

Oxidizing Ability of a Series of (Tropon-2-ylimino)pnictoranes (Pnictogen = P, As, Sb, and Bi) toward Some Alcohols

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In order to gain a better understanding of the oxidizing ability of a series of (tropon-2-ylimino)pnictoranes of the general structure $Ph_3M{=}NR$ (R = tropon-2-yl; M = P, As, Sb, and Bi), reactions were run with some alcohols such as benzopinacol (1,1,2,2-tetraphenyl-1,2-ethanediol), benzoin, cinnamyl alcohol, 1-phenylethanol, a mixture of *cis*- and *trans*-4-*t*-butylcyclohexanol, 2-phenylethanol, and 1-phenyl-1,3-propandiol. Iminophosphorane oxidized only benzopinacol to give benzophenone, while both arsorane and stiborane oxidized benzopinacol and benzoin to give benzophenone and benzil, respectively. On the other hand, iminobismuthorane has appreciable oxidizing ability, and reacted with the alcohols mentioned above, except the primary alcohol, to give the corresponding carbonyl compounds. Iminobismuthorane reacted with 1-phenyl-1,3-propandiol selectively to oxidize benzyl alcohol moiety, but not a primary alcohol moiety, to give 3-hydroxy-1-phenyl-1-propanone. Thus, the oxidizing ability of a series of (tropon-2-ylimino)pnictoranes is demonstrated to be in the order of iminophosphorane < iminoarsorane < iminostiborane < iminobismuthorane: the dipolar (degree of contribution of the $Ph_3M^+-{}^-NR$ canonical structure) and electrophilic character of pnictogen elements of a series of iminopnictoranes appear to increase their oxidizing ability when the pnictogen stands lower in the periodic table.

Iminopnictoranes (**1a–d**) ($Ph_3M = NR$; M = P, As, Sb, Bi) are a class of compounds having a formal double bond between the nitrogen and the pnictogen elements (Fig. 1). In contrast to extensive works on lighter pnictoranes, the chemistry of iminostiborane and iminobismuthorane has been studied less. The latter compounds have been receiving considerable attention in view of their chemical analogy to pnictogen ylides as well as their potential utility in organic synthesis.[1–5] The dipolar and nucleophilic character of the iminopnictoranes appear to increase, and their stability decrease when the pnictogen stands lower in the periodic table. The difference between iminophosphoranes and other iminopnictoranes is commonly ascribed to less efficient pπ–dπ overlap between the N-p orbitals and the larger and more diffuse 4d, 5d, and 6d orbitals of arsenic, antimony, and bismuth elements, and decreased electrostatic interaction across the imide bonds.[2,3] The utility of (vinylimino)phosphoranes (**2**) as useful building blocks for the synthesis of azaheterocycles has been demonstrated convincingly.[6–10] (Vinylimino)phosphoranes undergo a single-step annulation with compounds containing two electrophilic centers such as α-bromo ketones, α,β-unsaturated ketones and aldehydes, as well as the related Michael acceptors to give a variety of nitrogen heterocycles.[8] In relation to these studies, we have recently been interested in exploiting the synthesis, structure, and reactivities afforded by (tropon-2-ylimino)phosphorane (**3a**),[11] as well as a series of (tropon-2-ylimino)pnictoranes (**3b–d**) (M = As, Sb, Bi).[12,13] The X-ray crystallographic analysis of **3a**,**b** has revealed that the P–O and As–O distances are significantly shorter than the sum of the van der Waals radii of both elements, respectively, and the pnictogens (P and As) and the oxygen atom in **3a**,**b** are held together by coordination (Fig. 1).[11,13] Although compounds **3c**,**d** are not isolated in pure form and are prepared in situ due to their moisture sensitivity, the reaction of **3a–d** with heterocumulenes provides a new methodology for constructing new cyclohepta-annulated five-membered heterocycles.[11–13] Furthermore, the reactivity of **3a–d** has been clarified to be in the order of **3a** < **3b** < **3c** < **3d**.[11,13] Through these studies, coordination of the oxygen atom to Sb and Bi elements in **3c**,**d** is also suggested.[13] Iminoarsorane (M = As) appears to be more resistant to hydrolysis than the iminostiborane (M = Sb) and iminobismuthorane (M = Bi),[2,3,13,14] and can be handled in air, although it is more labile than its phosphorane analogue. Since the first preparation of several iminobismuthoranes according to Wittig's procedure,[15] other improved procedures have been developed to examine their chemistry in some detail. Iminopnictranes (M = Sb,[15,16] Bi[15–19]) thus far obtained as stable compounds have electron-withdrawing groups such as tosyl,[15,18] trifluoroacetyl, and trichloroacetyl[20] groups

