

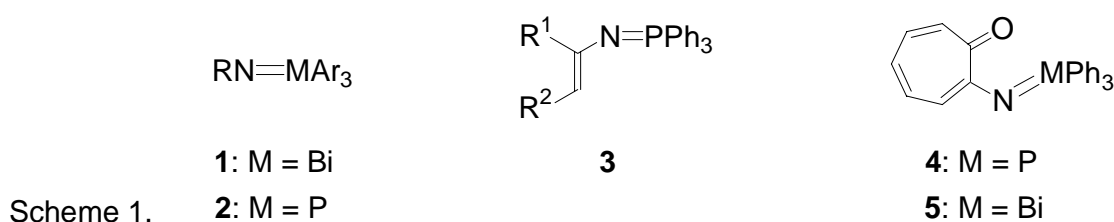
A CONVENIENT *IN SITU* PREPARATION OF TRIPHENYL-BISMUTHANE (TROPON-2-YL)IMIDE: REACTION WITH HETEROCUMULENES AND ACTIVATED ALCOHOLS

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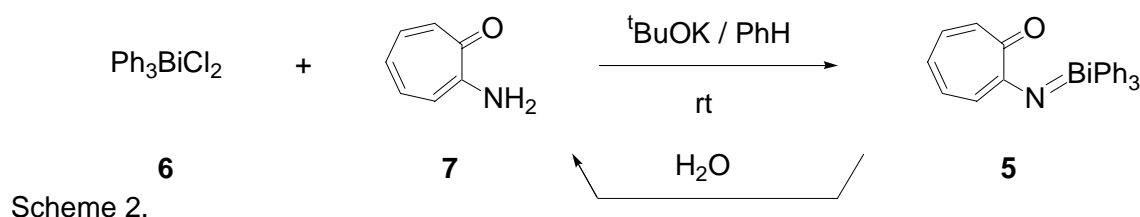
Abstract-The first *in situ* preparation of triphenylbismuthane (tropon-2-yl)imide has been accomplished by the reaction of triphenylbismuth dichloride with 2-aminotropone. The imide is not isolated due to its moisture sensitivity, while it undergoes aza-Wittig type reaction with heterocumulenes leading to cyclohepta-annulated heterocycles *in situ*, and reacts also as an oxidizing agent of activated alcohols to give the corresponding carbonyl compounds under mild conditions.

Among pnictorane imides of the general structure $RN=MAr_3$ ($M = P, As, Sb, Bi$), triarylbismuthane imide (**1**) are a class of compound bearing a formal double bond between the nitrogen and the bismuth elements, and they are analogues of iminotriarylphosphoranes (phosphorane imide) (**2**) (Scheme 1). They have been receiving considerable attention in view of their chemical analogy to pnictorane ylides as well as potential utility in organic synthesis.¹⁻³ The properties of pnictorane imides are very dependent on the identity of pnictogens. The dipolar and nucleophilic characters of the pnictorane imides appear to increase and their stability decreases when the pnictogen stands lower in the Periodic Table. Thus, all known bismuthane imides⁴⁻⁹ are stabilized by highly electronegative arenesulfonyl,⁵ trifluoromethanesulfonyl,⁸ and trifluoroacetyl⁹ groups on the nitrogen atom, but no bismuthane imide bearing a functional group other than organic sulfonyl and trifluoroacetyl groups has been reported to date. On the other hand, the utility of (vinylimino)phosphoranes (**3**) as useful building blocks for the synthesis of azaheterocycles has been demonstrated convincingly.¹⁰⁻¹⁴ (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 related Michael acceptors to give a variety of nitrogen heterocycles.¹² In relation to these studies, we have been interested recently in



exploiting the synthesis, structure, and reactivities afforded by (tropon-2-ylimino)phosphorane (**4**).¹⁵ The compound (**4**) has been clarified to react with heterocumulenes to provide a new methodology for constructing cyclohepta-annulated five-membered heterocycles. In order to gain a better understanding of bismuthane imide, we report herein the first *in situ* preparation of bismuthane (tropon-2-yl)imide (**5**) and its reaction with heterocumulenes and activated alcohols under mild conditions.

