Diverse Structures and Remarkable Oxidizing Ability of Triarylbismuthane Oxides. Comparative Study on the Structure and Reactivity of a Series of Triarylpnictogen Oxides

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A systematic series of triarylbismuthane oxides was prepared in order to disclose their structure and reactivity, which have been compared with those of lighter pnictogen counterparts. X-ray crystallographic analysis of tris(2-methoxyphenyl)bismuthane oxide and tris(2-methoxyphenyl)stibane oxide revealed that they exist as dimers with a flat bis(μ-oxo) ring, implying that the polarized Bi^+-O^- and Sb^+-O^- bonds aggregate to attain electrostatic stabilization. In sharp contrast to their phosphorus, arsenic, and antimony counterparts, triarylbismuthane oxides are thermally unstable and possess a high oxidizing ability. In particular, the bismuthane oxides bearing ortho-substituted aryl ligands oxidized primary and secondary alcohols to aldehydes and ketones, respectively, with high efficiency under mild conditions.

Introduction

Metal–oxo and heteroatom–oxo species have been receiving much attention because of their importance in synthetic, biological, and industrial oxidation processes.[1] Such compounds exist in monomeric, oligomeric, or polymeric forms, and their oxidizing abilities differ considerably, depending on the central elements as well as on the attached ligands. The pentavalent group 15 elements (pnictogens) can make a formal double bond with an oxygen atom to construct triorganylpnictogen oxides of the general formula $R_3M{=}O$ (M = P, As, Sb, Bi).[2] The M=O bond of this class of compounds is often described as a hybrid with the ionic canonical form M^+-O^-, but with its bonding characteristics such as bond order, polarization, and energy being strongly dependent on a relevant pnictogen atom. Triphenylphosphane oxide ($Ph_3P{=}O$) is known to exist as a monomer with a tetrahedral geometry at the phosphorus center, and X-ray crystallographic analysis of $Ph_3P{=}O$[3] disclosed that the P=O bond length (1.46 Å) is significantly shorter than the ideal value for the P–O single-bond length (1.65 Å).[4] Recent theoretical studies on a parent phosphane oxide ($H_3P{=}O$) have concluded that the contribution of the ionic canonical form P^+-O^- would be important for explaining this bond shortening.[5] $Ph_3P{=}O$ is readily produced by oxygenation of triphenylphosphane or by metathesis of phosphorus ylides and imides. Forming a strong P=O bond is the driving force of these transformations, and $Ph_3P{=}O$ is unreactive and thermally stable. Triphenylarsane oxide ($Ph_3As{=}O$) and triphenylstibane oxide ($Ph_3Sb{=}O$) are also formed as thermally stable solids by oxygenation or by metathesis. $Ph_3As{=}O$ is known to exist as a monomer,[6] whereas $Ph_3Sb{=}O$ has been obtained in various forms depending on the preparation methods.[7] Doak and coworkers isolated a crystalline, dimeric triphenylstibane

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[1] (a) *Comprehensive Organic Synthesis*; Trost, B. M. Ed.; Pergamon: New York, 1991; Vol. 7. (b) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981. (c) Nugent, W. A.; Mayer, J. M. *Metal–Ligand Multiple Bonds*; Wiley: New York, 1988. (d) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459–517. (e) Romao, C. C.; Kuhn, F. E.; Herrmann, W. A. *Chem. Rev.* **1995**, *95*, 2021–2040. (f) Grushin, V. V. *Chem. Rev.* **2004**, *104*, 1629–1662 and references therein.

[2] Unless otherwise noted, the bonds between the pnictogen and oxygen atoms in the oxides are represented as M=O, irrespective of the actual nature of the bonds.

[3] (a) Bandori, G.; Bortolozzo, G.; Clemente, D. A.; Croatto, U.; Panattoni, C. *J. Chem. Soc. A* **1970**, 2778–2780. (b) Thomas, J. A.; Hamor, T. A. *Acta Crystallogr.* **1993**, *C49*, 355–357.