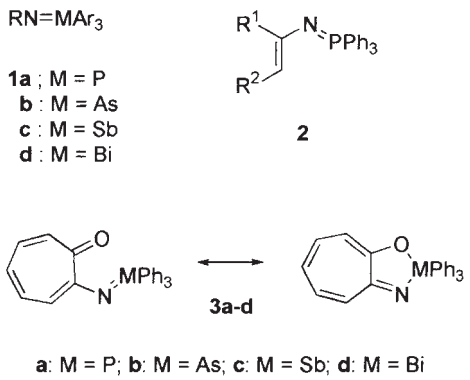


Fig. 1.

on the nitrogen atom. Triaryl(tosylimino)bismuthorane reacts with aromatic aldehyde, benzoyl chloride, and phenyl isocyanate to give *N*-arylmethylene-*p*-toluenesulfonamide, *N*-benzoyl-*p*-toluenesulfonamide, and *N*-aryl-*N*′-tosylurea, respectively.[17] Recently, triaryl(3,5-ditrifluoromethylbenzoylimino)-bismuthorane has been shown to oxidize even primary alcohols,[21] as in the case of triarylbismuthine oxide[22] and other pentavalent organobismuth reagents,[4,23] which act as efficient oxidizing agents toward a wide range of alcohols. Although triaryl(tosylimino)bismuthorane and triaryl(trifluoroacetylimino)bismuthorane have been shown to exhibit oxidizing properties toward some activated alcohols, converting them into the corresponding carbonyl compounds,[16,20] triaryl(tosylimino)stiborane oxidizes benzopinacol and benzoin to give benzophenone and benzil.[16] Thus, the oxidizing ability of iminopnictoranes seems to be dependent not only on the pnictogen element but also on the substituent involved in pnictoranes. Since the oxidizing ability of a series of iminopnictoranes (pnictogen = P, As, Sb, Bi) has not been demonstrated so far, we investigated the reaction of **3a–d** (pnictogen = P, As, Sb, Bi) with selected alcohols to give the corresponding carbonyl compounds. We report herein the results in detail.

