Synthesis, structure, and reactivity of (tropon-2-ylimino)arsorane and *in situ* generation of its stiborane and bismuthorane analogues: reactions with heterocumulenes and an activated acetylene giving heteroazulenes

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(Tropon-2-ylimino)pnictoranes of the general structure $RN{=}MPh_3$ (R = tropon-2-yl; M = As, Sb, and Bi) **4**–**6** have been prepared for the first time by the reaction of 2-aminotropone with Ph_3MX_2 (M = As, Sb, and Bi) in the presence of a base. The arsorane derivative (M = As) **4** is isolated as a stable crystalline compound, while the stiborane (M = Sb) and the bismuthorane (M = Bi) derivatives **5** and **6** are not isolated and are prepared *in situ* due to their moisture sensitivity. The X-ray crystal analysis revealed that compound **4** exhibits two different conformations in the solid state, and that the As–O bond distances (2.33 Å) lie below the sum of the van der Waals radii (3.37 Å), and thus, there is appreciable bonding interaction between the arsine and the oxygen atoms. With a view to constructing a series of cyclohepta-annulated heterocycles and in order to gain a better understanding of a series of iminopnictoranes, compounds **4**–**6** were allowed to react with heterocumulenes such as carbon disulfide, phenyl isothiocyanate, phenyl isocyanate, and diphenylcarbodiimide, in an aza-Wittig/electrocyclization or a formal [8 + 2] type cycloaddition eliminating triphenylpnictorane oxide to give 2*H*-cycloheptaoxazol-2-one, its thione, and imine derivatives. On the other hand, the reaction of compounds **4** and **5** with dimethyl acetylenedicarboxylate (DMAD) gives postulated dimethyl cyclohepta[*b*]pyrrole-2,3-dicarboxylate, which subsequently reacts with DMAD to result in the formation of tetramethyl 2*H*-cyclohepta[*gh*]pyrrolizine-1,2,4,5-tetracarboxylate, while the reaction of **6** gives only intractable tarry materials. The reactivity of the compounds **4**–**6**, which contain a formal N=M (M = As, Sb, and Bi) double bond, has been clarified to be in the order of **6** (M = Bi) > **5** (M = Sb) > **4** (M = As) > [the corresponding iminophosphorane derivative **3** (M = P)].

Introduction

Iminopnictoranes **1a**–**d** are a class of compounds bearing a formal double bond between the nitrogen and the pnictogen elements (Fig. 1). They have been receiving considerable attention in view of their chemical analogy to pnictogen ylides as well as their potential utility in organic synthesis.[1–3] The properties of iminopnictoranes are highly dependent on the identity of the pnictogen. The dipolar and nucleophilic character of the iminopnictoranes appears to increase, and their stability decreases, when the pnictogen stands lower in the Periodic Table. The difference between iminophosphoranes and other iminopnictoranes is commonly ascribed to the less efficient pπ–dπ overlap between the N-p orbitals and the larger and more diffuse 4d, 5d, and 6d orbitals of arsine, stibine, and bismuth elements, and the decreased electrostatic interaction across the imide bonds, but it is probable that these are not the only factors involved.[2] Iminoarsoranes (M = As) appear to be more resistant to hydrolysis than the corresponding iminostiboranes (M = Sb) and iminobismuthoranes (M = Bi) for even the simple example (R = H),[2,4] and can be handled in air, although they are less stable than their phosphorane analogues. All known iminopnictoranes (M = Sb,[5,6] Bi[5–9]) are stabilized by highly electronegative organic sulfonyl[5,8] and trifluoroacetyl[10] groups on the nitrogen atom, but no iminopnictoranes (M = Sb, Bi) bearing a functional group other than organic sulfonyl and trifluoroacetyl[10] groups have been reported to date. On the other hand, the utility of (vinylimino)phosphoranes **2** as

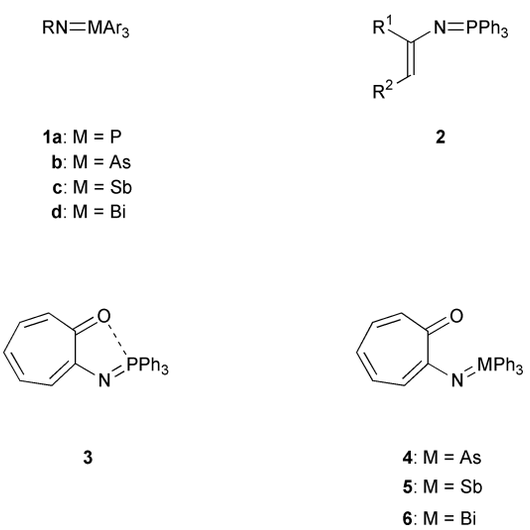

Fig. 1

useful building blocks for the synthesis of azaheterocycles has been demonstrated convincingly.[11–15] (Vinylimino)phosphoranes undergo a single-step annulation with compounds containing two electrophilic centers such as α-bromo ketones, α,β-unsaturated ketones and aldehydes, and related Michael acceptors to give a variety of nitrogen heterocycles.[13] In relation to these studies, we have been interested recently in exploiting