In our previous paper,¹⁵ we reported a Kirsanov reaction¹⁶ treating 2-aminotropone (**7**) with Ph_3PCl_2 in benzene to yield (tropon-2-ylimino)phosphorane (**4**) in good yield. In a similar fashion, the reaction of triphenylbismuth dichlorides (**6**) (0.5 mmol) with **7** (0.5 mmol) and $t\text{BuOK}$ (1 mmol) in benzene (5 mL) at room temperature proceeded smoothly in 5-10 min, but the usual workup did not afford the imide (**5**), and only the starting material (**7**) was recovered quantitatively. However, *in situ* preparation of **5** was carried out in a similar fashion using **6**, **7**, and $t\text{BuOK}$ in hexadeuteriobenzene, and the ^1H NMR spectrum, which is summarized in Table 1, confirmed the formation of imide (**5**). The addition of a trace amount of H_2O to a yellow solution of **5** generated *in situ* caused decomposition of **5**, and clean conversion to 2-aminotropone (**7**) was confirmed by the ^1H NMR spectrum (Scheme 1).

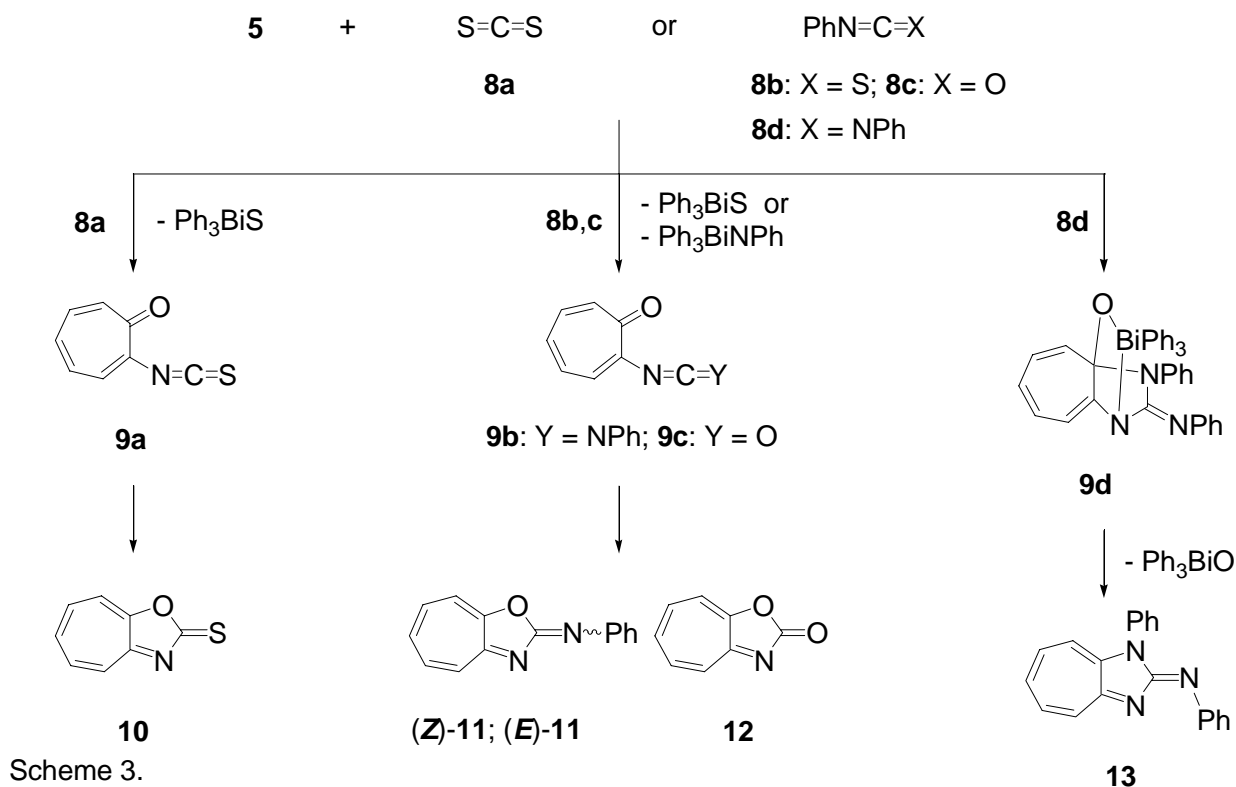


Compound (**4**) has been clarified to react with heterocumulenes (**8a-c**) in refluxing benzene or toluene to afford cyclohepta-annulated heterocycles.¹⁵ Thus, targeting clarification of the reactivity of the imide (**5**) and the construction of cyclohepta-annulated heterocycles, the reactions of **5** with heterocumulenes (**8a-d**) were investigated *via* similar intermediates to those of the reactions of phosphorane imide (**4**) with heterocumulenes¹⁵ under mild conditions at room temperature. Compound (**5**) reacted with carbon