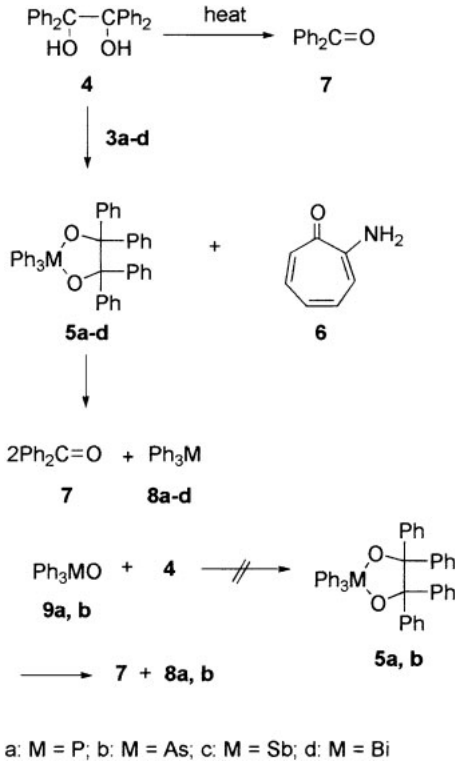
Results and Discussion

The preparation of iminophosphorane (**3a**)[11] and in situ preparation of iminoarsorane **3b**, iminostiborane (**3c**), and iminobismuthorane (**3d**) were accomplished according to the procedures described previously.[12,13] Since we have reported a preliminary study of a mild oxidation reaction of **3d** toward benzopinacol and cinnamyl alcohol to give benzophenone and cinnamaldehyde,[12] we now examine the reactions of **3a–d** with selected alcohols to gain insight into their oxidizing ability. The reaction conditions and the yields of the products are summarized in Table 1. Treatment of **3a–d** with some alcohols led to interesting results: the reaction of **3a** with benzopinacol (**4**) in refluxing xylene gave 2-aminotropone (**6**), benzophenone (**7**), and triphenylphosphine (**8a**), in addition to the recovery of **3a** (Scheme 1, Table 1, Run 1). In this reaction, **8a** was obtained in 17% yield, while **7** was obtained in 71% yield. Thus, ca. 54% of **7** would arise from the thermal reaction of **4** without intervention of **3a**. Actually, the thermal reaction of **4** in refluxing xylene afforded **7** in 41% yield (Table 1, Run 2). On the other hand, the reaction of **4** in the presence of triphenylphosphine oxide (**9a**) afforded **7** and recovery of **4** in yields similar to those of the thermal reaction (Table 1, Run 3). The compound **9a** was recovered without formation of triphenylphosphine (**8a**), and thus, **9a** does not act as an oxidizing agent.[22] Similarly, the reaction of **3b–d** with **4** in refluxing toluene, in PhH at rt, and in CH_2Cl_2 at rt, respectively, afforded **6**, **7**, and triphenylpnictine (**8b–d**) in good yields (Scheme 1, Table 1, Runs 4, 7, and 8). The thermal reaction of **4** in the absence or presence of triphenylarsine oxide **9b** afforded a small amount of **7**, which derives from the thermal process, in addition to recovery of **4** (Runs 5 and 6). Thus, triphenylarsine oxide **9b** also does not seem to have oxidizing ability toward **4**, as in the case of **9a**.[22]

Table 1. Results for the Reaction of Iminopnictoranes (**3a–d**) with Some Alcohols

Pnictorane			Reaction conditions			Product[a] (Yield/%)[b]	
Run	**3a–d**	Alcohol	Solvent	Temp	Time/h	Carbonyl compd	Remaining compd
1	**3a**	**4**	Xylene	reflux	1	**7** (71)	**3a** (9), **6** (37), **8a** (17)
2	**None**	**4**	Xylene	reflux	1	**7** (41)	**4** (50)
3	**9a**	**4**	Xylene	reflux	1	**7** (30)	**4** (58), **9a** (99)
4	**3b**	**4**	Toluene	reflux	1.5	**7** (88)	**6** (87), **8b** (92)
5	**None**	**4**	Toluene	reflux	1.5	**7** (5)	**4** (94)
6	**9b**	**4**	Toluene	reflux	1.5	**7** (16)	**4** (83), **9b** (86)
7	**3c**	**4**	PhH	rt	2	**7** (92)	**6** (97), **8c** (92)
8	**3d**	**4**	CH_2Cl_2	rt	1	**7** (95)	**6** (90), **8d** (92)
9	**3a**	**11**	Xylene	reflux	43	**12** (57)	**3a** (79), **11** (0), **8a** (0)
10	**None**	**11**	Xylene	reflux	43	**12** (91)	**11** (0)
11	**3b**	**11**	Toluene	reflux	25	**12** (97)	**6** (97), **8b** (97)
12	**None**	**11**	Toluene	reflux	25	**12** (42)	**11** (40)
13	**3c**	**11**	PhH	reflux	1.5	**12** (95)	**6** (100), **8c** (96)
14[c]	**3d**	**11**	CH_2Cl_2	rt	43	**12** (6)	**6** (100), **11** (75), **8d** (59)
15	**3b**	**14**	Toluene	reflux	19	**15** (0)	**6** (73), **14** (73), **9b** (66)
16[d]	**3c**	**14**	PhH	reflux	19	**15** (0)	**6** (90), **14** (94)
17	**3d**	**14**	CH_2Cl_2	rt	5	**15** (85)	**6** (96), **8d** (65)
18[d]	**3c**	**16**	PhH	reflux	15	**17** (0)	**6** (100), **16** (94)
19	**3d**	**16**	CH_2Cl_2	rt	5	**17** (53)	**6** (93), **8d** (57)
20[d]	**3c**	**18**	PhH	reflux	24	**19** (0)	**6** (87), **18** (100)
21	**3d**	**18**	CH_2Cl_2	rt	18	**19** (57)	**6** (93), **8d** (59)
22	**3d**	**20**	CH_2Cl_2	rt	46	**21** (0)	**6** (60), **20** (61), **8d** (70)
23	**3d**	**22**	CH_2Cl_2	rt	3	**23** (84)	**6** (95), **8d** (42)