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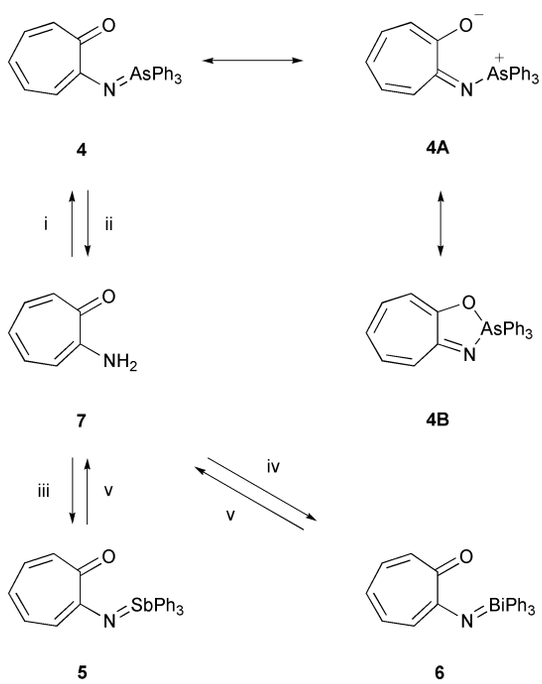
the synthesis, structure, and reactivities afforded by the (tropon-2-ylimino)phosphorane† **3**.[16] The X-ray crystallographic analysis of **3** has revealed that the P---O distance is significantly longer than a covalent bond, but the oxygen atom in **3** intramolecularly coordinates to the phosphorus atom. It is also clarified that the reaction of **3** with heterocumulenes provides a new methodology for constructing new cyclohepta-annulated five-membered heterocycles (heteroazulenes). In order to gain a better understanding of this class of iminopnictoranes, we have embarked on the preparation of a series of iminopnictoranes **4**–**6**, which could be stabilized by coordination of the oxygen atom to the pnictogenes like the phosphorus analogue **3**. We report herein the first synthesis, structure, and reactivity of the (tropon-2-ylimino)arsorane **4** as well as *in situ* generation of the (tropon-2-ylimino)stiborane **5** and bismuthorane **6** and their reaction with heterocumulenes and dimethyl acetylenedicarboxylate (DMAD).

Results and discussion

In our previous paper, we reported a Kirsanov reaction,[17] treating 2-aminotropone **7** with Ph_3PCl_2 in benzene to yield (tropon-2-ylimino)phosphorane in good yield (Scheme 1).[16]



Scheme 1 *Reagents and conditions*: i, Ph_3AsBr_2, NEt_3, PhH or C_6D_6, rt; ii, H_2O or H_3O^+; iii, Ph_3SbCl_2, Bu^{t}OK, PhH or C_6D_6, rt; iv Ph_3BiCl_2, Bu^{t}OK, PhH or C_6D_6, rt; v, H_2O.

This imination procedure is known to be useful also for the preparation of (tropon-2-ylimino)pnictoranes **4**, **5**, and **6**. 2-Aminotropone **7** reacted with Ph_3AsBr_2[18] in the presence of NEt_3 at room temperature to give (tropon-2-ylimino)arsorane **4** in good isolated yield. The structure of compound **4** was confirmed from an inspection of the spectroscopic data including ^{1}H NMR spectra (Table 1), IR, UV–visible, and mass spectral data as well as elemental analysis, and finally X-ray crystal structure analysis.

The X-ray crystal analysis revealed compound **4** exhibits two different conformations in the solid state. Two ORTEP drawings of the conformers **I** and **II** are shown in Fig. 2, where the arsine atoms of conformers **I** and **II** lie between the center of a trigonal bipyramidal configuration [(O1 and C11) and (O1′ and C11′) in apical positions, (N1, C21, and C31) and (N1′, C21′, and C31′) in equatorial positions, respectively] and the center of a tetrahedral configuration, with the bond angles shown in Fig. 3. On the other hand, the intramolecular As1---O1 and As1′---O1′ distances (2.33 Å for **I** and **II**) are longer than a covalent bond (1.74–1.90 Å) in spirobi(1,3,2λ^5-dioxarsolane) derivative,[19] and are significantly shorter than the sum of the van der Waals radii (3.37 Å).[20] Thus, evidently, the oxygen atom of compound **4** intramolecularly coordinates to the arsine atom. The As1–N1 (1.81 Å for **I**) and As1′–N1′ (1.82 Å for **II**) bonds are slightly longer than a standard formal As=N bond (1.71–1.78 Å).[21] This is also in accord with the observed relatively short N1–C2 (1.32 Å) and N1′–C2′ (1.28 Å) bond lengths for **I** and **II**, as compared with typical N–C(sp^2) bond length (1.38 Å).[22] Thus, the As1=N1 and As1′=N1′ bonds possess little double-bond character, and the canonical structures **4A** and **4B** best represent the actual bonding in **4**. The tropone moiety in compound **4** is nearly planar, and bond length alternation is clearly seen (1.37–1.46 Å for **I**; 1.37–1.47 Å for **II**); the result is also in agreement with the evidence obtained from the ^{1}H NMR spectra (Table 1). The carbonyl absorption appearing at ν_{max} 1590 cm^{-1} in the IR spectrum is slightly lower than those found in tropone (ν_{max} 1594 cm^{-1})[23] and compound **3** (ν_{max} 1596 cm^{-1}),[16] and the C=O bond lengths (1.27 Å for **I** and 1.24 Å for **II**) do not differ appreciably from those of tropone and compound **3** (1.26 Å).[16,24] Compound **4** is stable at room temperature for a month in dry nitrogen atmosphere, and it is not stable over silica gel. On treatment of **4** with water or acid, it underwent hydrolysis to afford 2-aminotropone **7** and triphenylarsine oxide (Scheme 1).

On the other hand, the reaction of **7** with Ph_3SbCl_2[25] and Ph_3BiCl_2[26] in the presence of Bu^{t}OK in benzene proceeded in 5–10 min, but the usual work-up did not afford the stiborane **5** and bismuthorane **6**, respectively, and only the starting material **7** was isolated. However, *in situ* generation of **5** and **6** in hexadeuteriobenzene (C_6D_6) was carried out, and the ^{1}H NMR spectra confirmed the formation of **5** and **6** (Scheme 1). The ^{1}H NMR spectral data of **5** and **6** as well as of isolated **4** and *in situ*-generated **4** are summarized in Table 1. The ^{1}H NMR spectral data of **4**–**6** resemble each other and clearly suggest the clean generation of **4**, **5**, and **6**. Compounds **5** and **6** are actually clarified by ^{1}H NMR spectral studies as being moisture sensitive. The addition of a trace amount of water caused decomposition of **5** and **6** leading to 2-aminotropone **7** (Scheme 1). Furthermore, compounds **4** and **5** are stable under heating in benzene (*cf.* Table 2), while compound **6** in benzene seems to eliminate the tropon-2-ylnitrene moiety to give Ph_3Bi in 84% yield after heating under reflux for 1 h (see Experimental section).[10] Thus, the moisture sensitivity of (tropon-2-ylimino)-iminopnictoranes **4**–**6** seems to increase and the thermal stability decreases when the pnictogen element stands lower in the Periodic Table.

