On the reactions of (vinylimino)phosphoranes and related compounds. Part 30.[1] Short new synthesis of 5-azaazulene derivatives. Some comments on reactivities of (vinylimino)phosphoranes[2]

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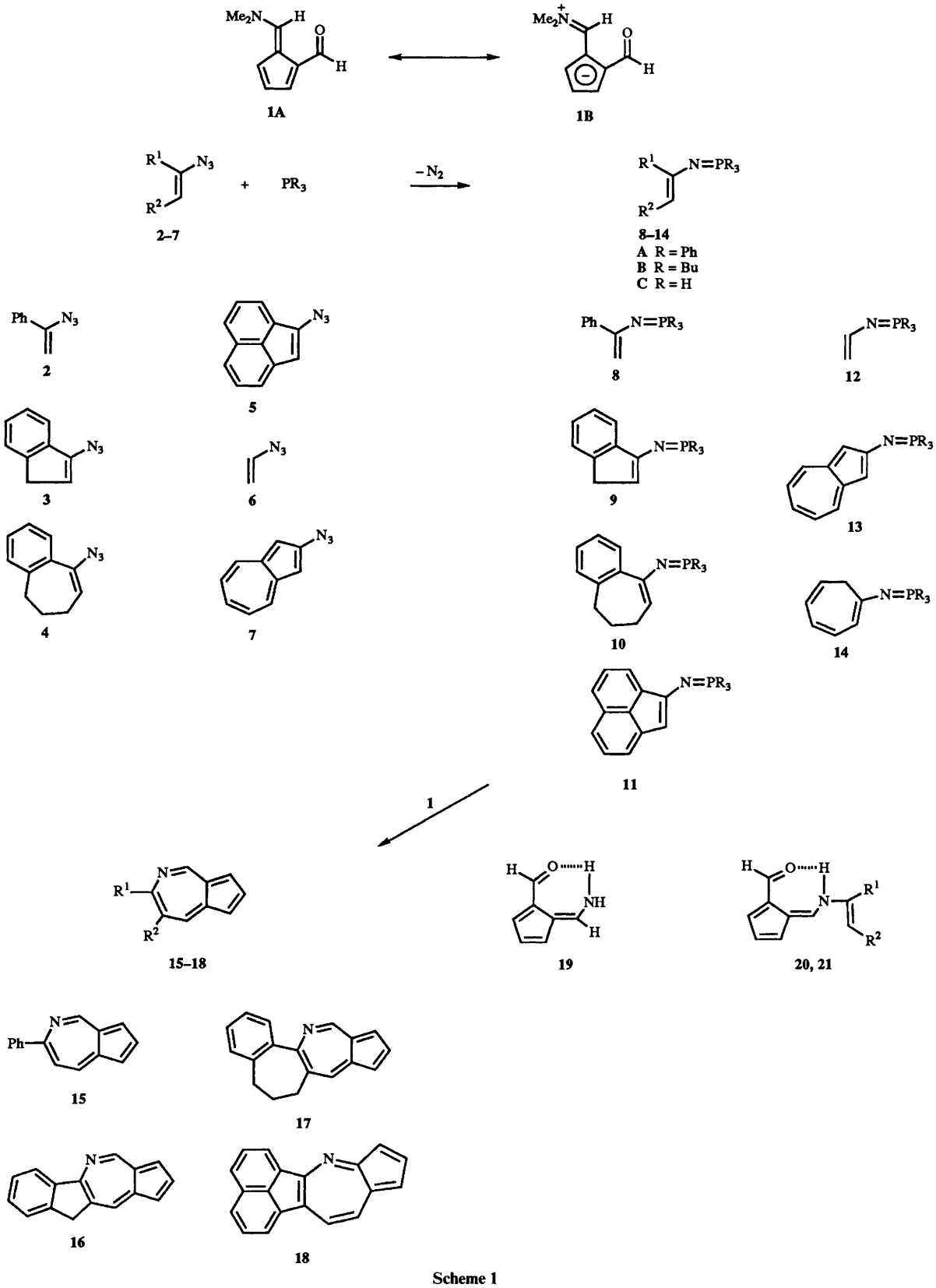
A short new synthesis of phenyl-substituted and annulated 5-azaazulene (cyclopenta[*c*]azepine) derivatives **15–18** consists of the reaction of [(1-phenylvinyl)imino]- and benz-annulated [(cycloalkenyl)imino]-phosphoranes **8–11** with 5-(dimethylaminomethylene)cyclopenta-1,3-dienecarbaldehyde **1** in an enamine alkylation (Michael addition) process, subsequent proton migration–ketonization, and condensation of the formyl group with the iminophosphorane moiety (aza-Wittig reaction). On the other hand, reactions of aldehyde **1** with (vinylimino)phosphoranes **12–14**, which have no phenyl group at the α-position relative to the nitrogen atom, consist of a intramolecular aza-Wittig reaction or a substitution reaction of aldehyde **1** with phosphoranes **12–14** and subsequent hydrolysis to afford 5-(aminomethylene)cyclopenta-1,3-dienecarbaldehyde **19** and its derivatives **20** and **21**, respectively. In the context of selectivity observed in the reaction of phosphoranes **8–11** and **12–14** with aldehyde **1**, respectively, MNDO calculations on compounds **1** and **12A**, **12B** as well as on model compounds **8C–12C** were performed to gain insight *via* a theoretical interpretation based upon frontier molecular orbital theory (FMO): the former reaction, giving 5-azaazulene derivatives, would be an FMO-controlled reaction, while the latter is a charge-controlled reaction. Several spectral and chemical properties of heterocycles of **16–18** are analysed.