[4] The average P–O single bond length of P_4O_6. See: Jansen, M.; Moebs, M. *Inorg. Chem.* **1984**, *23*, 4486-4488.

[5] (a) Dobado, J. A.; Martínez-García, H.; Molina, J. M.; Sundberg, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 8461–8471. (b) Chesnut, D. B. *J. Am. Chem. Soc.* **1998**, *120*, 10504–10510. (c) Chesnut, D. B. *Heteroat. Chem.* **2000**, *11*, 341–352.

[6] Shao, M.; Jin, X.; Tang, Y.; Huang, Q.; Huang, Y. *Tetrahedron Lett.* **1982**, *23*, 5343–5346.

[7] (a) Doak, G. O.; Freedman, L. D. *Organometallic Compounds of Arsenic, Antimony, and Bismuth*; Wiley: New York, 1970; pp 298–307. (b) Briles, G. H.; McEwen, W. E. *Tetrahedron Lett.* **1966**, 5299–5302. (c) Doak, G. O.; Long, G. G.; Freedman, L. D. *J. Organomet. Chem.* **1968**, *12*, 443–450. (d) Venezky, D. L.; Sink, C. W.; Nevett, B. A.; Fortescue, W. F. *J. Organomet. Chem.* **1972**, *35*, 131–142. (e) McEwen, W. E.; Briles, G. H.; Schulz, D. N. *Phosphorus* **1972**, *2*, 147–153. (f) Carmalt, C. J.; Crossley, J. G.; Norman, N. C.; Orpen, A. G. *Chem. Commun.* **1996**, 1675–1676 and references therein.

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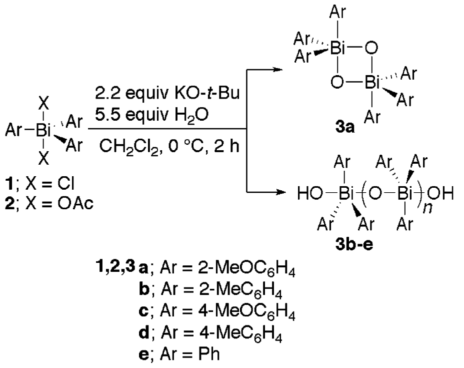
oxide and revealed its structure by X-ray crystallography, in which each antimony center was found to adopt a trigonal-bipyramidal geometry with a flat four-membered Sb_2O_2 ring.[8] In organic synthesis, $Ph_3P{=}O$ and $Ph_3As{=}O$ are well-known as the side products of the Wittig reactions[9] and have been used as Lewis base catalysts in transition-metal-catalyzed reactions,[10] and $Ph_3Sb{=}O$ has been used as a catalyst in amidation and sulfation of carboxylic acids and carbonylation of amines.[11] In these transformations, the pentavalent oxidation state of the phosphorus, arsenic, and antimony is retained.

On the other hand, the chemistry of triorganylbismuthane oxides ($R_3Bi{=}O$) has been explored much less than that of lighter pnictogen counterparts, probably due to the limited access to this class of compounds.[12] In 1934, Challenger and Richards reported the synthesis of triphenylbismuth dihydroxide, a hydrated form of triphenylbismuthane oxide.[13] It was found that the dihydroxide decomposes in ethanol and 2-propanol to afford acetaldehyde and acetone, respectively, with recovery of triphenylbismuthane. Goel and Prasad obtained triphenylbismuthane oxide as a polymeric substance in 10−40% yield by metathesis of Ph_3BiX_2 (X = Cl, CN) with silver oxide or mercury oxide.[14] These authors proposed the polymeric, oxo-bridged Bi−O−Bi network for this amorphous oxide on the basis of the IR spectra as well as their insolubility.[15] Triarylbismuthane oxides were also obtained by oxygenation of the corresponding triarylbismuthanes with iodosylbenzene[16] and by hydrolysis of triarylbismuthane imides.[17] To our knowledge, however, no well-characterized examples have been reported for triarylbismuthane oxides, and the nature of the Bi=O bond still remains to be clarified. Importantly, triarylbismuthane oxides are attractive oxidants, due to the potent oxidizing ability of the pentavalent bismuth.[18] Thus, it is of utmost importance to investigate the chemistry of triorganylbismuthane oxides from both structural and synthetic points of view.