Previously, the iminophosphorane **3** was revealed to react with heterocumulenes to afford cyclohepta-annulated heterocycles (Table 2, Entries 1, 5, 15, and 20).[16] In relation to that study and to clarify the reactivities, the reactions of pnictoranes **4**–**6** with heterocumulenes **8a**–**d** were investigated. The reaction of compounds **4** and *in situ*-generated **5** and **6** with carbon disulfide **8a** was accomplished to give 2*H*-cycloheptaoxazole-2-thione **11** (Scheme 2). Similarly, the reactions of compounds **4** and *in situ*-generated **4**–**6** with phenyl isothiocyanate **8b** were also carried out to give *N*-phenyl-2*H*-cycloheptaoxazole-2-imine **12**, which is a mixture of (***Z***)- and (***E***)-isomers in the ratio 7 : 3.[16] The reaction conditions and the yields of the products are summarized in Table 2 (Entries 2–4 and 6–9). The reaction of isolated **4** with **8b** gave a good yield of **12**, while that of *in situ*-generated **4** with **8b** gave a modest yield of **12** (Table 2, Entries 6 and 7). The structures of compounds **11** and **12** were confirmed on the basis of a comparison of their physical data with those of the authentic specimens.[16] The iminopnictoranes

† The non-systematic term 'tropon-2-yl' will be used in both this section and the Results and discussion; systematic nomenclature (7-oxo cyclohepta-1,3,5-trienyl) will be used in the Experimental section.

Table 1 ^{1}H NMR spectral data (500 MHz) of pnictoranes **4**–**6**

Compd		H3		H4		H5		H6		H7	Remaining signals
4[a]	δ_H	7.66		7.12		6.54		6.98		6.75	7.36–7.42 (9H, m, Ph),
	J		10.5		9.3		9.5		10.7		7.62–7.66 (6H, m, Ph),
4[b]	δ_H	8.01		6.99		6.36		6.76		7.03	7.08–7.13 (9H, m, Ph)
	J		11.0		9.4		9.4		10.8		7.72–7.90 (6H, m, Ph)
4[c]	δ_H	7.36		6.85		6.31		6.77		7.11	7.15–7.22 (9H, m, Ph),
	J		11.6		9.0		10.0		10.3		7.72 (6H, d, *J* 6.6, Ph)
5[c]	δ_H	7.04		6.52		6.05		6.42		6.06	7.07–7.30 (15H, Ph)
	J		10.4		9.5		9.1		11.0		
6[c]	δ_H	7.91		6.93		6.36		6.80		7.25	7.18–7.21 (9H, m, Ph),
	J		11.9		9.4		9.0		10.2		7.95 (6H, d, *J* 7.0, Ph)

[a] Isolated compound in $CDCl_3$. [b] Isolated compound in C_6D_6. [c] Compound prepared *in situ* in C_6D_6.

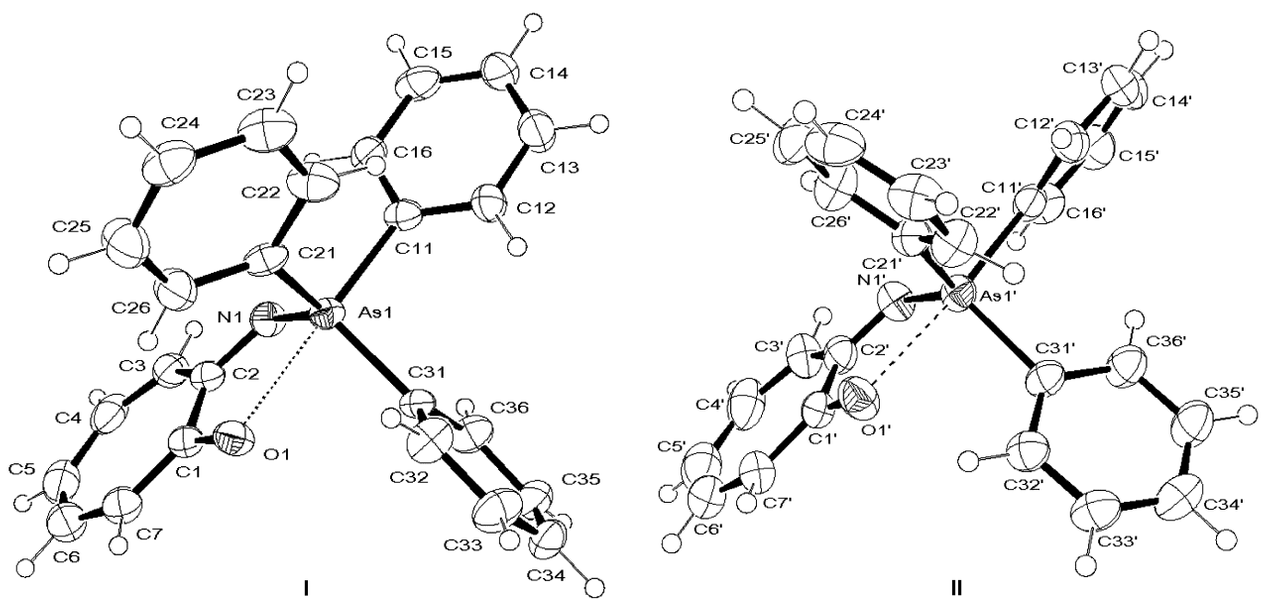


Fig. 2 ORTEP drawing of conformations **I** and **II** for **4** with thermal ellipsoid plot (40% probability) (with crystallographic numbering). Selected bond lengths (Å). For **I**: As1–O1 2.326, As1–C11 1.964(5), As1–C21 1.957(5), As1–C31 1.940(5), As1–N1 1.814(5), O1–C1 1.274(7), N1–C2 1.315(7), C1–C2 1.462(8). C2–C3 1.409(8), C3–C4 1.369(9), C4–C5 1.435(10), C5–C6 1.378(11), C6–C7 1.395(9), C7–C1 1.370(8). For **II**: As1′–O1′ 2.332, As1′–C11′ 1.976(5), As1′–C21′ 1.948(5), As1′–C31′ 1.961(5), As1′–N1′ 1.820(5), O1′–C1′ 1.237(7), N1′–C2′ 1.284(7), C1′–C2′ 1.471(8), C2′–C3′ 1.405(8), C3′–C4′ 1.420(10), C5′–C6′ 1.370(11), C6′–C7′ 1.419(9), C7′–C1′ 1.391(8).