Table 1. ^1H NMR spectral data of imide (**5**) and 2-aminotropone (**7**), and physical data of product (**13**)

5: ^1H NMR (500 MHz, C_6D_6) δ 6.36 (1H, dd, $J=9.0, 9.4$, H-5), 6.80 (1H, dd, $J=9.0, 10.2$, H-6), 6.93 (1H, dd, $J=9.4, 11.9$, H-4), 7.25 (1H, d, $J=10.2$, H-7), 7.91 (1H, d, $J=11.9$, H-3), 7.18-7.21 (9H, m, Ph), 7.95 (6H, d, $J=7.0$, Ph).

13: dark red prisms; mp 140-142 °C (AcOEt); ^1H NMR (600 MHz, CDCl_3) δ 6.66 (1H, d, $J=9.8$, H-8), 6.91 (1H, dd, $J=10.0, 9.8$, H-6), 7.02 (1H, m, Ph), 7.19 (1H, dd, $J=9.8, 10.0$, H-7), 7.31 (4H, m, Ph), 7.44 (1H, dd, $J=9.8, 11.1$, H-5), 7.50 (2H, d, $J=7.8$, Ph), 7.52 (1H, t, $J=7.5$, Ph), 7.60 (1H, d, $J=11.1$, H-4), 7.62 (1H, dd, $J=7.5, 7.8$, Ph); ^{13}C NMR (150.8, MHz, CDCl_3) δ 110.2 (C-8), 122.7 (Ph), 123.3 (Ph), 127.1 (C-4), 127.9 (C-6), 128.1 (Ph), 128.5 (Ph), 128.9 (Ph), 129.8 (Ph), 134.6 (quart), 136.2 (C-7), 138.7 (C-5), 149.1 (quart), 152.2 (quart), 159.3 (quart), 165.8 (quart); IR (CHCl_3) 1634, 1580 cm^{-1} ; MS (m/z), 297 (M^+ , 72%), 77 (100). *Anal.* Calcd for $\text{C}_{20}\text{H}_{15}\text{N}_3$: C; 80.78; H; 5.08, N; 14.13. Found: C; 80.51, H; 4.98, N; 13.86.



disulfide (**8a**) to give *2H*-cycloheptoxazol-2-thione, which probably arises from the aza-Wittig-type reaction of **5** with **8a** giving the intermediate (**9a**) and subsequent 10- π electron cyclization.¹⁵ Similarly, compound (**5**) with phenyl isothiocyanate (**8b**) and phenyl isocyanate (**8c**) reacted to give a mixture of *2H*-cycloheptoxazol-2-imines (**Z**)-**11** and (**E**)-**11** in a ratio of 7/3 and *2H*-cycloheptoxazol-2-one (**12**) in modest yields, probably *via* the intermediates (**9b**) and (**9c**), respectively.¹⁵ On the other hand, the reaction of **5** with diphenylcarbodiimide (**8d**), which was prepared *in situ* by heating **8c** and a catalytic amount of triphenylarsine oxide in benzene,¹⁷ afforded *N*-phenyl-*2H*-cycloheptoxazol-2-imine (**13**) probably *via* the intermediate (**9d**), which suggests a Bi--O interaction in **5**, in modest yield (Scheme 3). The reaction conditions and the yields of the products are summarized in Table 2 (Entries 1-4). The structures of the known compounds (**10**), a mixture of (**Z**)-**11** and (**E**)-**11**, and (**12**) were confirmed on the basis of the spectroscopic data of an authentic specimen.¹⁵ The structure of new compound (**13**) was assigned on the basis of the ¹H and ¹³C NMR spectra, IR spectrum, MS spectral data, analytical data, as well as a comparison of the physical data with those of the related derivatives.¹⁸ Furthermore, it was found compound (**13**) is not a mixture of (**E**)- and (**Z**)-isomers. Although no evidence for the stereochemical situation for **13** obtained, we prefer the (**Z**)-isomer for **13**, because of the steric hindrance of the phenyl groups.