The chemistry of azaazulenes is still of interest to organic chemists, particularly in comparison with that of azulene, and has played a major role in the advancement of our understanding of cyclic conjugation.[3] Development of methodology for effective construction of azaazulenes has attracted considerable attention for a few decades.[4] All the monoazaazulenes are known in the form of their derivatives, and the parent 1-,[5] 4-,[6] 5-[7] and 6-azaazulenes[8] have also been prepared. Among monoazaazulene derivatives, examples of 5-azaazulenes are few and only a condensed system, azuleno[1,8-*c*,*d*]azepine,[9] has been prepared in addition to 4-, 6-,[10] 7,8-[11] and 2,4,6,7,8-substituted derivatives. Recently, the preparation of nitrogen heterocycles by means of the aza-Wittig reaction has been widely utilized because of the ready availability of functionalized iminophosphoranes.[12] Previously, we have also demonstrated a simple preparation of (vinylimino)phosphoranes,[13] which were found to react with the compounds bearing two electrophilic centres, α-bromo ketones,[14] α,β-unsaturated ketones,[15] tropone derivatives[16] and methano[11]annulenones[17] in an enamine alkylation process (Michael addition) followed by aza-Wittig reaction to provide a convenient route to pyrroles, pyridines, 1-azaazulenes and methanocycloundeca[*b*]pyrroles. Regarding 5-(dimethylaminomethylene)cyclopenta-1,3-diene carbaldehyde **1**, it reacts with nucleophilic and electrophilic reagents indicating a participation of the polar structure **1B**.[18] Thus, compound **1** is considered to have two electrophilic centres, the C-6 carbon and the carbonyl carbon atoms (Scheme 1).[18] Now we planned to take advantage of the methodology using (vinylimino)phosphoranes **8–14** and aldehyde **1** for construction of 5-azaazulene (cyclopenta[*c*]azepine) derivatives. The organic azides **2–7** with tertiary phosphines gave the corresponding iminophosphoranes **8–13** after evolution of nitrogen.[13] The iminophosphorane **14** was obtained by successive 1,5-hydrogen migration of [(cyclohepta-2,4,6-trienyl)imino]phosphorane.[13] The reaction of phosphoranes **8–11** with aldehyde **1** afforded 5-azaazulene derivatives **15–18**, while that of triphenyl(vinylimino)phosphorane **12A**, [(azulen-2-yl)imino]tributylphosphorane **13B** and [(cyclohepta-1,3,5-trienyl)imino]tributylphosphorane **14B**, gave only 5-(aminomethylene)cyclopenta-1,3-dienecarbaldehyde **19**, 5-[(azulen-2-yl)aminomethylene]cyclopenta-1,3-dienecarbaldehyde **20** and 5-(cyclohepta-1,3,5-trienylaminomethylene)-cyclopenta-1,3-dienecarbaldehyde **21**, respectively (Scheme 1). In order to gain insight into the selectivity, minimal neglect of differential overlap (MNDO) calculations on structures **1**, **12A**, **12B** and model compounds **8C–14C** were also performed. We describe here the results in detail.

Results and discussion

Annulation of 5-azaazulene ring system

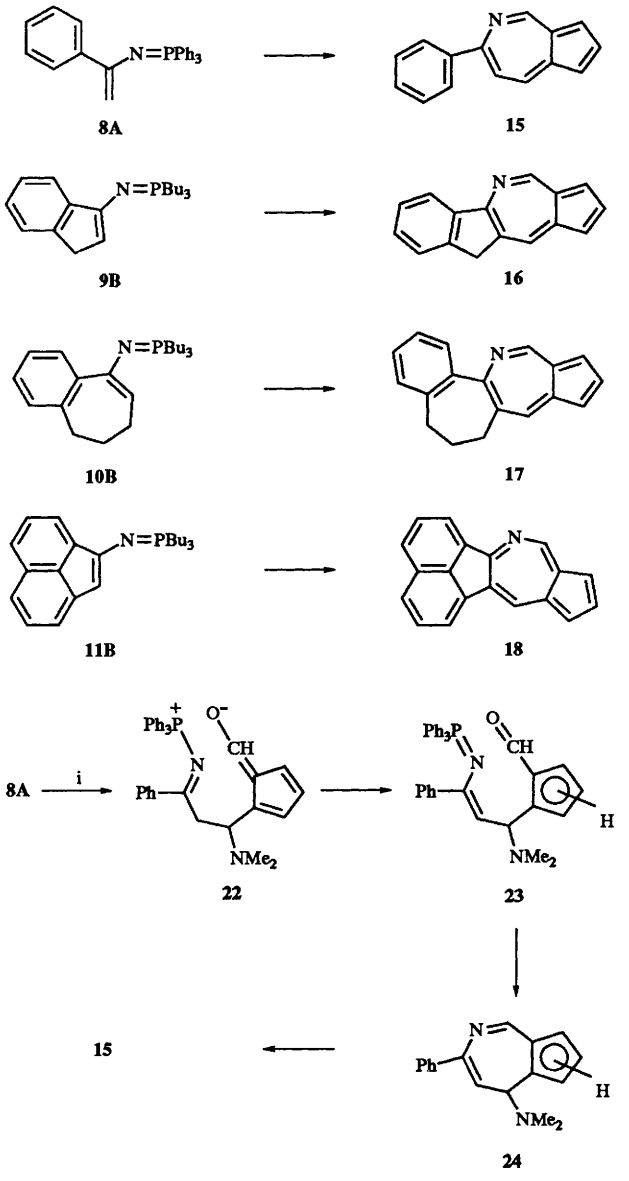
Reaction of triphenyl[(1-phenylvinyl)imino]phosphorane **8A**[16] with aldehyde **1** in anhydrous bromobenzene was carried out to give 6-phenyl-5-azaazulene **15** (Scheme 2). The reaction was also carried out in a one-flask operation: after a solution of 2-phenylvinyl azide **2** and triphenylphosphane in anhydrous bromobenzene had been stirred for 1 h at 80 °C, to this reaction mixture was added aldehyde **1**, and the mixture was refluxed to give product **15**. The structure of compound **15** was unequivocally assigned on the basis of a comparison of its physical data with those reported in the literatures.[7,10a] Further examples of the construction of annulated 5-azaazulenes are shown in Scheme 2. Several (vinylimino)phosphoranes are prepared easily by the Staudinger reaction[19] of the corresponding organic azides with a tertiary phosphane in an anhydrous solvent.[20–22] Since tributyl(vinylimino)phosphoranes seemed more reactive than the triphenyl analogues and generally to be less stable,[21] *in situ* preparation of phosphoranes **9–11** and subsequent reaction with aldehyde **1** in a one-flask operation was carried out. Reaction of tributyl-[(inden-3-yl)imino]phosphorane **9B**[22] with aldehyde **1** afforded the cyclopenta[*e*]indeno[1,2-*b*]azepine **16**. Similarly, tributyl {(6,7-dihydro-5*H*-benzo[7]annulen-9-yl)imino}phosphorane **10B** (see Experimental section) reacted with aldehyde **1** to