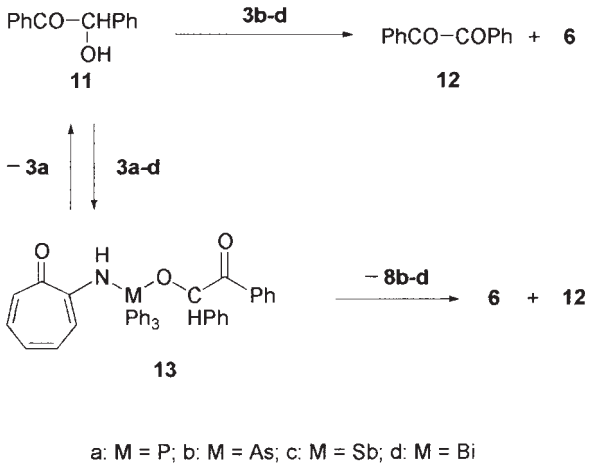
a) Identified on the basis of comparison of physical data with those of the authentic specimens. b) Isolated yield through column chromatography and/or TLC. c) Reaction carried out under reflux did not improve the yields. d) Formation of Ph_3SbO is expected through hydrolysis of unreacted **3c** and/or pentavalent intermediates under workup conditions (column chromatography and/or TLC), but it is known to exist as polymer and not isolated here (Ref. 24).



Scheme 1.

Plausible reaction pathways for these oxidations are depicted in Scheme 1. Iminopnictoranes (**3a–d**) with **4** react to form cyclic pentavalent intermediates (**5a–d**),[16,20,21,23] which undergo ligand cleavage to give **7**. Regarding the reactivities of **3a–d** toward **4**, the formation of **5b–d** and their concomitant elimination of **6**, and subsequent reaction to give **7** and **8b–d** seems to proceed smoothly, while **3a** would form **5a** inefficiently, and an appreciable amount of the thermal decomposition of **4** occurs to give **7** (Runs 1 and 2 vs Runs 4 and 5). The structures and properties of a series of (acylimino)pnictoranes ($Ar_3M{=}NCO–$ and $H_3M{=}NCOCF_3$; M = P, As, Sb, Bi) are compared based on spectroscopy, X-ray analysis, and ab initio molecular orbital calculations.[21] It was found that the contribution of the $M^+–N{=}C–O^-$ canonical structure becomes more prominent and the single bond character of the M=N bond increases progressively as the pnictogen atom becomes heavier, probably due to the difference in orbital size and electronegativity between the pnictogen and nitrogen atoms. These features are expected for compounds **3a–d** based on the reactivity toward heterocumulenes.[13] Thus, the formation **5a–d** occurs more easily in the order of **3a** < **3b** < **3c** < **3d**, and their reductive elimination of **7** would also be efficient in that order. Consequently, regarding the reaction time and the reaction temperature concerning **3a–d** (Runs 1, 4, 7, and 8), the oxidizing ability is clearly suggested to be in the order of **3a** < **3b** < **3c** < **3d**. Triphenylstibine and triphenylbismuthine oxides are known to exist as dimeric and polymeric substances, and they are known to oxidize both benzopinacol (**4**) and benzoin (**11**) to give **7** and benzil (**12**), however, compounds **9a**,**b** are clarified to be inert toward **4**.[22,24]