Triarylbismuthane tosylimide prepared *in situ*⁵ and stabilized triarylbismuthane imides^{8,9} have been reported to exhibit oxidizing ability toward activated alcohols, converting them into the corresponding carbonyl compounds. Thus, the attempted reactions of imide (**5**) with benzopinacol (**14**) proceeded smoothly at room temperature to give benzophenone (**17**), in addition to 2-aminotropone (**7**) and

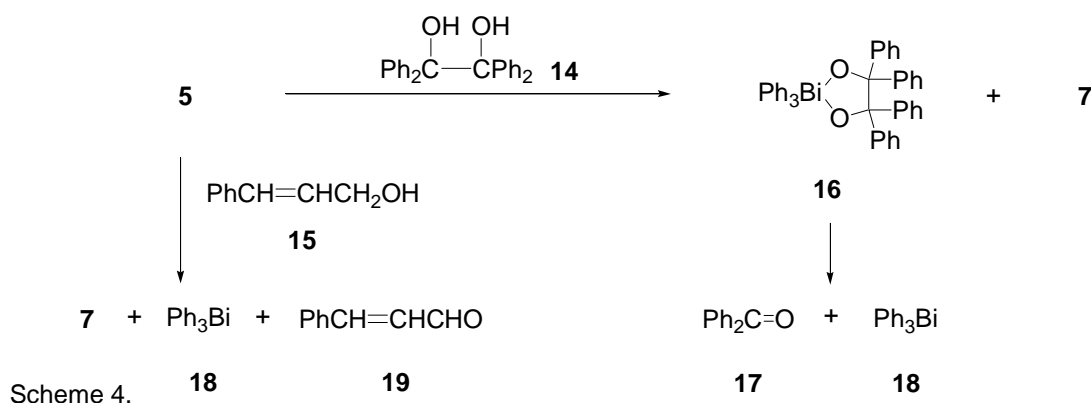


Table 2. Results for the reactions of imide (**5**) with heterocumulenes (**8a-d**) and alcohols (**14**) and (**15**)

Entry	Cumulene or	Ratio of	Reaction conditions ^b	
	Alcohol		8a-d, 14 or 15/5 ^a	Time/min
1	8a	excess	240	10 (21)
2	8b	10	180	(<i>Z, E</i>)- 11 (26)
3	8c	10	10	12 (34)
4	8d ^d	10	10	13 (56)
5 ^e	14	1	30	17 (95), 7 (90), 18 (92)
6 ^e	15	1	300	19 (85), 7 (96), 18 (65)

a. All *in situ* preparations of imide (**5**) were carried out by stirring a mixture of **6** (0.5 mmol), **7** (0.5 mmol) and ^tBuOK (1.0 mmol) in benzene (5 mL) at room temperature for 5-10 min. b. Stirred at room temperature. c. Isolated yield through TLC on SiO₂. Yield was based on 2-aminotropone (**7**) used. d. Prepared *in situ* by heating **8c** and a catalytic amount of triphenylarsine oxide in benzene.¹⁷ e. CH₂Cl₂ was used instead of benzene.

triphenylbismuthane (**18**) in good yields, respectively, suggesting the possible intermediacy of **16**.⁵ Similarly, the reaction of **5** with 3-phenylprop-2-enol (**15**) afforded cinnamaldehyde (**19**) in addition to **7** and **18** (Scheme 4). The results are summarized in Table 2 (Entries 5 and 6).

In conclusion, the present study demonstrates a practical and convenient preparation of triphenylbismuthane (tropon-2-yl)imide (**5**). The compound (**5**), which contains a formal N=Bi double bond, is found to possess enhanced reactivity toward heterocumulenes as compared with the phosphorus analogue (**4**) and oxidizing ability toward activated alcohols converting them to the corresponding carbonyl compounds. Further studies of the synthesis and reactivities of a series of pnictorane imides are now underway.

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