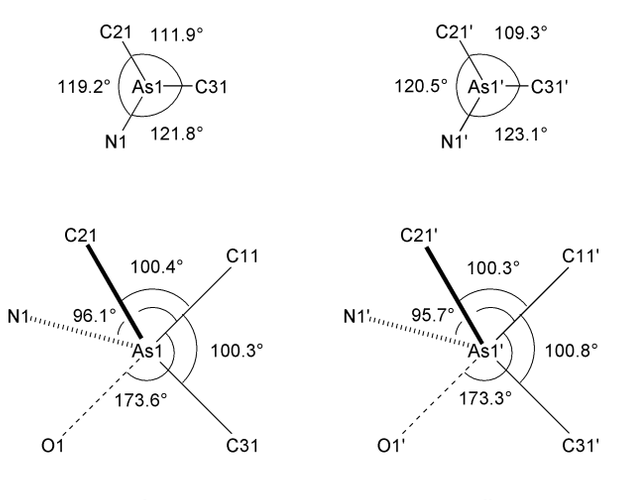
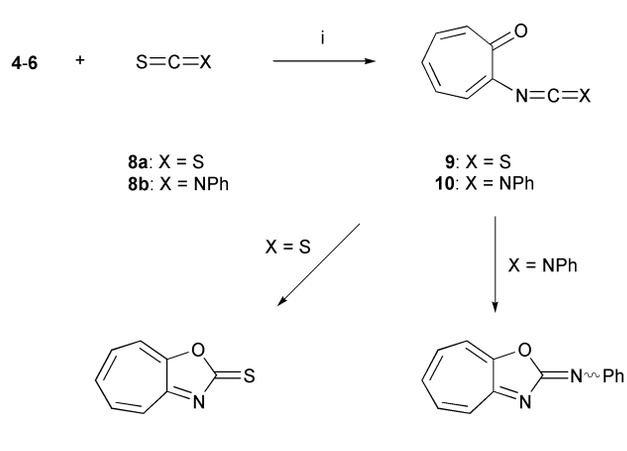


Fig. 3 Bond angles around nearly the trigonal bipyramidal structure of conformations **I** and **II** for **4**.



Scheme 2 *Conditions*: i, heat.

4–**6** undergo an aza-Wittig-type reaction to eliminate the sulfur atom of **8a**,**b** to lead to the intermediates **9** and **10**, which then undergo 10π-electron cyclization to give **11** and **12**, respectively.[16] This is similar to the reaction of **3** with carbon disulfide **8a** and phenyl isothiocyanate **8b**, respectively (Table 2, Entries 1 and 5). Compounds **3** and **4** undergo the reaction at elevated temperature, while reactions of **5** and **6** proceeded smoothly at lower temperature (Table 2). Thus, it is clear that the reactivity of **3**–**6** is in the order **3** < **4** < **5** < **6**. The reactivity due to the dipolar and nucleophilic character of the iminopnictoranes **3**–**6** appears to increase when the pnictogen stands lower in the Periodic Table.

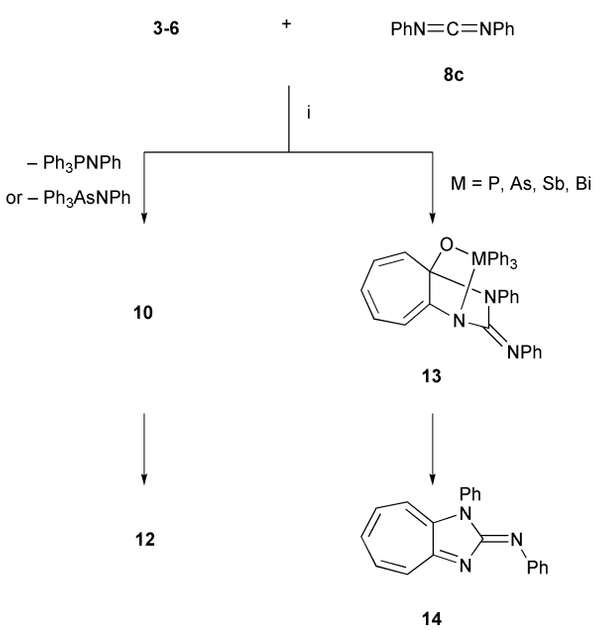
Since the reaction of the iminophosphorane **3** (Fig. 1) with diphenylcarbodiimide **8c** has not been investigated,[16] the iminopnictoranes **3**–**6** were allowed to react with diphenylcarbo-

Table 2 Results for the reactions of compounds **3**, **4**, **5** and **6** with heterocumulenes **8a**–**d** and DMAD **17**

