino)propylphosphonium Bromide* **4**.—In a dried, argon-filled, round-bottomed flask was stirred a mixture of the λ^5-phosphazene **1** (0.89 g, 2.5 mmol) and phosphonium salt **2** (0.95 g, 2.5 mmol) in methylene dichloride (20 cm^3) for 40 h at room temperature. The mixture was poured into ice–water (100 cm^3), extracted with methylene dichloride (150 cm^3) and the organic phase was dried (Na_2SO_4). The bulk of the solvent was evaporated off and then the residue was added to ethyl acetate to afford a solid, which was recrystallized from ethyl acetate–methylene dichloride to give a mixture of isomeric compounds **5**/**4** (0.95 g, 87%) with the tautomer composition ratio 80:20 (^{31}P NMR). The *mixture* had m.p. 185–186 °C (decomp.) (Found: C, 68.45; H, 5.2; N, 3.0. $C_{27}H_{25}BrNP$ requires C, 68.3; H, 5.3; N, 2.9%); ν_{max}(NaCl)/cm^{-1} 3150 (NH) and 1100 (C–N); δ_H 2.1 (3 H, s, Me), 4.75 (1 H, d, $^2J_{PH}$ 14.5 Hz, CH=), 6.9–7.9 (m, ArH) and 10.6 (d, $^4J_{PH}$ 3.1 Hz, NH) for compound **5** and 2.6 (3 H, s, Me) and 5.92 (2 H, d, $^2J_{PH}$ 11.4 Hz) for compound **4**; δ_C 22.4 (Me), 57.9 (d, $^1J_{PC}$ 117.0 Hz, CH=), 122.4–138.4 (C_{arom}) and 164.5 (d, $^2J_{PC}$ 14.0 Hz, CNH) for compound **5**; δ_P 17.0 (80%) for compound **5** and 20.0 (20%) for compound **4**; *m*/*z* 393 (M^+ − HBr).

Synthesis of β-*Enamino Phosphonium Salts* **7**. *General Procedure. 2-Anilino-4-phenylbuta-*1,3-*dienyl(triphenyl)phosphonium Bromide* **7a**.—λ^5-Phosphazene **1** (0.89 g, 2.5 mmol) was added to a solution of phosphonium salt **2** (0.95 g, 2.5 mmol) in dry methylene dichloride (20 cm^3). The reaction mixture was stirred for 20 h at room temperature and then a solution of benzaldehyde (0.32 g, 3 mmol) in methylene dichloride (5 cm^3) was added. After being stirred for several hours the bulk of the solution was evaporated and the residue was taken up in ethyl acetate until formation of a crystalline solid, which was recrystallized from ethyl acetate–methylene dichloride to give *tautomeric compounds* **7a**/**6a** (1.30 g, 93%), m.p. 157–158 °C (decomp.); isomer ratio 83:17 (^{31}P NMR) (Found: C, 72.3; H, 5.7; N, 2.3. $C_{34}H_{29}BrNP$ requires C, 72.53; H, 5.20; N, 2.49%); ν_{max}(NaCl)/cm^{-1} 3200 (NH) and 1100 (C–N); δ_H 4.85 (1 H, d, $^2J_{PH}$ 14.1 Hz, CH=), 6.1 (1 H, d, $^3J_{HH}$ 15.8 Hz, CH=), 6.8–7.85 (m, ArH), 8.0 (1 H, d, $^3J_{HH}$ 15.8 Hz, CH=) and 10.38 (d, $^4J_{PH}$ 3.7 Hz, NH) for compound **7a** and 5.69 (2 H, d, $^2J_{PH}$ 12.1 Hz, CH_2), 6.42 (1 H, dd, $^3J_{HH}$ 16.5, $^4J_{PH}$ 3.0 Hz, CH=), 8.45 (1 H, d, $^3J_{HH}$ 16.5 Hz, CH=) for compound **6a**; δ_C 61.4 (d, $^1J_{PC}$ 117.9 Hz, CH=), 119.7 (d, $^3J_{PC}$ 7.0 Hz, CH=), 122.6–148.3 (C_{arom}), 140.1 (CH=) and 161.0 (d, $^2J_{PC}$ 11.6 Hz, CNH) for compound **7a** and 34.5 (d, $^1J_{PC}$ 60.5 Hz, CH_2), 117.5 (CH=), 144.5 (CH=) and 159.4 (C=N) for compound **6a**; δ_P 16.5 (83%) for **7a** and 24.1 (17%) for **6a**; *m*/*z* 481 (M^+ − HBr).