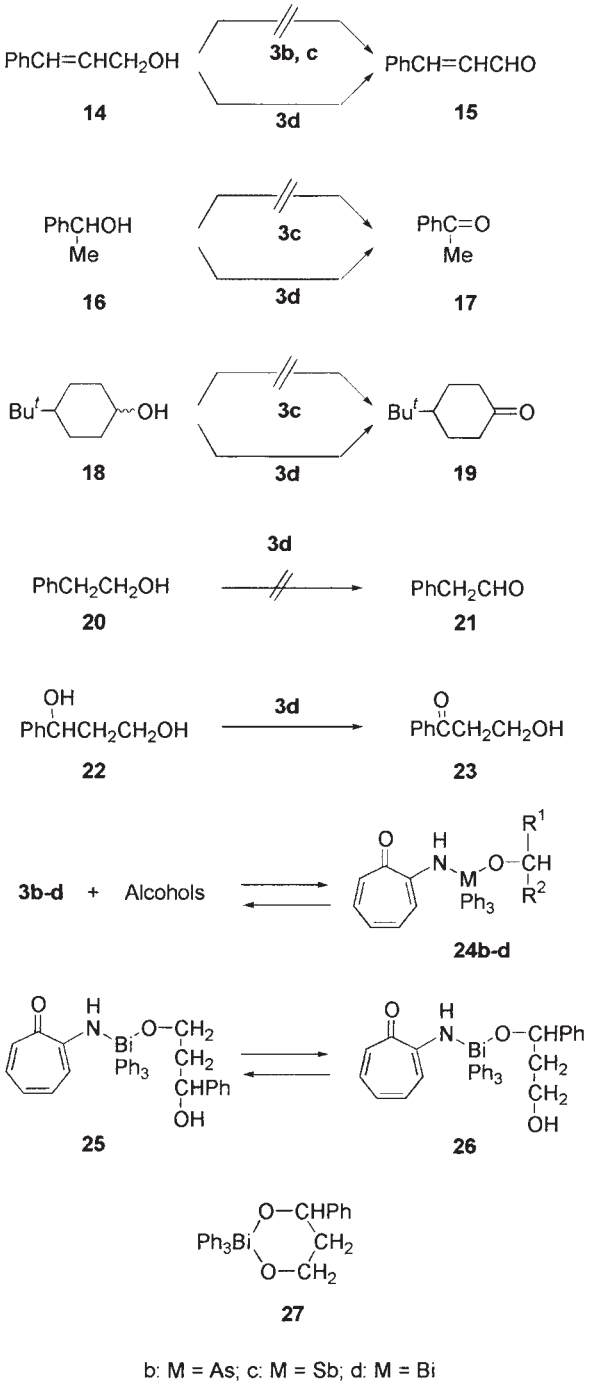
On the other hand, the reaction of **3a** with **11** in refluxing xylene did not give **8a**, and benzil (**12**) is obtained in addition



Scheme 2.

to the recovery of **3a** (Scheme 2, Table 1, Run 9). The formation of **12** is similar to the thermal reaction of **11** (Run 10). Thus, **3a** does not act as oxidizing agent toward **11**. Unlike in the case of **3a**, iminoarsorane (**3b**) oxidizes **11** to give **6**, **12**, and **8b** in quantitative yields, respectively (Run 11). Although the thermal reaction of **11** also gives **12** in modest yield (Run 12), the quantitative yield of **8b** (Run 11) suggests that the oxidation reaction of **3b** occurs smoothly as compared with the pure thermal process. Similarly, the oxidation reactions of **3c** and **3d** with **11** in refluxing PhH and in refluxing CH_2Cl_2, respectively, to yield **6**, **12**, and triphenylpnictanes (**8c**,**d**), suggests the appreciable oxidizing ability of **3c** and **3d** (Runs 13 and 14). Details are ambiguous at this stage, however, repeated reactions of **11** and **3d** did not cause complete consumption of **11** (Run 14). Regarding the hydrolysis of **3a–d**[13] and the nature of the M=N bond (vide supra),[21] **11** and **3a–d** would react to give **13a–d**, which probably exist in an equilibrium with **3a–d** and **11**. The intermediates **13b–d** then eliminate the tropon-2-ylamino group and the α-hydrogen of the alkoxy function simultaneously to form **6**, **12**, and **8b–d**.[16] In the reaction of **3a** with **11**, the formation of **13a** and its reductive elimination of the (tropon-2-yl)amino group, **12**, and **8a** would become less efficient.