Entry	Compd.	Cumulene or **17**	Ratio of **8a**–**d** or **17** : **3**–**6**[a]	Reaction conditions		Product (Yield/%)
				Solvent[b]	Time *t*/h	
1[c]	**3**	**8a**	excess	CS_2[d]	1 week	**11** (82)
2	**4**[e]	**8a**	excess	CS_2[d]	2 days	**11** (92)
3	**5**	**8a**	excess	PhH–CS_2	30	**11** (82)
4	**6**	**8a**	excess	PhH–CS_2[f]	4	**11** (21)
5[c]	**3**	**8b**	2	PhMe	9	**12** (72), **16** (7)
6	**4**[e]	**8b**	10	PhH	5	**12** (81)
7	**4**	**8b**	10	PhH	1	**12** (42)
8	**5**	**8b**	10	PhH	4.5	**12** (72)
9	**6**	**8b**	10	PhH[f]	3	**12** (26)
10	**3**	**8c**	5	Xylenes	7	**12** (63), **14** (11)
11	**4**[e]	**8c**	5	PhH	10	**12** (20), **14** (57)
12	**4**	**8c**	5	PhH	4.5	**12** (3), **14** (42)
13	**5**	**8c**	5	PhH	1	**14** (63)
14	**6**	**8c**	5	PhH[f]	10 min	**14** (54)
15[c]	**3**	**8d**	2	PhH	1	**12** (26), **16** (74)
16	**4**	**8d**	10	PhH	1	**16** (42)
17	**5**	**8d**	10	PhH	30 min	**16** (53)
18	**6**	**8d**	10	PhH[f]	5 min	**16** (34)
19	**4**[e]	**8d**	10	Xylenes	25	**12** (15), **14** (34)
20[c]	**3**	**17**	3	PhBr	4.5	**23** (43)
21	**4**[e]	**17**	5	PhBr	20	**23** (60)
22	**5**	**17**	10	PhBr	1	**23** (10)

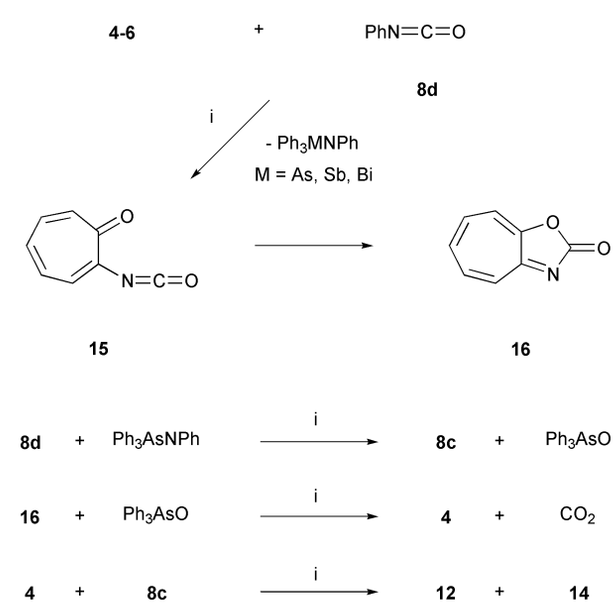
[a] In the case of *in situ* generation of **4**–**6**, the amounts correspond to the amount of 2-aminotropone **7** used. [b] Unless otherwise specified, the reaction was carried out under reflux. [c] Ref. 16. [d] Reaction was carried out in an autoclave at 100 °C. [e] Isolated compound. [f] Stirred at room temperature.

diimide **8c**, which was prepared *in situ* by the reaction of phenyl isocyanate **8d** in the presence of a catalytic amount of Ph_3AsO.[27] The reaction conditions and the yields of the products are summarized in Table 2 (Entries 10–14). The reactions of **3** and **4** with **8c** proceeded at relatively high temperature to give products **12** and **14** (Scheme 3; Table 2, Entries 10–12). On the other hand, the reactions of **5** and **6** with **8c** proceeded selectively under mild conditions to give the single product **14** (Entries 13 and 14). The structure of new compound **14** was assigned on the basis of its ^1H and ^{13}C NMR spectra, IR, UV–visible spectra, mass spectral data, and analytical data, as well as a comparison of its physical data with those of related derivatives.[28] Furthermore, it was found that compound **14** is not a mixture of (***E***)- and (***Z***)-isomers. Although no evidence for the stereochemical situation for **14** was obtained, we prefer the (***Z***)-isomer for **14**, because of the steric hindrance of the phenyl groups. The reactions of **3** and **4** with **8c** are considered to proceed *via* an aza-Wittig reaction giving the intermediate **10** and *via* a formal [8 + 2]-type electrocyclization to give the intermediate **13**, while those of **5** and **6** with **8c** proceed *via* the intermediate **13**. The intermediates **10** and **13** then collapse to result in the formation of **12** and **14**, respectively. The formation of **13** is suggestive of the M---O (M = P, As, Sb, Bi) coordinating interaction in compounds **3**–**6**, and the interaction may appear to be larger when the pnictogen atom is lower in the Periodic Table.



Scheme 3 *Conditions*: i, heat.

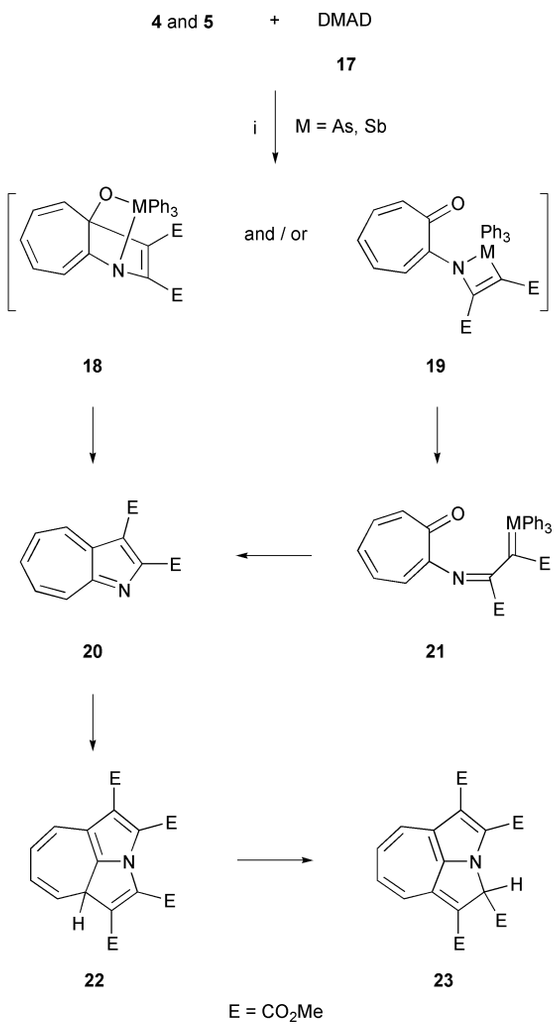
On the other hand, the reactions of **4**–**6** prepared *in situ* with phenyl isocyanate **8d** afforded 2*H*-cycloheptaoxazol-2-one **16**, which probably arises from an aza-Wittig-type reaction giving the intermediate **15**, in modest yields (Scheme 4, Table 2, Entries 16–18). In these cases, the reactions of **5** and **6** seem to proceed quickly or under mild conditions as compared with that of **4**. In the reaction of isolated **4** with **8d** at elevated temperature of refluxing xylenes, products **12** and **14**, instead of **16**, were