*2-Anilino-4-(*p-*tolyl)buta-*1,3-*dienyl(triphenyl)phosphonium Bromide* **7b**.—The *isomeric compounds* **7b**/**6b** (1.23 g, 86%) had m.p. 138–140 (decomp.); tautomer ratio 84:16 (Found: C, 72.6; H, 5.5; N, 2.5. $C_{35}H_{31}BrNP$ requires C, 72.92; H, 5.42; N, 2.43%); ν_{max}(NaCl)/cm^{-1} 3250 (NH) and 1100 (C–N); δ_H 2.22 (3 H, s, Me), 4.93 (1 H, d, $^2J_{PH}$ 14.5 Hz, CH=), 6.14 (1 H, d, $^3J_{HH}$ 16.3 Hz, CH=), 6.85–8.1 (m, ArH + CH=) and 10.3 (d, $^4J_{PH}$ 3.4 Hz, NH); δ_C 21.1 (Me), 61.4 (d, $^1J_{PC}$ 117.9 Hz, CH=), 119.0 (d, $^3J_{PC}$ 7.0 Hz, CH=), 122.6–148.3 (C_{arom}), 139.6 (CH=) and 161.1 (d, $^2J_{PC}$ 11.5 Hz, CNH); δ_P 16.5 (84%) for **7b** and 24.2 (16%) for **6b**; *m*/*z* 495 (M^+ − HBr).

*2-Anilino-4-(*o-*nitrophenyl)buta-*1,3-*dienyl(triphenyl)phosphonium Bromide* **7c**.—The *isomeric compounds* **7c**/**6c** (1.33 g, 88%) had m.p. 191–193 °C (decomp.); tautomer ratio 92:8 (Found: C, 67.3; H, 4.6; N, 4.65. $C_{34}H_{28}BrN_2O_2P$ requires C, 67.22; H, 4.64; N, 4.61%); ν_{max}(NaCl)/cm^{-1} 3200 (NH) and 1150 (C–N); δ_H 5.12 (1 H, d, $^2J_{PH}$ 13.9 Hz, CH=), 6.05 (1 H, d, $^3J_{HH}$ 15.9 Hz, CH=), 7.2–8.0 (m, ArH + CH=) and 10.7 (d, $^4J_{PH}$ 3.5 Hz, NH); δ_C 62.1 (d, $^1J_{PC}$ 118.1 Hz, CH=), 116.2–147.2 (C_{arom} + 2 CH=) and 161.3 (d, $^2J_{PC}$ 12.5 Hz, CNH); δ_P 16.6 (92%) for **7c** and 24.1 (8%) for **6c**; *m*/*z* 562 (M^+ − HBr).