Scheme 1

give 6,7-dihydro-5*H*-benzo[7]annuleno[5,6-*b*]cyclopenta[*e*]-azepine **17**. Furthermore, [(acenaphthylen-1-yl)imino]tributylphosphorane **11B**[23] reacted with aldehyde **1** to give acenaphtho[1,2-*b*]cyclopenta[*e*]azepine **18**. The results and reaction conditions are summarized in Table 1.

The proposed reaction pathways for the formation of heterocycles **15–18** is also outlined in Scheme 2 by using compound **8A** as an example. As expected, the enamine-type alkylation of the iminophosphoranes **8A** onto the methylene carbon of aldehyde **1** occurs to give the intermediate **22**. The following proton transfer and ketonization in intermediate **22** generates iminophosphorane **23**. The intermediate **23** then



Scheme 2 *Reagents and conditions:* i, **1**, heat

undergoes intramolecular aza-Wittig reaction to give heterocycle **24**, which eliminates $HNMe_2$ to give compound **15**.

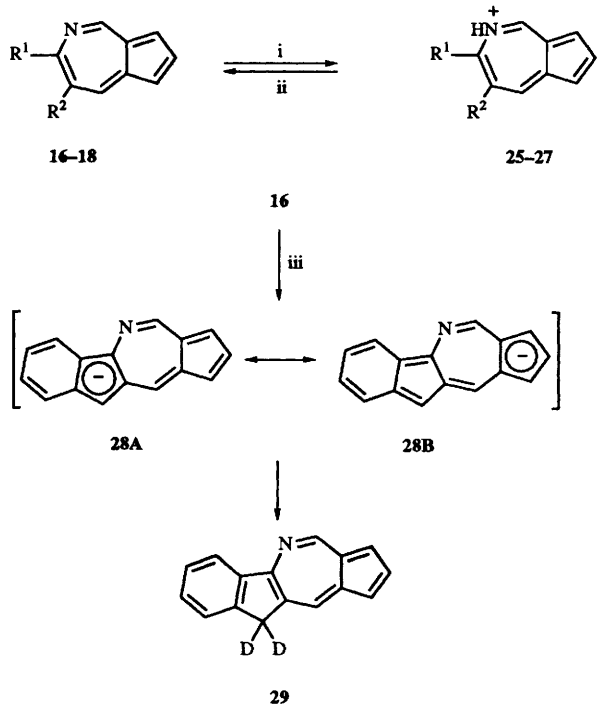
The spectral data of new compounds **16–18** are appropriate for their structures: the ^1H NMR spectra were assigned completely with the aid of pseudocontact spectra obtained by using tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium [Eu(fod)$_3$] and are consistent with the proposed structures. Their electronic spectra in EtOH are similar to that of compound **15**.[7] In particular, compound **18**, involving an acenaphthylene moiety, exhibits an additional longer-wavelength absorption maximum at 738 nm, suggesting the presence of extended conjugation. Furthermore, the absorption maxima in the visible region of compounds **16–18** in EtOH–trifluoroacetic acid (TFA) show hypsochromic shifts, and the features are similar to those of compound **15**[7] (Table 2). These findings indicate that compounds **16–18** exist as 5-azaazulenium ions **25–27** in acidic media (Scheme 3), protonated at the nitrogen atom, being consistent with the theoretical prediction.[8,24] The protonation process is reversible and the compounds were recovered by neutralization with aq. $NaHCO_3$.

Interesting chemical properties of compound **16** were also

Table 1 Reaction of phosphoranes **8–11** with aldehyde **1**

Compound	Solvent	Reaction conditions	Reaction time (t/h)	Product, yield (%)[a]
8A[b]	PhBr	reflux	4	**15** (24)
8A	PhBr	reflux	4	**15** (25)
9B	PhMe	reflux	3	**16** (32)
10B	PhBr	reflux	10	**17** (21)
11B	PhMe	reflux	20	**18** (34)

[a] Yields are based on fulvene **1** used. [b] Isolated phosphorane **8** was used for the reaction.