Scheme 4 *Conditions*: i, heat.

isolated (Table 2, Entry 19). This process is similar to the reaction of **4** with **8c** (Table 2, Entries 11 and 12). Ph_3AsNPh is generated in the reaction of **4** with **8d** giving the intermediate **15**, which probably reacts with excess of **8d** to generate carbodiimide **8c** and Ph_3AsO. The latter compound further reacts with **8d** to generate Ph_3AsNPh, and thus, **8c** is generated in a catalytic process.[27] The independent reaction of **16** with Ph_3AsO in refluxing xylenes gives compound **4**, which is detected by its ^1H NMR spectrum. Thus, compound **16**, which is generated by the reaction of isolated **4** with **8d** at first, collapses to give **4**, which reacts with **8c** to result in the formation of **12** and **14** (Scheme 4).

Finally, as in the case of the reaction of the phosphorane **3**, the isolated **4** and *in situ*-prepared **5** reacted with DMAD **17** to give tetramethyl 2*H*-cyclohepta[*gh*]pyrrolizine-1,2,4,5-tetracarboxylate **23** (Scheme 5; Table 2, Entries 21 and 22). The reaction of **6** with DMAD **17** at rt, however, did not give compound **23**, and only intractable tarry materials were obtained. In these reactions, the reactivity of **4**–**6** seems to be also in the order **4** < **5** < **6**. The structure of compound **23** was assigned on the basis of a comparison of its physical data with those of the authentic specimen.[16] Michael-type addition of the nitrogen atom of compound **4** and **5** to DMAD **17** gives the intermediates **18** and/or **19**. Then the M–O (M = As and Sb)-bonded intermediate **18** eliminates Ph_3MO (M = As and Sb) to result in the formation of 1-azaazulene derivative **20**.[16] An intermediate similar to **20** has also been postulated in the reaction of 2-(triphenylphosphoranylidenemethyl)tropone with DMAD giving an azulene derivative.[29] An alternative pathway is a ring-opening of **19** to give the intermediate **21** and the following aza-Wittig-type reaction to result in the formation of **20**. Reactions similar to the formation of **21** have been shown in the reaction of simple iminophosphoranes,[30] iminoarsoranes,[2] and iminostiboranes[31] with DMAD. 1-Azaazulene has been shown to react with DMAD to give an intermediate such as **22**,[32] in which hydrogen migration results in the formation of the product **23**.



Scheme 5 *Conditions*: i, heat.

In conclusion, we have demonstrated the synthesis of a series of (tropon-2-ylimino)pnictoranes **4**–**6** and their reactions with heterocumulenes and an activated acetylene to provide a variety of cyclohepta-annulated five-membered heterocycles (heteroazulenes). The arsorane **4** was isolated as a stable crystalline compound and clarified by X-ray structure analysis to be stabilized by not only the electron-withdrawing tropone but also by coordination of the carbonyl oxygen to the arsine element. The stiborane and bismuthorane analogues **5** and **6** prepared *in situ* seemed also to be stabilized by a similar coordination as in the case of **4**, as demonstrated through their reaction with diphenylcarbodiimide **8c**. Through the reactions of **4**–**6** and the phosphorane **3** in part with heterocumulenes, the dipolar and nucleophilic character of a series of pnictoranes **3**–**6** appears to increase and their stability decreases when the pnictogen stands lower in the Periodic Table. Further studies concerning the synthesis of pnictoranes and their synthetic applicability are underway.

Experimental

IR spectra were recorded on a Horiba FT-710 spectrometer. UV–visible spectra were recorded on a Shimadzu UV-3101PC spectrometer. Mass spectra and high-resolution mass spectra (FAB) were run on JEOL JMS-AUTOMASS150 and JMS-SX102A spectrometers. ^1H NMR spectra and ^{13}C NMR spectra were recorded on a JEOL JNM-LA500 spectrometer using $CDCl_3$ and C_6D_6 as solvents, and the chemical shifts are given relative to internal or external $SiMe_4$ standard; *J*-values are given in Hz. Compounds Ph_3AsBr_2,[18] Ph_3SbCl_2,[25] and Ph_3BiCl_2[26] were prepared according to the procedure reported in the literature. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. All the reactions except hydrolysis were carried out under anhydrous conditions and dry nitrogen atmosphere.

Preparation of (7-oxocyclohepta-1,3,5-trienylimino)triphenylarsorane 4

To a stirred solution of Ph_3As (919 mg, 3.0 mmol) in benzene (5 cm^3) was added a solution of bromine (479 mg, 3.0 mmol) in benzene (2 cm^3) dropwise at rt, and the mixture was stirred for another 30 min. To this mixture was added a solution of 2-aminotropone **7** (363 mg, 3.0 mmol) and NEt_3 (627 mg, 6.2 mmol) in benzene (2 cm^3), and the mixture was stirred for 16 h at rt. The reaction mixture was then filtered through Celite and the filtrate was concentrated. The residue was washed with diethyl ether under dry nitrogen atmosphere to give **4** (1.15 g, 90%) as yellow prisms; mp 154–158 °C (decomp. from AcOEt); δ_C ($CDCl_3$) 119.0 (C7), 121.7 (C5), 123.2 (C3), 128.7 (Ph), 130.2 (Ph), 131.7 (Ph), 136.3 (C4), 138.8 (Ph), 170.1 (C2), 173.6 (C1); ν_{max} ($CHCl_3$)/cm^{-1} 1590, 1498, 1424, 1400, 1354, 1086; λ_{max} (MeCN)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 252 (4.48), 364 (4.11), 397sh (3.64), 421sh (3.68), 444 (3.86) (Found: $M^+ + 1$, 426.0861; C, 70.4; H, 4.6; N, 3.2. $C_{25}H_{20}AsNO$ requires $M + 1$, 426.0840; C, 70.59; H, 4.74; N, 3.29%).