2-*Anilino*-4-(2-*furyl*)*buta*-1,3-*dienyl*(*triphenyl*)*phosphonium Bromide* **7d**.—The *tautomeric compounds* **7d**/**6d** (1.09 g, 79%) had m.p. 210–212 °C (decomp.); isomer ratio 81:19 (Found: C, 69.6; H, 4.9; N, 2.6. $C_{32}H_{27}BrNOP$ requires C, 69.57; H, 4.93; N, 2.53%); ν_{max}(NaCl)/cm^{-1} 3300 (NH) and 1050 (C–N); δ_H 4.88 (1 H, d, $^2J_{PH}$ 14.4 Hz, CH=), 6.13 (1 H, d, $^3J_{HH}$ 16.0 Hz, CH=), 7.15–8.05 (m, ArH + CH=) and 10.3 (d, $^4J_{PH}$ 3.0 Hz, NH); δ_C 62.0 (d, $^1J_{PC}$ 118.0 Hz, CH=), 117.1 (d, $^3J_{PC}$ 7.1 Hz, CH=), 112.1–150.6 (C_{arom} + CH=) and 160.4 (d, $^2J_{PC}$ 12.2 Hz, CNH); δ_P 16.6 (81%) for **7d** and 24.1 (19%) for **6d**; *m*/*z* 472 (M^+ − HBr).

2-*Anilinobuta*-1,3-*dienyl*(*triphenyl*)*phosphonium Bromide* **7e**.—The *tautomeric compounds* **7e**/**6e** (1.15 g, 95%) had m.p. 217–218 °C (decomp.); isomer ratio 90:10 (Found: C, 69.25; H, 5.1; N, 3.0. $C_{28}H_{25}BrNP$ requires C, 69.14; H, 5.18; N, 2.88%); ν_{max}(NaCl)/cm^{-1} 3300 (NH) and 1100 (C–N); δ_H 4.84 (1 H, d, $^2J_{PH}$ 13.9 Hz, CH=), 5.40 (1 H, d, $^3J_{HH}$ 11.1 Hz, CH=), 5.90 (1 H, dd, $^3J_{HH}$ 11.1, $^3J_{HH}$ 17.3 Hz, CH=), 6.58 (1 H, d, $^3J_{HH}$ 17.3 Hz), 7.2–8.1 (m, ArH) and 10.4 (d, $^4J_{PH}$ 3.6 Hz, NH); δ_C 61.4 (d, $^1J_{PC}$ 111.7 Hz, CH=), 124.3–147.9 (C_{arom} + 2 CH=) and 160.8 (d, $^2J_{PC}$ 12.2 Hz, CNH); δ_P 16.5 (90%) for **7e** and 24.1 (10%) for **6e**; *m*/*z* 404 (M^+ − HBr).

2-*Anilinohexa*-1,3-*dienyl*(*triphenyl*)*phosphonium Bromide* **7f**.—The *isomeric compounds* **7f**/**6f** (1.15 g, 68%) had m.p. 146–147 °C (decomp.); tautomer ratio 93:7 (Found: C, 70.2; H, 5.45; N, 2.8. $C_{30}H_{29}BrNP$ requires C, 70.04; H, 5.68; N, 2.72%); ν_{max}(NaCl)/cm^{-1} 3350 (NH) and 1150 (C–N); δ_H 0.6 (3 H, t, Me), 1.91 (2 H, m, CH_2), 4.75 (1 H, d, $^2J_{PH}$ 14.8 Hz, CH=), 5.53 (1 H, d, $^3J_{HH}$ 15.7 Hz, CH=), 7.1–8.1 (m, ArH + CH=) and 10.05 (d, $^4J_{PH}$ 3.7 Hz, NH); δ_C 11.2 (Me), 25.2 (CH_2), 59.7 (d, $^1J_{PC}$ 118.5 Hz, CH=), 121.1 (d, $^3J_{PC}$ 6.8 Hz, CH=), 122.3–145.7 (C_{arom} + CH=) and 161.2 (d, $^2J_{PC}$ 12.8 Hz, CNH); δ_P 16.7 (93%) for **7f** and 24.0 (7%) for **6e**; *m*/*z* 433 (M^+ − HBr).