Scheme 1



We report herein the first comprehensive studies on the synthesis, structure, and reactions of triarylbismuthane oxides.[19] Due to the high polarity of the bismuth(V)−oxygen bond and a large difference in orbital size between bismuth and oxygen atoms, the bismuthane oxides readily undergo dimerization, polymerization, or hydration. In marked contrast to the lighter pnictogen counterparts, the bismuthane oxides, especially those bearing ortho substituents, are thermally unstable and oxidize alcohols to carbonyl compounds with high efficiency under mild conditions.

Results and Discussion

Synthesis. Treatment of tris(2-methoxyphenyl)bismuth dichloride (**1a**) with 2.2 equiv of KO-*t*-Bu in the presence of 5.5 equiv of H_2O in CH_2Cl_2 at 0 °C afforded tris(2-methoxyphenyl)bismuthane oxide (**3a**) as a pale yellow solid (Scheme 1).[19] The present method is simple and efficient for obtaining **3a**, which is otherwise difficult to prepare.[20] Other triarylbismuth dichlorides (**1b**−**e**) similarly reacted with H_2O/KO-*t*-Bu to afford the corresponding triarylbismuth dihydroxides and/or μ-oxo-bridged dihydroxides (**3b**−**e**) quantitatively.[21] Compounds **3a**−**e** were also available from triarylbismuth

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[8] Bordner, J.; Doak, G. O.; Everett, T. S. *J. Am. Chem. Soc.* **1986**, *108*, 4206−4213.

[9] (a) Johnson, A. W. *Ylid Chemistry*; Academic Press: New York, 1966. (b) Johnson, A. W. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993. (c) Lloyd, D.; Gosney, I. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; Wiley: Chichester, U.K., 1994; Chapter 16, pp 657−693.

[10] (a) Ryan, K. M.; Bousquet, C.; Gilheany, D. G. *Tetrahedron Lett.* **1999**, *40*, 3613−3616. (b) Yamasaki, S.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2001**, *123*, 1256−1257. (c) Nemoto, T.; Ohshima, T.; Yamaguchi, K.; Shibasaki, M. *J. Am. Chem. Soc.* **2001**, *123*, 2725−2732.

[11] (a) Nomura, R.; Wada, T.; Yamada, Y.; Matsuda, H. *Chem. Lett.* **1986**, 1901−1904. (b) Nomura, R.; Yamada, Y.; Matsuda, H. *Appl. Organomet. Chem.* **1989**, *3*, 355−357. (c) Nomura, R.; Miyazaki, S.; Nakano, T.; Matsuda, H. *Appl. Organomet. Chem.* **1991**, *5*, 513−516. (d) Nomura, R.; Nakano, T.; Yamada, Y.; Matsuda, H. *J. Org. Chem.* **1991**, *56*, 4076−4078. (e) Nomura, R.; Miyazaki, S.; Nakano, T.; Matsuda, H. *Chem. Ber.* **1990**, *123*, 2081−2082. (f) Nomura, R.; Hasegawa, Y.; Ishimoto, M.; Toyosaki, T.; Matsuda, H. *J. Org. Chem.* **1992**, 57, 7339−7342.