Hydrolysis of 4 in acidic and neutral conditions

A solution of **4** (51 mg, 0.12 mmol) in 0.5 M H_2SO_4 (water–EtOH 10 : 1; 5 cm^3) was stirred at rt for 30 min. This mixture was neutralized with aq. $NaHCO_3$, the mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4. After evaporation of the mixture, the residue was separated by TLC

on SiO_2 (AcOEt) to give **7** (13 mg, 89%) and Ph_3AsO (32 mg, 83%).

A solution of **4** (85 mg, 0.2 mmol) in water–EtOH (1 : 1; 5 cm^3) was stirred at rt for 4.5 h. Then the reaction mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4. After evaporation of the mixture, the residue was separated by TLC on SiO_2 (AcOEt) to give **7** (20 mg, 83%) and Ph_3AsO (50 mg, 78%).

^{1}H NMR studies of (7-oxocyclohepta-1,3,5-trienylimino)triphenylpnictoranes 4, 5, and 6

A suspension of **7** (29 mg, 0.24 mmol), NEt_3 (61 mg, 0.6 mmol), and Ph_3AsBr_2 (112 mg, 0.24 mmol) in C_6D_6 (5 cm^3) was stirred at room temperature for 10 min to give a suspension of **4**. In a similar manner, suspensions of **7** (29 mg, 0.24 mmol), Bu^{t}OK (67 mg, 0.6 mmol), and Ph_3SbCl_2 (102 mg, 0.24 mmol) or Ph_3BiCl_2 (123 mg, 0.24 mmol) in C_6D_6 (5 cm^3) were stirred for 5 min to make clean suspension of the product **5** or **6**. The suspensions were filtered through glass wool quickly, the filtrate was introduced into an NMR tube under dry nitrogen atmosphere, and the ^{1}H NMR spectra of the solutions of **4**, **5**, and **6** were recorded using Me_4Si as external standard. The results are summarized in Table 1.

Thermal reaction of the bismuthorane 6

A solution of **7** (30 mg, 0.25 mmol), Bu^{t}OK (50 mg, 0.5 mmol), and Ph_3BiCl_2 (128 mg, 0.25 mmol) in benzene (2 cm^3) was stirred at rt for 5 min. The reaction mixture was heated under reflux for 1 h. After evaporation of the mixture, the residue was separated by column chromatography on SiO_2 (hexane–AcOEt 5 : 1) to give Ph_3Bi (92 mg, 84% base on **7**).

Reaction of isolated 4 with carbon disulfide 8a

A solution of **4** (85 mg, 0.2 mmol) in carbon disulfide (8 cm^3) was heated at 100 °C in an autoclave for 2 days. After evaporation of the mixture, the residue was crystallized from CH_2Cl_2 to give **11** (30 mg, 92%) (Table 2, Entry 2).

Reactions of isolated 4 with heterocumulenes 8b,c

A solution of **4** (64 mg, 0.15 mmol) and **8b**,**c** in benzene (3 cm^3) was heated under reflux. After evaporation of the mixture, the residue was purified by TLC on SiO_2 (AcOEt) to give the products, **12** and **14** (Table 2, Entries 6 and 11).

In the reaction with carbodiimide **8c**, a solution of phenyl isocyanate **8d** (179 mg, 1.5 mmol) and Ph_3AsO (10 mg, 0.03 mmol) in benzene (1 cm^3) was heated under reflux for 2 h. The generation of **8c** was confirmed by its IR spectrum. This solution was subsequently used for the reaction with **4** as described above.

Reaction of isolated 4 with 8d at high temperature

A solution of **4** (64 mg, 0.15 mmol) and **8d** (179 mg, 1.5 mmol) in xylenes (3 cm^3) was heated under reflux for 25 h. After evaporation of the mixture, the residue was separated by TLC on SiO_2 (AcOEt) to give the products, **12** and **14** (Table 2, Entry 19).

For *N,1-diphenylcycloheptaimidazol-2(1H)-imine* **14**: dark red prisms, mp 140–142 °C (from CH_2Cl_2–hexane); δ_H ($CDCl_3$) 6.66 (1H, d, *J* 9.8, H8), 6.91 (1H, dd, *J* 10.8, 9.8, H6), 7.02 (1H, m, Ph), 7.19 (1H, dd, 9.8, 10.0, H7), 7.31 (4H, m, Ph), 7.44 (1H, dd, 9.8, 11.1, H5), 7.50 (2H, d, *J* 7.8, Ph), 7.52 (1H, t, *J* 7.5, Ph), 7.60 (1H, d, *J* 11.1, H4), 7.62 (2H, dd, *J* 7.5, 7.8, Ph); δ_C ($CDCl_3$) 110.2 (C8), 122.7 (Ph), 123.3 (Ph), 127.1 (C4), 127.9 (C6), 128.1 (Ph), 128.5 (Ph), 128.9 (Ph), 129.8 (Ph), 134.6 (quart), 136.2 (C7), 138.7 (C5), 149.1 (quart), 152.2 (quart), 159.3 (quart), 165.8 (quart); ν_{max}/cm^{-1} ($CHCl_3$) 1634, 1580, 1528, 1493, 1475, 1445, 1388; λ_{max} (MeCN)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 266 (4.64), 422 (4.39); *m*/*z* 297 (M^+, 72%), 77 (100) (Found M^+ + 1, 298.1307; C, 80.8; H, 5.0; N, 14.1. $C_{20}H_{15}N_3$ requires *M* + 1, 298.1344; C, 80.78; H, 5.08; N, 14.13%).