Scheme 3 *Reagents and conditions:* i, EtOH–TFA; ii, aq. $NaHCO_3$; iii, Bu^{t}OK–MeOD, THF

clarified. On treatment of compound **16** with Bu^{t}OK in MeOD at −45 °C, the methylene hydrogens at C-10 were exchanged almost completely with deuterium to give compound **29** in 90% yield (Scheme 3). The clean deuterium exchange, however, did not proceed at above −40 °C, and significant decomposition was then observed. Therefore the formation of an anion **28**, which is a benzo-annulated aza-analogue of a 14π-electron system, cyclopenta[*f*]azulenide,[25] was suggested. Regarding the canonical structures **28A** and **28B**, the former involves benzene and 5-azaazulene in addition to cyclopentadienide ion, while the latter has 5-azaazulene annulated with quinonoid benzene and cyclopentadienide ion. Since deuterium is not incorporated onto C-1 and/or C-3, the former canonical structure **28A** is suggested to be the more stable thermodynamically.

Intermolecular aza-Wittig reaction or a substitution reaction of aldehyde 1 with phosphoranes 12–14

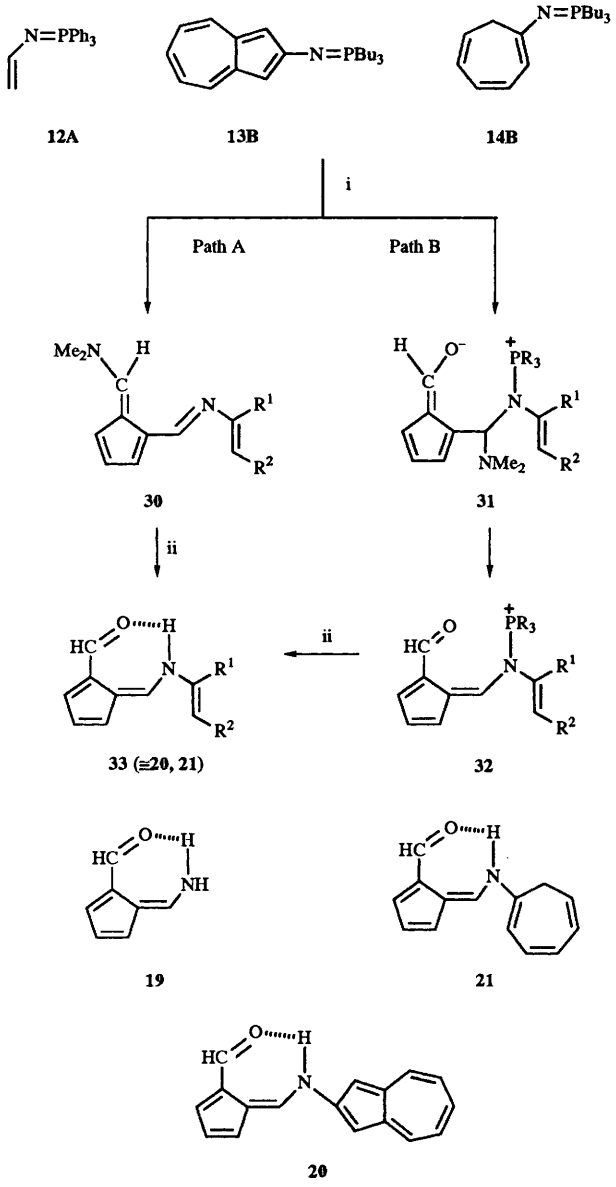
Reaction of unsubstituted (vinylimino)phosphorane **12A**[26] afforded 5-(aminomethylene)cyclopenta-1,3-dienecarbaldehyde **19**[27] albeit in low yield. Furthermore, we found that [(azulen-2-yl)imino]tributylphosphorane **13B**[28] reacted with aldehyde **1** to yield only 5-[(azulen-2-yl)aminomethylene]cyclopenta-1,3-dienecarbaldehyde **20**. Similarly, tributyl[(cyclohepta-1,3,5-trienyl)imino]phosphorane **14B**[21] reacted with aldehyde **1** to give 5-[(cyclohepta-1,3,5-trienyl)aminomethylene]cyclopenta-

Table 2 Electronic spectral data of 5-azaazulene derivatives

Compound	Solvent	λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1})
16	EtOH	301 (4.71), 332 (4.46), 394 (4.16), 558 (3.14), 581 (3.08), 608 (3.02), 670 (2.03)
	EtOH–TFA	302 (4.70), 356 (4.31), 402 (4.06), 537 (3.60), 588 (3.58), 582 (3.51), 638 (3.09)
17	EtOH	285 (4.60), 376 (3.62), 564 (2.91), 610 (2.87)
	EtOH–TFA	284 (4.60), 337 (4.31), 376 (3.91), 541 (3.24), 588 (3.16), 645 (2.87)
18	EtOH	320 (4.95), 353 (4.93), 372 (4.67), 452 (3.32), 610 (2.56), 667 (2.45), 738 (1.91)
	EtOH–TFA	341 (4.90), 427 (3.95), 453 (3.92), 593 (2.93), 648 (2.84), 715 (2.51)

1,3-dienecarbaldehyde **21** (Scheme 4). The results and reaction conditions are summarized in Table 3. The structure of product **19** was unequivocally determined on the basis of a comparison of its spectral data with those reported in the literature.[27] The structures of products **20** and **21** were also determined on the basis of ^{1}H NMR, IR and high-resolution mass spectral data. Typical characteristics of products **20** and **21** are the signals of protons on the methylene carbon of the fulvene moiety. The protons appear at δ 8.17 for compound **20** and δ 7.72 for compound **21**, each of which is coupled with the –NH– proton by J 10.1 and J 13.0 Hz, respectively. Thus the structural assignment was confirmed.