[12] Many attempts to prepare triarylbismuthane oxides have been unsuccessful. (a) Challenger, F.; Goddard, A. E. *J. Chem. Soc.* **1920**, *117*, 762−773. (b) Monagle, J. J. *J. Org. Chem.* **1962**, *27*, 3851−3855. (c) Agolini, F.; Bonnett, R. *Can. J. Chem.* **1962**, *40*, 181−183. (d) Bernstein, J.; Halman, M.; Pinchas, S.; Samuel, D. *J. Chem. Soc.* **1964**, 821−824. (e) Davies, A. G.; Hook, S. C. W. *J. Chem. Soc. C* **1971**, 1660−1665. (f) Brandes, D.; Blaschette, A. *J. Organomet. Chem.* **1974**, *73*, 217−227. (g) Glidewell, C. *J. Organomet. Chem.* **1976**, *116*, 199−209. (h) El Sheikh, S. I. A.; Patel, M. S.; Smith, B. C.; Waller, C. B. *J. Chem. Soc., Dalton Trans.* **1977**, 641−644. (i) Suzuki, H.; Ikegami, T.; Matano, Y.; Azuma, N. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2411−2415.

[13] Challenger, F.; Richards, O. V. *J. Chem. Soc.* **1934**, 405−411.

[14] (a) Goel, R. G.; Prasad, H. S. *J. Organomet. Chem.* **1972**, *36*, 323−332. (b) Goel, R. G.; Prasad, H. S. *J. Organomet. Chem.* **1973**, *50*, 129−134.

[15] Goel, G.; Prasad, H. S. *Spectrochim. Acta* **1976**, *32A*, 569−573. The Bi−O−Bi asymmetric stretching mode appears at 620−625 cm^{-1} in the IR spectrum.

[16] Suzuki, H.; Ikegami, T.; Matano, Y. *Tetrahedron Lett.* **1994**, *35*, 8197−8200.

[17] (a) Pasenok, S. V.; Kirij, N. V.; Yagupolskii, Y. L.; Naumann, D.; Tyrra, W. *J. Fluorine Chem.* **1993**, *63*, 179−183. (b) Matano, Y.; Nomura, H.; Suzuki, H.; Shiro, M.; Nakano, H. *J. Am. Chem. Soc.* **2001**, *123*, 10954−10965.

[18] Pentavalent organobismuth compounds have been used as oxidizing agents. For example, see: (a) Barton, D. H. R.; Kitchin, J. P.; Lester, D. J.; Motherwell, W. B.; Papoula, M. T. B. *Tetrahedron* **1981**, *37* (Supplement 1), 73−79. (b) Dodonov, V. A.; Gushchin, A. V.; Brilkina, T. G. *J. Gen. Chem. USSR* **1985**, *55*, 63−68; *Zh. Obshch. Khim.* **1985**, *55*, 73−80. (c) Barton, D. H. R.; Yadav-Bhatnagar, N.; Finet, J.-P.; Khamsi, J.; Motherwell, W. B.; Stanforth, S. P. *Tetrahedron* **1987**, *43*, 323−332. (d) Matano, Y.; Nomura, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3028−3031. (e) Komatsu, N. In *Organobismuth Chemistry*; Suzuki, H., Matano, Y. Eds.; Elsevier: New York, 2001; Chapter 5, pp 371−440. (f) Matano, Y. In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Chapter 14, pp 753−811, and references therein.

[19] For preliminary results, see: Matano, Y.; Nomura, H. *J. Am. Chem. Soc.* **2001**, *123*, 6443−6444.

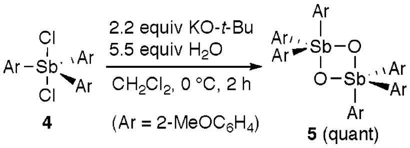
[20] An attempt to prepare **3a** using tris(2-methoxyphenyl)bismuthane and iodosylbenzene resulted in the formation of tetrakis(2-methoxyphenyl)bismuthonium salts: Suzuki, H.; Ikegami, T.; Azuma, N. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1609−1616.

diacetates (**2a**–**e**). When K_2CO_3, KOH, and $NaHCO_3$ were used in place of KO-*t*-Bu, **3** could not be formed efficiently.