In order to evaluate further the oxidizing properties of **3b–d**, they were treated with an allylic alcohol and a cinnamyl alcohol (**14**) in refluxing toluene, in refluxing benzene, and in CH_2Cl_2 at rt, respectively, (Scheme 3). The former two pnictoranes do not exhibit oxidizing ability and compound **6**, which arises from the hydrolysis of **3b**,**c** under workup conditions, along with most of the starting material **14** were recovered (Runs 15 and 16). In contrast, compound **3d** exhibited remarkable oxidizing ability to give **6**, aldehyde (**15**), and **8d** in good yields (Run 17). Similarly, **3c** did not oxidize secondary alcohols, 1-phenylethanol (**16**) and a mixture of *cis*- and *trans*-4-*t*-butylcyclohexanol (**18**) (Runs 18 and 20), but **3d** oxidized **16** and **18** to give acetophenone (**17**) and cyclohexanone (**19**), along with **6** and **8d** (Runs 19 and 21). However, compound **3d** did not oxidize primary alcohol (**20**) even under prolonged reaction time, and **20** was recovered (Run 22). In this case, compound **6** and **8d** were also obtained, suggesting the thermal decomposition of **3d** occurs in the protic media of **20**.[13] So we



Scheme 3.

next investigated the selectivity for dihydroxy compound (**22**), which is composed of benzylic and primary hydroxy groups (Run 23). In this case, the IR spectrum of the product **23** exhibited one carbonyl absorption due to a ketone but not an aldehyde, and the structure was confirmed on the basis of comparison of the spectral data with those of the authentic specimen. The reactions of **3b–d** with alcohols (**14**), (**16**), (**18**), (**20**), and (**22**) would proceed also via a common pentavalent intermediate (**24b–d**) (vide supra). In these reactions, the concomitant elimination of the tropon-2-ylamino group, the oxidized carbonyl compounds, and **8b–d** from **24** is considered to depend on the oxidizing ability of the pnictogen elements and the reactivity of the α-hydrogen of the incorporated alkoxy moiety. Since selective oxidation of compound **22** occurs to give **23**, the pentavalent intermediate (**24d**) would exist in equilibrium between the intermediates (**25**) and (**26**), and the more active α-hydrogen is eliminated via **26**. Although details are ambiguous at this stage, an alternative pathway for the selective oxidation of **22** would be a formation of **27**, which eliminates the more active α-hydrogen. In addition, only the oxidation reaction of **4** with **3d** resulted in the formation of **8d** in good yield (Run 8), while reactions with other alcohols resulted in the modest yields of **8d** (Runs 14, 17, 19, 21 and 23). A plausible explanation would be the following: during the reductive elimination of alcohols, 2-aminotropone (**6**), and triphenylbismuthine (**8d**) from the pentavalent intermediates (**13**) (M = Bi) and (**24d**) (M = Bi), the α-hydrogen is abstracted alternatively by the phenyl group on the bismuth element to result in the formation of benzene and a bismuth compound, which are not isolated at the present stage.[21,23]