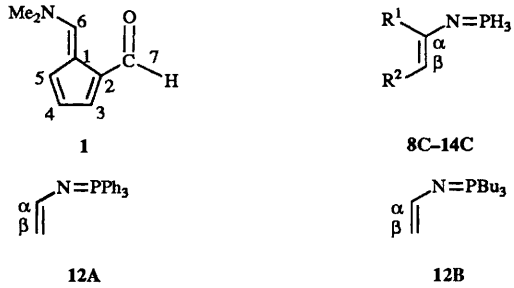
The proposed mechanistic pathways for the formation of products **19–21** are also outlined in Scheme 4. The condensation (aza-Wittig reaction,[19] Path A) of the formyl group of aldehyde **1** with the iminophosphorane moiety of reagents **12–14** gives enimine **30**. This process is very useful in the chemistry of simple iminophosphoranes.[12] Compound **30** is then hydrolysed in the presence of adventitious water or under work-up conditions to give a compound of type **33** (**20** and **21**). The alternative pathway (Path B) is the nucleophilic attack of the nitrogen moiety of phosphoranes **12–14** onto the methylene of aldehyde **1** to give zwitterion **31**, which undergoes elimination of the dimethylamino group to give phosphonium ion **32**. Hydrolysis of the P–N bond of ion **32** gives enamine **33** (**20** and **21**). Unlike the cases of compounds **20** and **21**, the enamine moiety of compounds **33** would be unstable because of the absence of conjugative stabilization, and it would further undergo hydrolysis to give enamine **19**.



Scheme 4 *Reagents and conditions:* i, **1**, heat; ii, adventitious water or SiO_2

Explanation of the selectivity in the reaction of phosphoranes 8–14 with aldehyde 1 by FMO theory

One of the most useful aspects of the principle of hard and soft acids and bases is the way in which it classifies our ideas on ambient reactivity (Schemes 2 and 4).[29] The site where most of the charge exists (the hard centre) will be the site of attack by charged, or relatively charged, electrophiles (hard electrophiles) and the site of the largest coefficient in the highest occupied molecular orbital (HOMO) of the nucleophile (soft centre) will be the site of attack by electrophiles with a relatively low-energy lowest unoccupied molecular orbital (LUMO) (soft electrophile). Thus the selectivity in the reaction of (vinylimino)-phosphoranes **8–14** with aldehyde **1** are now explicable in terms of Frontier Molecular Orbital theory (FMO).[30] Table 4 presents LUMO energy and coefficients as well as charge densities of aldehyde **1** as obtained by the MNDO method.[31] The (vinylimino)phosphoranes **8–14** are large molecules, except for compounds **12**. In the case of **12A**, it consists of fewer than 50 atoms and a MOPAC program is available for the calculations. The calculation on compound **12B** as well as on model compound **12C** (Scheme 5) was also performed, and HOMO energies and coefficients, as well as charge densities of (vinylimino)phosphoranes, are listed in Tables 5 and 6. In the



Scheme 5

rest of the (vinylimino)phosphoranes, calculation on the model compounds **8C–11C**, **13C** and **14C**, all of which involve PH_3 in place of the corresponding PBu_3 or PPh_3 of displayed structures **8–11**, **13** and **14**, respectively, was performed (Tables 5 and 6). Regarding the calculated values of **12A**, **12B** and **12C**, similar relative magnitudes of the coefficients and charge densities are obtained for C^{β}, C^{α} and C^{N}; however, energies of HOMOs are higher for **12A** and **12B**, as compared with that of the model compound **12C**. The relative ratios of HOMO coefficients of C^{β} and C^{N} (C^{β}/C^{N}) are similar for each for compounds **12A**, **12B** and **12C**. Thus we assume that HOMO energies of phosphoranes **8–11**, **13** and **14** must be higher than those of the model compounds **8C–11C**, **13C** and **14C**, but coefficients and charge densities must be similar for compounds **8–11**, **13** and **14** to those of the corresponding model compounds. The values of C^{β}/C^{N} (Table 5) are relatively large for compounds **8C–11C** as compared with those of compounds **12A**, **12B** and **12C**, indicating that enamine-type alkylation is favourable for species **8C–11C**, and thus for all **8–11**. Since the values of C^{β}/C^{N} for compounds **12C** (as well as **12A** and **12B**) are small as compared with those of phosphoranes **8C–11C**, enamine-type alkylation is unfavourable in this case and aza-Wittig reaction of the iminophosphorane moiety (hard centre, high charge density) (Table 6) with the carbonyl carbon atom (hard centre, high positive charge density) (Table 4) must be favoured (Path A in Scheme 4). An alternative pathway is substitution reaction of the iminophosphorane moiety onto the relatively positive centre methylene of aldehyde **1** (Path B in Scheme 4). On the other hand, HOMO levels of compounds **13C** and **14C** are slightly high and C^{β}/C^{N}-values are also large for compounds **13C** and **14C**, as compared with those values for phosphoranes **8C–11C**. However, the charge densities on the nitrogen atom of compounds **13C** and **14C** is extremely high. This fact is suggestive that the aza-Wittig reaction (Path A in Scheme 4) or the substitution reaction (Path B in Scheme 4) predominates for phosphoranes **13C** and **14C**, thus for other phosphoranes **13** and **14**, as in the case of the vinylphosphoranes **12**. Regarding Path A and Path B (Scheme 4), we have no evidence as to which pathway is favoured at this stage; however, the selectivity of the reaction of (vinylimino)phosphoranes **8–14** is suggestive. In addition, the iminophosphoranes **8–14** have been demonstrated to undergo enamine-type alkylation with tropone or 2-chlorotropone to result in the formation of a 1-azaazulene ring system.†,[13] We therefore suggest that the selectivity of the (vinylimino)phosphorane is also dependent on the nature of the Michael acceptor.