Reaction of 2*H*-cycloheptaoxazol-2-one 16 with Ph_3AsO to give 4

A solution of **16** (22 mg, 0.15 mmol) and Ph_3AsO (49 mg, 0.15 mmol) in benzene (2 cm^3) was heated under reflux for 15 h. After evaporation of the mixture, the residue was monitored by ^{1}H NMR to contain **4** and **7** in the ratio 7 : 4. The residue was then separated by TLC on SiO_2 (AcOEt) to give **7** (16 mg, 89%; R_f = 0.5). The base line on the TLC plates was further developed by CH_2Cl_2–EtOH 10 : 1 to give Ph_3AsO (47 mg, 96%; R_f = 0.7).

In situ preparation of 4 and reactions with heterocumulenes 8b–d

To a stirred solution of Ph_3As (153 mg, 0.5 mmol) in benzene (5 cm^3) was added bromine (80 mg, 0.5 mmol) and the mixture was stirred for 5 min at room temperature. To this mixture were added **7** (61 mg, 0.5 mmol) and NEt_3 (111 mg, 1.1 mmol) and the mixture was stirred for another 30 min. To this solution was added a heterocumulene **8**, and the mixture was heated for the period indicated in Table 2. The reaction mixture was concentrated and the resulting residue was separated by TLC on SiO_2 (AcOEt) to give the products, **12**, **14**, and **16** (Table 2, Entries 7, 12, and 16).

In the reaction with diphenylcarbodiimide **8c**, a solution of **8d** (596 mg, 5.0 mmol) and Ph_3AsO (32 mg, 0.1 mmol) in benzene (3 cm^3) was heated under reflux for 2 h. The generation of **8c** was confirmed by its IR spectrum. This solution was subsequently used for the reaction with a solution of **4** prepared above.

Reaction of the phosphorane 3 with the carbodiimide 8c

A solution of **8d** (357 mg, 3 mmol) and Ph_3AsO (10 mg, 0.03 mmol) in xylenes (5 cm^3) was heated at 90 °C for 2 h. To this reaction mixture was added the phosphorane **3** (114 mg, 0.3 mmol), and the mixture was heated under reflux for 7 h. After evaporation of the mixture, the residue was separated by TLC on SiO_2 (AcOEt) to give the products, **12** and **14** (Table 2, Entry 10).

In situ preparation of 5 and reactions with heterocumulenes 8a–d

To a stirred solution of Ph_3SbCl_2 (212 mg, 0.5 mmol) and **7** (61 mg, 0.5 mmol) in benzene (3 cm^3) was added Bu^{t}OK (112 mg, 1.0 mmol), and the mixture was stirred for 30 min at rt. To this solution was added a heterocumulene **8** and the mixture was heated under reflux for the period indicated in Table 2. After evaporation of the mixture, the resulting residue was separated by TLC on SiO_2 (AcOEt) to give the products, **11**, **12**, **14**, and **16** (Table 2, Entries 3, 8, 13, and 17).

In the reaction with diphenylcarbodiimide **8c**, a solution of **8d** (596 mg, 5.0 mmol) and Ph_3AsO (32 mg, 0.1 mmol) in benzene (3 cm^3) was heated under reflux for 2 h. The generation of **8c** was confirmed by its IR spectrum. This solution was subsequently used for the reaction with a solution of **5** prepared above.

In situ generation of 6 and reactions with heterocumulenes 8a–d

To a stirred solution of Ph_3BiCl_2 (256 mg, 0.5 mmol) and **7** (61 mg, 0.5 mmol) in benzene (3 cm^3) was added Bu^{t}OK (112 mg, 1.0 mmol), and the mixture was stirred for 5 min at rt. To this solution was added a substrate **8**, and the mixture was stirred for the period indicated in Table 2. After the mixture was filtered through Celite, the filtrate was concentrated and the resulting residue was separated by TLC on SiO_2 (AcOEt) to give the products, **11**, **12**, **14**, and **16** (Table 2, Entries 4, 9, 14, and 18).

In the reaction with the carbodiimide **8c**, a solution of **8d** (596 mg, 5.0 mmol) and Ph_3AsO (32 mg, 0.1 mmol) in benzene (3 cm^3) was heated under reflux for 2 h. The generation of **8c** was confirmed by its IR spectrum. This solution was subsequently used for the reaction with a solution of **6** prepared above.

Reaction of 4 with DMAD 17

A solution of **4** (64 mg, 0.15 mmol) and DMAD **17** (101 mg, 0.75 mmol) in bromobenzene (3 cm^3) was heated under reflux for 20 h. After evaporation of the mixture, the residue was purified by TLC on SiO_2 (AcOEt) to give **23** (35 mg, 60%), which is identical with the authentic specimen (Table 2, Entry 21).

In situ preparation of 5 and reaction with DMAD 17

To a stirred solution of Ph_3SbCl_2 (212 mg, 0.5 mmol) and **7** (61 mg, 0.5 mmol) in bromobenzene (3 cm^3) was added Bu^tOK (112 mg, 1.0 mmol) and the mixture was stirred for 30 min at rt. To this solution was added a solution of DMAD **17** (711 mg, 5 mmol) in bromobenzene (2 cm^3) and the mixture was heated under reflux for 1 h. The reaction mixture was then filtered through Celite, the filtrated was concentrated, and the residue was purified by TLC on SiO_2 (hexane–AcOEt 1 : 2) to give **23** (Table 2, Entry 22).

Crystal structure determination of 4 ‡

Single crystal of [$C_7H_5ON{=}AsPh_3$] **4** were recrystallised from AcOEt.

Crystal data. $C_{25}H_{20}AsNO$, $M = 425.37$, orthorhombic, $a = 25.5308(0)$, $b = 28.5381(0)$, $c = 10.7821(0)$ Å, $V = 7855.86(0)$ Å^3, $T = 298$ K, space group *Pcnb* (no. 60), $Z = 16$, μ(Cu-Kα) = 2.4413 mm^{-1}, 8598 reflections measured, 7190 unique ($R_{int} = 0.019$). The final $R(F^2)$ and $wR(F^2)$ were 0.067 and 0.080 for 6515 observed reflections [$F^2 > 2\sigma(F^2)$] used in all calculations.[33]

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