In conclusion, we have demonstrated the oxidizing ability of a series of (tropon-2-ylimino)pnictoranes (**3a–d**). It is clarified for the first time that the iminophosphorane (**3a**) oxidizes only benzopinacol (**4**), while iminoarsorane (**3b**) and iminostiborane (**3c**) oxidize benzopinacol (**4**) and benzoin (**11**). Compounds (**3b**,**c**) do not oxidize allylic and benzylic alcohols (**14**) and (**16**). On the other hand, iminobismuthorane (**3d**) oxidizes allylic alcohol (**14**), benzylic alcohol (**16**), and even *trans*-4-*t*-butylcyclohexanol (**18**). Compound (**3d**) is inert toward primary alcohol, 2-phenylethanol (**20**), and selective oxidation of 1-phenyl-1,3-propanediol (**22**) occurrs to give **23**. Through the present investigations, the oxidizing ability of a series of iminopnictoranes (**3a–d**) toward alcohols is demonstrated to be in the order of **3a** < **3b** < **3c** < **3d**: the dipolar (degree of contribution of the $Ph_3M^+-{}^-NR$ canonical structure) and electrophilic character of pnictogen elements of a series of iminopnictoranes appear to increase their oxidizing ability when the pnictogen stands lower in the periodic table.

Experimental

General. Compounds Ph_3AsBr_2,[25] Ph_3SbCl_2,[26] and Ph_3BiCl_2[27] were prepared according to the procedures reported in the literature. (Tropon-2-ylimino)phosphorane (**3a**) was prepared by the method reported in the previous paper.[11] In situ generation of iminoarsorane (**3b**), iminostiborane (**3c**), and iminobismuthorane (**3d**) was performed according to the previous paper.[13] All the reactions were carried out under anhydrous conditions and dry nitrogen atmosphere.

Reaction of (Tropon-2-ylimino)phosphorane (3a) with Benzopinacol (4) and Benzoin (11). A solution of **3a** (95 mg, 0.25 mmol) and an alcohol [**4** (92 mg, 0.25 mmol); **11** (53 mg, 0.25 mmol)], in dry xylene (5 cm^3) was heated under reflux for the period indicated in Table 1. After evaporation of the solvent, the residue was separated by TLC on SiO_2 (hexane:AcOEt/5:1) to give the products (Table 1, Runs 1 and 9).

Thermal Reaction of Benzopinacol (4) in the Absence or Presence of Ph_3PO. A solution of **4** (95 mg, 0.25 mmol) in xylene (5 cm^3) in the absence or presence of Ph_3PO (70 mg, 0.25 mmol) was heated under reflux for 1 h. After evaporation of the solvent, the residue was separated by TLC on SiO_2 (hexane: AcOEt/5:1) to give the products (Table 1, Runs 2 and 3).

Thermal Reaction of Benzoin (11). A solution of **11** (53 mg, 0.25 mmol) in xylene (5 cm^3) was heated under reflux for 43 h. After evaporation of the solvent, the residue was purified by TLC on SiO_2 (hexane:AcOEt/5:1) to give the products (Table 1, Run 10).

Reaction of (Tropon-2-ylimino)arsorane (3b) with Benzopinacol (4), Benzoin (11), and Cinnamyl Alcohol (14). To a stirred solution of Ph_3AsBr_2 (117 mg, 0.25 mmol) and **6** (30 mg, 0.25 mmol) in toluene (6 cm^3) was added NEt_3 (51 mg, 0.50 mmol) in toluene (1 cm^3), and then stirred for 2 h at rt. To this mixture was added an alcohol [**4** (92 mg, 0.25 mmol), **11** (53 mg, 0.25 mmol), **14** (33 mg, 0.25 mmol)], and then this mixture was heated under reflux for the period indicated in Table 1. After evaporation of the solvent, the residue was separated by TLC on SiO_2 (hexane:AcOEt/5:1) to give the products (Table 1, Runs 4, 11, and 15).

Thermal Reaction of Benzopinacol (4) in the Absence or Presence of Ph_3AsO. A solution of **4** (95 mg, 0.25 mmol) in toluene (5 cm^3) in the absence or presence of Ph_3AsO (81 mg, 0.25 mmol), was heated under reflux for 1.5 h. After evaporation of the solvent, the residue was separated by TLC on SiO_2 (hexane:AcOEt/5:1) to give the products (Table 1, Runs 5 and 6).