In conclusion, the utility of phenyl-substituted and benz-annulated (vinylimino)phosphoranes **8–11** and 5-(dimethylaminomethylene)cyclopenta-1,3-dienecarbaldehyde **1** for the preparation of phenyl-substituted and annulated 5-azaazulene (cyclopenta[*c*]azepine) ring systems was demonstrated. The (vinylimino)phosphoranes **8–11** are suggested to react in an FMO-controlled manner, while phosphoranes **12–14** do so in a charge-controlled fashion on the basis of MNDO calculations on model compounds. Further application of the synthetic methodology using (vinylimino)phosphoranes and related compounds is now in progress in our laboratory.

Table 3 Reaction of phosphoranes **12–14** with aldehyde **1**

Compound	Solvent	Reaction conditions	Reaction time (*t*/h)	Product, yield (%)[a]
12A[b]	PhH	reflux	2	**19** (24)
13B	PhMe	reflux	3	**20** (34)
14B[b]	PhMe	reflux	11	**21** (15)

[a] Yields are based on fulvene **1** used. [b] Isolated (vinylimino)phosphorane was used for the reaction.

Experimental

IR spectra were recorded on a Shimadzu IR-400 spectrometer. Electronic spectra were measured on a Shimadzu UV-3101PC spectrometer. Mass spectra and high-resolution mass spectra were run on a Shimadzu GCMS QP-1000 and a JEOL DX-300 spectrometer. Unless otherwise specified, ^1H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded in $CDCl_3$ solutions on a JNM-GSX400 and spectrometer and the chemical shifts are given relative to internal $SiMe_4$ standard. *J*-Values are given in Hz. Microanalyses were performed at the Materials Characterization Central Laboratory of Waseda University. Mps were recorded on a Yamato mp-21 apparatus and are uncorrected. Triphenyl-[(1-phenylvinyl)imino]phosphorane **8A**,[15] triphenyl(vinylimino)phosphorane **12A**[26] and tributyl[(cyclohepta-1,3,5-trienyl)imino]phosphorane **14B**[21] were prepared and characterized previously. Preparation of tributyl[(inden-3-yl)imino]phosphorane **9B**,[22] [(acenaphthylen-1-yl)imino]tributylphosphorane **11B**,[23] [(azulen-2-yl)-imino]tributylphosphorane **13B**[26] are carried out *in situ* as described previously. The preparation and characterization of [(6,7-dihydro-5*H*-benzo[7]annulen-9-yl)imino]triphenylphosphorane **10A** is described in this paper, and the corresponding tributylphosphorane **10B**[32] was prepared *in situ* and used subsequently for the preparative reaction.

Preparation and characterization of 9-azido-6,7-dihydro-5*H*-benzo[7]annulene 4 and the corresponding iminophosphorane

A solution of NaN_3 (230 mg, 3.5 mmol) and ICl (179 mg, 1.1 mmol) in CH_2Cl_2 (5 cm^3) was stirred at 0 °C for 30 min. To this solution was added 6,7-dihydro-5*H*-benzo[7]annulene

† Iminophosphorane **10B** reacts with 2-chlorotropone to give the 1-azaazulene derivative (ref. 32).

Table 4 FMO energies and coefficients and charge densities of the fulvene **1**[a]

	Coefficient								
LUMO/eV	C-1	C-2	C-3	C-4	C-5	C-6	C^N	C-7	C^O
−0.853	−0.295	−0.013	−0.005	0.322	−0.388	0.562	−0.025	−0.058	0.038
	Charge density								
	C-1	C-2	C-3	C-4	C-5	C-6	C^N	C-7	C^O
	−0.072	−0.166	−0.003	−0.087	−0.064	0.136	−0.395	0.329	−0.305

[a] Numbering scheme is that for fulvene, and is shown in Scheme 5.

Table 5 FMO energies and coefficients of (vinylimino)phosphoranes **8C–11C** and **12A–C**

Compound	HOMO/eV	Coefficient				
		C^{β}	C^{α}	C^{N}	C^{P}	C^{β}/C^{N}
8C	−7.821	0.683	0.330	−0.501	−0.074	1.36
9C	−7.584	0.694	0.327	−0.491	−0.070	1.41
10C	−7.714	0.683	0.324	−0.530	−0.069	1.29
11C	−7.645	0.523	0.389	−0.322	−0.018	1.62
12C	−7.612	0.656	0.368	−0.610	−0.077	1.09
12A	−7.076	0.671	0.342	−0.618	−0.065	1.09
12B	−6.922	0.670	0.328	−0.624	−0.042	1.07
13C	−7.389	0.487	0.392	−0.367	−0.085	1.33
14C	−7.228	0.492	0.358	−0.281	−0.067	1.75

Table 6 Charge densities of phosphoranes **8C–14C**, **12A** and **12B**

Compound	C^{β}	C^{α}	C^{N}	C^{P}
8C	−0.242	0.084	−0.472	0.583
9C	−0.305	0.108	−0.460	0.583
10C	−0.287	0.113	−0.467	0.575
11C	−0.073	0.057	−0.472	0.600
12C	−0.163	0.013	−0.467	0.583
12A	−0.203	0.042	−0.524	0.752
12B	−0.210	0.046	−0.519	0.399
13C	−0.346	0.321	−1.342	3.114
14C	−0.317	0.303	−1.368	3.110

(144 mg, 1 mmol), and the mixture was stirred for 2.5 h at room temp. The reaction was quenched with $Na_2S_2O_3$, the mixture was extracted with CH_2Cl_2, and the extract was dried over $MgSO_4$. Removal of solvent under reduced pressure gave 9-azido-8-iodo-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (302 mg, 97%).