Synthesis of Substituted Tetrahydropyridines **9**. *General Procedure. Synthesis of Triphenyl*-[(1-*phenyl*-1,2,5,6-*tetrahydropyridin*-2-*ylidene*)*methyl*]*phosphonium Bromide* **9a**.—This was prepared by the same method as for compound **7a** in acetonitrile as solvent at reflux. This *compound* had m.p. 158–160 °C (decomp.) (from ethyl acetate–methylene dichloride) (Found: C, 70.4; H, 5.2; N, 2.9. $C_{30}H_{27}BrNP$ requires C, 70.32; H, 5.31; N, 2.73%); ν_{max}(NaCl)/cm^{-1} 1150 (C–N); δ_H 2.60 (2 H, m, CH_2), 3.69 (2 H, t, $^3J_{HH}$ 7.1 Hz, CH_2), 3.86 (1 H, d, $^2J_{PH}$ 13.6 Hz, CH=), 5.73 (1 H, d, $^3J_{HH}$ 10.0 Hz, CH=), 6.34 (1 H, m, CH=) and 7.3–7.9 (m, ArH); δ_C 24.2 (CH_2), 48.9 (CH_2N), 62.3 (d, $^1J_{PC}$ 116.2 Hz, CH=), 120.9 (d, $^3J_{PC}$ 7.5 Hz, CH=), 121.6–143.4 (C_{arom} + CH=) and 158.5 (d, $^2J_{PC}$ 13.2 Hz, CN); δ_P 15.5; *m*/*z* 431 (M^+ − HBr).

Synthesis of [(6-*Methyl*-1-*phenyl*-1,2,5,6-*tetrahydropyridin*-2-*ylidene*)*methyl*]*triphenylphosphonium Bromide* **9b**.—This *compound* had m.p. 138–139 °C (decomp.) (from ethyl acetate–methylene dichloride) (Found: C, 70.9; H, 5.4; N, 2.7. $C_{31}H_{29}BrNP$ requires C, 70.72; H, 5.55; N, 2.66%); ν_{max}(NaCl)/cm^{-1} 1150 (C–N); δ_H 1.23 (3 H, d, $^3J_{HH}$ 6.6 Hz, Me), 2.60 (2 H, m, CH_2), 3.78 (1 H, d, $^2J_{PH}$ 13.4 Hz, CH=), 4.00 (1 H, m, CHN), 5.83 (1 H, d, $^3J_{HH}$ 10.0 Hz, CH=), 6.35 (1 H, m, CH=) and 7.4–7.9 (m, ArH); δ_C 18.8 (Me), 31.4 (CH_2), 53.7 (CHN), 62.6 (d, $^1J_{PC}$ 115.8 Hz, CH=), 120.4 (d, $^3J_{PC}$ 7.6 Hz, CH=), 121.8–141.6 (C_{arom} + CH=) and 157.9 (d, $^2J_{PC}$ 13.0 Hz, CN); δ_P 15.7; *m*/*z* 445 (M^+ − HBr).

Synthesis of 2-*Vinyl*-1-*aza*-1,3-*dienes* **11**. *General Procedure. Synthesis* of 1,5-*Diphenyl*-3-*phenyliminopenta*-1,4-*diene* **11a**.—*Method A*. In a dried, argon-filled, round-bottomed flask a suspension of β-enamino phosphonium salt **7a** (1.41 g, 2.5 mmol) in THF (50 cm^3) was treated with BuLi (2.5 mol dm^{-3}) (1 cm^3, 2.5 mmol) at −70 °C and the mixture was stirred for 1 h, after which benzaldehyde (0.32 g, 3 mmol) was added at −70 °C. The mixture was allowed to reach room temperature and was then hydrolysed with ice–water. Aqueous work-up afforded an oil, which was purified by means of short silica gel column chromatography in diethyl ether to give compound **11a** (0.66 g, 86%) (recrystallized from hexane).