Reaction of (Tropon-2-ylimino)stiborane (3c) with Benzopinacol (4) and Benzoin (11). To a stirred solution of Ph_3SbCl_2 (106 mg, 0.25 mmol) and **6** (30 mg, 0.25 mmol) in dry PhH (3 cm^3) was added Bu^{t}OK (56 mg, 0.5 mmol) and then stirred for 30 min at rt. To this reaction mixture was added an alcohol [**4** (92 mg, 0.25 mmol); **11** (53 mg, 0.25 mmol)], and stirred at rt or heated under reflux for the period indicated in Table 1. After evaporation of the solvent, the residue was separated by column chromatography on SiO_2. Fractions eluted with CH_2Cl_2 gave a mixture of **8c** and oxidized product. Fractions eluted with AcOEt afforded **6**. The former mixture was further separated by TLC on SiO_2 (hexane:AcOEt/5:1) to give **8c** and oxidized product (Table 1, Runs 7 and 13).

Reaction of (Tropon-2-ylimino)stiborane (3c) with Alcohols (14) and (16). To a stirred solution of Ph_3SbCl_2 (106 mg, 0.25 mmol) and **6** (30 mg, 0.25 mmol) in dry PhH (5 cm^3) was added Bu^{t}OK (56 mg, 0.5 mmol) and then stirred for 30 min at rt. To this reaction mixture was added an alcohol [**14** (33 mg, 0.25 mmol); **16** (31 mg, 0.25 mmol)], and heated under reflux for the period indicated in Table 1. After evaporation of the solvent, the residue was separated by column chromatography on SiO_2. The fractions eluted with AcOEt gave **6** and unreacted **14** and **16** (Table 1, Runs 16 and 18).

Reaction of (Tropon-2-ylimino)bismuthorane (3d) with Benzopinacol (4), Benzoin (11), and Alcohols (14), (16), and (18). To a solution of Ph_3BiCl_2 (128 mg, 0.25 mmol) and 2-aminotropone **6** (30 mg, 0.25 mmol) in CH_2Cl_2 (3 cm^3) was added Bu^{t}OK (56 mg, 0.5 mmol), and then stirred for 5 min at rt. To this mixture was added an alcohol [**4** (92 mg, 0.25 mmol); **11** (53 mg, 0.25 mmol); **14** (33 mg, 0.25 mmol); **16** (31 mg, 0.25 mmol); **18** (39 mg, 0.25 mmol), **20** (31 mg, 0.25 mmol), **22** (38 mg, 0.25 mmol)], and then stirred at rt for the period indicated in Table 1. After evaporation of the solvent, the residue was chromatographed on SiO_2. The fractions eluted with CH_2Cl_2 afforded a mixture of **8d** and oxidized product, and the mixture was further separated by TLC on SiO_2 (hexane:AcOEt/5:1) to give **8d** and oxidized product. The fractions eluted with AcOEt afforded **6** (Table 1, Runs 8, 14, 17, 19, and 21).

Reaction of (Tropon-2-ylimino)bismuthorane (3d) with Alcohols (20) and (22). To a solution of Ph_3BiCl_2 (256 mg, 0.5 mmol) and **6** (60 mg, 0.5 mmol) in CH_2Cl_2 (6 cm^3) was added Bu^{t}OK (112 mg, 1 mmol), and then stirred for 5 min at rt. To this mixture was added an alcohol [**20** (62 mg, 0.5 mmol) or **22** (78 mg, 0.5 mmol)], and then stirred at rt for the period indicated in Table 1. After evaporation of the solvent, the residue was chromatographed on SiO_2. The fractions eluted with CH_2Cl_2 afforded a mixture of **8d** and alcohol **20**, and the mixture was further separated by TLC on SiO_2 (hexane:AcOEt/5:1) to give **8d** and **20** or **8d** and **23**. The fractions eluted with AcOEt afforded **6** (Table 1, Runs 22 and 23).

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