After a solution of this compound (313 mg, 1 mmol) and Bu^{t}OK (210 mg, 2 mmol) had been stirred at room temp. for 2.5 h, aq. NH_4Cl was added to the reaction mixture. The mixture was extracted with CH_2Cl_2, and the extract was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting residue was purified through column chromatography on alumina to give 9-azido-6,7-dihydro-5*H*-benzo[7]annulene **4** (144 mg, 78%) as an oil; δ_H($CDCl_3$; 60 MHz) 1.67–2.39 (4 H, m, 6- and 7-H_2), 2.39–3.04 (2 H, m, 5-H_2), 5.62–6.09 (1 H, m, 8-H) and 6.95–7.53 (4 H, m, ArH).

To a stirred solution of compound **4** (185 mg, 1 mmol) in anhydrous benzene (2 cm^3) was added a solution of PPh_3 (236 mg, 0.9 mmol) in benzene (1 cm^3) dropwise at room temp., and the mixture was stirred at room temp. for 1.5 h. To this reaction mixture was added hexane (8 cm^3), and the precipitate was collected by filtration to give [(6,7-*dihydro*-5H-*benzo*[7]*annulen*-9-*yl*)*imino*]*triphenylphosphorane* **10A** (331 mg, 82%) as yellow prisms, mp 115–116 °C (from hexane–benzene); δ_H($CDCl_3$; 60 MHz) 1.38–2.20 (4 H, m, 5- and 7-H_2), 2.20–2.68 (2 H, m, 6-H_2), 4.80–5.17 (1 H, m, 8-H) and 6.83–8.04 (19 H, m, 1-, 2-, 3- and 4-H and Ph_3); *m*/*z* (rel. intensity) 419 (M^+, 64%) and 183 (100) (Found: C, 83.0; H, 6.1; N, 3.2. $C_{29}H_{26}NP$ requires C, 83.03; H, 6.25; N, 3.34%).

Reaction of phosphorane 8A with 5-(dimethylaminomethylene)-cyclopenta-1,3-dienecarbaldehyde 1

A solution of phosphorane **8A** (379 mg, 1 mmol) and aldehyde **1** (134 mg, 0.9 mmol) in anhydrous bromobenzene (2 cm^3) was heated under reflux for 4 h. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel with benzene as eluent. The fractions eluted with benzene were further purified by TLC on silica gel (CH_2Cl_2) to give 3-phenylcyclohepta[*c*]azepine **15** as violet plates, mp 156–158 °C (from hexane) (lit.,[7] mp 158–159 °C).

In one-flask operation. After a solution of 1-phenylvinyl azide (174 mg, 1.2 mmol) and PPh_3 (315 mg, 1.2 mmol) in bromobenzene (2 cm^3) had been stirred at 80 °C for 1 h, compound **1** (149 mg, 1 mmol) was added to the reaction mixture, and the mixture was refluxed for another 4 h. Work-up similar to that described above gave compound **15**. The results and reaction conditions are summarized in Table 1.

General procedure for the reaction of phosphoranes 9–11 with aldehyde 1

A solution of the corresponding organic azide **3–5** (1 mmol) and tributylphosphane (202 mg, 1 mmol) in anhydrous solvent (2 cm^3) was stirred at room temperature for 40 min. To this mixture was added a solution of aldehyde **1** (134 mg, 0.9 mmol) in the same solvent (1 cm^3), and the mixture was heated under reflux for the period indicated in Table 1. The reaction mixture was then filtered through Celite, and the resulting residue was purified by TLC on silica gel (CH_2Cl_2) to give 5-azaazulene derivatives **16–18**. The results and reaction conditions are summarized in Table 1.

11*H*-Cyclopenta[*e*]indeno[1,2-*b*]azepine 16. *Violet needles*, mp 190 °C (from EtOH); δ_H 4.16 (2 H, s, 10-H_2), 7.45 (1 H, d, *J* 3.7, 1-H), 7.49–7.52 (2 H, m, 7- and 8-H), 7.56–7.59 (1 H, m, 9-H), 7.62 (1 H, d, *J* 3.7, 3-H), 7.82 (1 H, d, *J* 3.7, 2-H), 8.26–8.30 (1 H, m, 6-H), 8.48 (1 H, s, 11-H), 9.41 (1 H, s, 4-H); relative downfield shifts (ppm/mol) obtained by using Eu(fod)$_3$: 1.0 (3-H), 2.5 (9-H), 3.0 (2-H), 8.8 (1-H), 13.5 (11-H), 61.0 (5-H), 99.9 (6-H), unresolved (7-, 8- and 10-H); δ_C 38.8, 120.8, 123.0, 123.9, 124.6, 127.6, 130.1, 130.8, 133.2, 136.2, 137.2, 137.7, 144.5, 145.1, 152.7 and 163.7; ν_{max}($CHCl_3$)/cm^{-1} 1583 and 1551; *m*/*z* (rel. intensity) 217 (M^+, 100%) (Found: M^+, 217.0899. $C_{16}H_{11}N$ requires M, 217.0892).

6,7-Dihydro-5*H*-benzo[7]annuleno[5,6-*b*]cyclopenta[*e*]azepine 17. *Violet needles*, mp 116–117 °C (from EtOH); δ_H 2.21–2.40 (2 H, m, 6-H_2), 2.58–2.64 (4 H, m, 5- and 7-H_2), 7.23 (1 H, d, *J* 1.5, 9-H), 7.36–7.46 (2 H, m, 2- and 3-H), 7.44–7.47 (1 H, m, 4-H), 7.54 (1 H, d, *J* 1.5, 11-H), 7.88–7.93 (2 H, m, 1- and 10-H), 8.34 (1 H, s, 8-H) and 9.42 (1 H, s, 12-H); δ_C 30.5, 33.4, 35.7, 120.5, 121.5, 126.9, 128.0, 129.4, 129.6, 129.9, 131.9, 137.9, 138.2, 139.1, 142.5, 144.2, 149.7 and 164.6; ν_{max}($CHCl_3$)/cm^{-1} 1584 and 1548; *m*/*z* (rel. intensity) 245 (M^+, 100%) (Found: M^+, 245.1197. $C_{18}H_{15}N$ requires M, 245.1206).