Method B. The procedure was as indicated for method A, and used phosphonium salts **7** directly prepared from starting materials as described for compounds **7** without isolation in a one-pot reaction to give *compound* **11a** (0.64 g, 84%) as a solid, m.p. 97–98 °C (from hexane) (Found: C, 89.4; H, 6.0; N, 4.5. $C_{23}H_{19}N$ requires C, 89.28; H, 6.19; N, 4.53%); ν_{max}(NaCl)/cm^{-1} 1550 (C=N); δ_H 6.76 (1 H, d, $^3J_{HH}$ 16.5 Hz, CH=), 6.91–7.6 (m, ArH) and 7.58 (1 H, d, $^3J_{HH}$ 16.5 Hz, CH=); δ_C 123.8 (CH=), 125.8 (CH=), 120.8–136.1 (C_{arom}), 138.0 (CH=), 138.3 (CH=), 150.5 (CH=) and 162.8 (C=N); *m*/*z* 309 (M^+).

1-(o-*Nitrophenyl*)-5-*phenyl*-3-*phenyliminopenta*-1,4-*diene* **11b**.—*Compound* **11b** (0.75 g, 84%) had m.p. 109–110 °C (from hexane) (Found: C, 78.0; H, 5.0; N, 8.0. $C_{23}H_{18}N_2O_2$ requires C, 77.95; H, 5.12; N, 7.90%); ν_{max}(NaCl)/cm^{-1} 1550 (C=N); δ_H 6.62 (1 H, d, $^3J_{HH}$ 16.1 Hz, CH=), 6.78 (1 H, d, $^3J_{HH}$ 16.4 Hz, CH=) and 6.98–8.13 (m, ArH + 2 CH=); δ_C 120.7 (d, CH=), 127.5 (d, CH=), 121.1–133.7 (C_{arom}), 135.6 (CH=), 139.5 (CH=) and 163.0 (C=N); *m*/*z* 354 (M^+).

1,7-*Diphenyl*-5-*phenyliminohepta*-1,3,6-*triene* **11c**.—This *oil* (0.65 g, 78%) had R_f 0.8 (Found: C, 89.6; H, 6.2; N, 4.2. $C_{25}H_{21}N$ requires C, 89.51; H, 6.31; N, 4.17%); ν_{max}(NaCl)/cm^{-1} 1500 (C=N); δ_H 6.35 (d, 1 H, $^3J_{HH}$ 16.2 Hz, CH=) and 6.6–7.7 (m, ArH + 5 CH=); δ_C 120.6–151.2 (C_{arom} + 6 CH=) and 161.5 (C=N); *m*/*z* 335 (M^+).

7-*Furyl*-1-*phenyl*-5-*phenyliminohepta*-1,3,6-*triene* **11d**.—This *oil* (0.63 g, 72%) had R_f 0.9 (Found: C, 82.2; H, 5.6; N, 4.3. $C_{23}H_{19}NO$ requires C, 82.35; H, 5.71; N, 4.17%); ν_{max}(NaCl)/cm^{-1} 1500 (C=N); δ_H 6.32 (1 H, d, $^3J_{HH}$ 15.9 Hz, CH=) and 6.6–7.5 (m, ArH + 5 CH=); δ_C 119.8–152.7 (C_{arom} + 6 CH=) and 162.6 (C=N); *m*/*z* 325 (M^+).

1-*Phenyl*-3-*phenyliminopenta*-1,4-*diene* **11e**.—This *oil* (0.49 g, 85%) had R_f 0.7 (Found: C, 87.4; H, 6.6; N, 6.2. $C_{17}H_{15}N$ requires C, 87.52; H, 6.48; N, 6.00%); ν_{max}(NaCl)/cm^{-1} 1500 (C=N); δ_H 5.61 (1 H, dd, $^3J_{HH}$ 11.3, $^2J_{HH}$ 1.5 Hz, CH=), 6.07 (1 H, dd, $^3J_{HH}$ 17.6, $^2J_{HH}$ 1.5 Hz, CH=), 6.28 (1 H, dd, $^3J_{HH}$ 17.6, $^3J_{HH}$ 11.3 Hz, CH=), 6.61 (1 H, d, $^3J_{HH}$ 16.5 Hz, CH=) and 6.70–7.70 (m, ArH + CH=); δ_C 119.6 (CH=), 123.4 (CH=), 126.4–148.6 (C_{arom} + 2 CH=) and 166.3 (C=N); *m*/*z* 233 (M^+).

Synthesis of Penta-1,4-*dien*-3-*ones* **12**. *General Procedure. Synthesis of* 1,5-*Diphenylpenta*-1,4-*dien*-3-*one* **12a**.—*Method A*. A solution of ketimine **11a** (0.77 g, 2.5 mmol) in THF (30 cm^3) was treated with 1 mol dm^{-3} H_2SO_4 (10 cm^3) at room temperature for 1 h. Then the mixture was extracted with methylene dichloride (100 cm^3), the extract was evaporated and the resulting oil was recrystallized from hexane to give compound **12a** (0.51 g, 88%).

Method B. The procedure was as described in method B for the preparation of compound **11a**, but with acid hydrolysis (1 mol dm^{-3} H_2SO_4, 30 cm^3) instead of ice–water in a one-pot reaction to yield *compound* **12a** (0.48 g, 82%) as a solid, m.p. 105–106 °C (from hexane) (Found: C, 87.3; H, 5.95. $C_{17}H_{14}O$ requires C, 87.15; H, 6.02%); ν_{max}(NaCl)/cm^{-1} 1550 (C=O); δ_H 7.12 (1 H, d, $^3J_{HH}$ 15.8 Hz, CH=), 7.25–7.60 (m, ArH) and 7.64 (1 H, d, $^3J_{HH}$ 15.8 Hz, CH=); δ_C 125.2–134.6 (C_{arom} + 2 CH=), 143.1 (CH=) and 188.7 (C=O); *m*/*z* 234 (M^+).

1-(o-*Nitrophenyl*)-5-*phenylpenta*-1,4-*dien*-3-*one* **12b**.—*Com-*

pound **12b** (0.58 g, 84%) had m.p. 92–93 °C (from hexane) (Found: C, 73.2; H, 4.75; N, 4.9. $C_{17}H_{13}NO_3$ requires C, 73.11; H, 4.69; N, 5.01%); ν_{max}(NaCl)/cm^{-1} 1650 (C=O); δ_H 6.85 (1 H, d, $^3J_{HH}$ 16.8 Hz, CH=), 7.02 (1 H, d, $^3J_{HH}$ 16.0 Hz, CH=) and 7.25–8.09 (m, ArH + 2 CH=); δ_C 124.2–134.3 (C_{arom} + 2 CH=), 138.2 (CH=), 144.3 (CH=) and 188.6 (C=O); *m/z* 279 (M^+).

1,7-*Diphenylhepta*-1,4,6-*trien*-3-*one* **12c**.—This *oil* (0.51 g, 79%) had R_f 0.8 (Found: C, 87.55; H, 6.2. $C_{19}H_{16}O$ requires C, 87.66; H, 6.19%); ν_{max}(NaCl)/cm^{-1} 1700 (C=O); δ_H 6.71 (1 H, d, $^3J_{HH}$ 15.7 Hz, CH=), 6.78–7.7 (m, ArH + 5 CH=) and 7.75 (1 H, d, $^3J_{HH}$ 15.7 Hz, CH=); δ_C 125.3–135.9 (C_{arom} + 3 CH=), 141.5 (CH=), 142.8 (CH=), 143.3 (CH=) and 188.8 (C=O); *m/z* 260 (M^+).