Acenaphtho[1,2-*b*]cyclopenta[*e*]azepine 18. *Green prisms*, mp 170 °C (from EtOH); δ_H 7.53 (1 H, d, *J* 3.7, 10-H), 7.57 (1 H, d, *J* 3.7, 8-H), 7.64 (1 H, dd, *J* 8.1 and 7.0, 2-H), 7.75 (1 H, dd, *J* 8.1 and 7.0, 5-H), 7.79 (1 H, t, *J* 3.7, 9-H), 7.84 (1 H, d, *J* 8.4, 4-H), 7.93 (1 H, d, *J* 7.0, 1-H), 7.99 (1 H, d, *J* 8.1, 4-H), 8.39 (1 H, d, *J* 7.0, 1-H), 8.82 (1 H, s, 7-H) and 9.30 (1 H, s, 11-H); relative downfield shifts (ppm/mol) obtained by using Eu(fod)$_3$: 0.0 (9-H), 1.0 (2-H), 2.0 (3-H), 8.6 (4-H), 8.6 (8-H), 9.1 (7-H), 9.6 (2-H), 10.5 (1-H), 10.6 (8-H), 68.5 (7-H) and 125.9 (6-H); δ_C

119.7, 122.8, 123.6, 124.5, 126.7, 127.4, 128.4, 128.8, 129.2, 130.0, 131.5, 133.2, 134.2, 136.6, 136.8, 136.9, 139.0, 150.5 and 162.8; $\nu_{max}(CHCl_3)/cm^{-1}$ 1583 and 1551; *m/z* (rel. intensity) 253 (M^+, 100%) (Found: M^+, 253.0883. $C_{19}H_{11}N$ requires M, 253.0892).

Deuterium-exchange reaction of compound 16

A solution of Bu^{t}OK (11.2 mg, 0.1 mmol) in MeOD (0.6 cm^3)–tetrahydrofuran (THF) (1 cm^3) was cooled to −45 °C. To this solution was added a solution of compound **16** (22 mg, 0.1 mmol) in THF (1 cm^3), and the mixture was stirred at −45 °C for 2 h. D_2O (1 cm^3) was added and the mixture was stirred for 10 min before being poured into water, extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4. After evaporation of the solvent, deuterium-incorporated product **29** (20 mg, 90%) was obtained.

Reaction of phosphoranes 12A and 14B with aldehyde 1

A solution of a phosphorane **12A** or **14B** (1 mmol) and aldehyde **1** (134 mg, 0.9 mmol) in an appropriate solvent (3 cm^3) was heated under reflux for a period indicated in Table 3. After evaporation of the solvent, the residue was purified through column chromatography on silica gel. Fractions eluted with hexane–AcOEt (1:1) were concentrated and the residue was further separated by TLC on silica gel (CH_2Cl_2) to give products **19** and **21**, respectively. Compound **19** was identified on the basis of a comparison of its IR and ^1H NMR spectral data with those reported in the literature.[27] The results are summarized in Table 3.

5-(Cyclohepta-1′,3′,5′-trienylaminomethylene)cyclopenta-1,3-dienecarbaldehyde 21. *Yellow oil*; $\delta_H(CDCl_3$; 90 MHz) 2.72 (2 H, d, *J* 6.8, 7′-H_2), 5.37 (1 H, dt, *J* 9.0 and 6.8, 6′-H), 6.09–6.50 (3 H, m, 3-, 2′- and 5′-H), 6.50–6.60 (2 H, m, 3′- and 4′-H), 6.97–7.04 (1 H, m, 2-H), 7.30–7.40 (1 H, m, 4-H), 7.72 (1 H, dd, *J* 13.0 and 0.9, =CH–N), 9.47 (1 H, s, CHO), 12.95–13.50 (1 H, br, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3011, 1656 and 1607; *m/z* (rel. intensity) 211 (M^+, 77%) and 91 (100) (Found: M^+, 211.0985. $C_{14}H_{13}NO$ requires M, 211.0988).

Reaction of compound 13B with aldehyde 1

A solution of 2-azidoazulene **7** (66 mg, 0.5 mmol) and tributylphosphane (101 mg, 0.5 mmol) in toluene (2 cm^3) was stirred at room temp. for 30 min. To this mixture was added a solution of aldehyde **1** (67 mg, 0.45 mmol) in toluene (1 cm^3), and the mixture was heated under reflux for 3 h. The reaction mixture was then filtered through Celite and the filtrate was purified by TLC on silica gel (CH_2Cl_2) to give **20**. The results are summarized in Table 3.

5-(Azulen-2′-ylaminomethylene)cyclopenta-1,3-dienecarbaldehyde 20. *Violet oil*; $\delta_H(CDCl_3$; 90 MHz) 6.51 (1 H, dd, *J* 4.2 and 3.3, 3-H), 7.05–7.50 (5 H, m, 2-, 4-, 5′-, 6′- and 7′-H), 7.12 (2 H, s, 1′- and 3′-H), 8.02–8.24 (2 H, m, 4′- and 8′-H), 8.17 (1 H, dd, *J* 10.1 and 0.9, =CH–N), 9.55 (1 H, s, CHO) and 13.60–14.10 (1 H, br, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3016, 1649 and 1608; *m/z* (rel. intensity) 247 (M^+, 48%) and 218 (100) (Found: M^+, 247.0991. $C_{17}H_{13}NO$ requires M, 247.0998).

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