1-*Furyl*-7-*phenylhelpta*-1,4,6-*trien*-3-*one* **12d**.—This *oil* (0.46 g, 74%) had R_f 0.9 (Found: C, 81.7; H, 5.6. $C_{17}H_{14}O$ requires C, 81.58; H, 5.64%); ν_{max}(NaCl)/cm^{-1} 1700 (C=O); δ_H 6.62 (1 H, d, $^3J_{HH}$ 15.7 Hz, CH=) and 6.38–7.5 (m, ArH + 5 CH=); δ_C 112.5–136.0 (C_{arom} + 3 CH=), 141.4 (CH=), 143.0 (CH=), 144.7 (CH=) and 188.3 (C=O); *m/z* 250 (M^+).

Synthesis of Hydroxy Phosphonium Salt **16**.—In a dried, argon-filled, round bottomed flask were placed the λ^5-phosphazene **1** (0.89 g, 2.5 mmol) and the phosphonium salt **2** (0.95 g, 2.5 mmol) in dry methylene dichloride (20 cm^3). The reaction mixture was stirred for 36 h at room temperature and then a solution of phthalaldehyde (0.38 g, 3 mmol) in methylene dichloride (5 cm^3) was added. After the mixture had been vigorously stirred for 8 h at room temperature, the solvent was evaporated off and the residue was taken up in ethyl acetate until formation of a crystalline solid, which was recrystallized from ethyl acetate–methylene dichloride to give *compound* **16** (1.0 g, 80%), m.p. 159–160 °C (decomp.) (Found: C, 71.0; H, 5.1; N, 2.5. $C_{35}H_{29}BrNOP$ requires C, 71.19; H, 4.95; N, 2.37%); ν_{max}(NaCl)/cm^{-1} 3350 (OH) and 1480 (C=N); δ_H 1.91 (s, OH), 3.32 (1 H, d, $^3J_{HH}$ 12.5 Hz, C*H*OH), 6.12 (1 H, d, $^3J_{HH}$ 12.0 Hz, CH=), 6.35 (d, CHP), 6.66 (1 H, d, $^3J_{HH}$ 12.0 Hz, CH=) and 7.1–7.95 (m, ArH); δ_C 57.6 (d, $^1J_{PC}$ 112.7 Hz, CP), 81.5 (d, $^2J_{PC}$ 12.2 Hz, COH), 122.5–141.8 (C_{arom} + 2 CH=) and 164.3 (d, $^2J_{PC}$ 14.2 Hz, C=N); δ_P 15.9; *m/z* 509 (M − HBr).

Synthesis of the N-*Phenyl Benztroponeimine* **17**.—To a suspension of NaH (0.1 g) in dry DMF (5 cm^3) was added dropwise a solution of compound **16** (0.95 g, 1.6 mmol) in DMF (15 cm^3) under nitrogen. The mixture was stirred for 10 h, quenched with ice–water and extracted with methylene dichloride. The extract was evaporated and the crude yellow solid was purified by means of short silica gel column chromatography in diethyl ether to yield *compound* **17** (0.3 g, 83%), m.p. 112–113 °C (Found: C, 88.0; H, 5.8; N, 6.2. $C_{17}H_{13}N$ requires C, 88.28; H, 5.66; N, 6.06%); ν_{max}(NaCl)/cm^{-1} 1480 (C=N); δ_H 6.38 (1 H, dd, $^3J_{HH}$ 12.7, $^4J_{HH}$ 2.6 Hz, CH=), 6.65 (1 H, dd, $^3J_{HH}$ 12.7, $^4J_{HH}$ 2.6 Hz, CH=), 6.68 (1 H, d, $^3J_{HH}$ 12.7 Hz, CH=), 6.90 (1 H, d, $^3J_{HH}$ 12.7 Hz, CH=) and 7.0–7.70 (m, ArH); δ_C 123.4 (CH=), 129.7 (CH=), 132.7 (CH=), 133.1 (CH=), 161.7 (C=N), 119.8–150.5 (C_{arom}) and 161.7 (C=N); *m/z* 231 (M^+).

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