Compounds **3a**–**e** are pale yellow or colorless solids, soluble in $CHCl_3$ and CH_2Cl_2 but almost insoluble in acetonitrile, diethyl ether, DMSO, and DMF. The structures of **3a**–**e** were characterized by ^{1}H NMR, IR, and FAB mass spectrometry as well as by X-ray crystallography (for **3a**). In the ^{1}H NMR spectra, the hydroxy protons appeared at δ 1.07 (ca. 1H vs methyl 9H) for **3b**, δ 0.56 (ca. 2H vs methyl 9H) for **3c,d**, and δ 0.65 (ca. 2H vs phenyl 15H) for **3e**, respectively. These signals disappeared on the addition of excess D_2O. On the other hand, no hydroxy proton was observed for **3a**. Thus, **3b**–**e** were obtained as hydrated forms of the corresponding oxides, whereas **3a** was obtained as an anhydride. The *o*-methoxy groups of **3a** probably interact with the bismuth center to prevent hydration of the $Bi^+–O^-$ bond (vide infra). In the IR spectra, characteristic absorptions were observed at around 530–610 cm^{-1}, which are consistent with the Bi–O–Bi stretching modes of the oxo-bridged triarylbismuth(V) compounds.[14,15] The FAB mass spectra exhibited a fragment ion peak at *m/z* 969 for **3a**,**c**, *m/z* 889 for **3b**,**d**, and *m/z* 819 for **3e**, respectively, attributable to a cation with a $Ar_5Bi_2O^+$ framework, together with weak fragment ion peaks due to higher oligomers, indicating that the aggregated species may be present in solution or generated during the ionization processes.

When they were allowed to stand in vacuo for several hours, **3c**–**e** were converted to amorphous powders, insoluble in most organic solvents. On treatment with a small amount of water in $CDCl_3$, the solids dissolved, and the parent soluble hydrates with a set of relatively sharp peaks were observed by ^{1}H NMR. Thus, the amorphous powders formed from **3c**–**e** were assigned as polymeric triarylbismuthane oxides. Such a polymerization was not observed for **3a**,**b**. The ortho substituents in **3a**,**b** may prevent polymerization of the $Bi^+–O^-$ bond both sterically and electronically.

The present methodology was also applicable to the synthesis of a stibane oxide. Thus, treatment of tris(2-methoxyphenyl)antimony dichloride (**4**) with 5.5 equiv of water in the presence of 2.2 equiv of KO-*t*-Bu afforded tris(2-methoxyphenyl)stibane oxide (**5**) quantitatively (eq 1).[22]



4 **5** (quant)

(1)

Structure. The structures of **3a** and **5** were further elucidated by X-ray crystallography. ORTEP diagrams are shown in Figures 1 and 2, data collection parameters are summarized in Table 1, and selected bond lengths and angles are listed in Table 2. As shown in Figure 1, bismuthane oxide **3a** exists in crystalline form as a dimer containing a flat bis(μ-oxo) Bi_2O_2 ring. Each bismuth center adopts a distorted-trigonal-bipyramidal geometry with two ipso carbon atoms and one oxygen atom at the equatorial sites and one ipso carbon and one oxygen at the apical sites. The $Bi–O_{bridge}$ bond lengths of known oxo-bridged binuclear organobismuth compounds range from 2.02(3) to 2.12(3) Å.[23,24] Thus, the $Bi–O_{eq}$ bond length of 2.013(5) Å lies at the shorter end of this range. On the other hand, the $Bi–O_{ap}$ bond length of 2.309(6) Å lies at the longer end of the $Bi–O_{ap}$ bond lengths observed for $Ph_3Bi(OR)_2$.[25] These findings suggest that both the $Bi–O_{eq}$ and the $Bi–O_{ap}$ bonds are best represented as Bi–O single bonds. The *o*-methoxy oxygens lean ca. 3–7° toward the bismuth center, indicating the attractive interaction between these two atoms. This intramolecular coordination

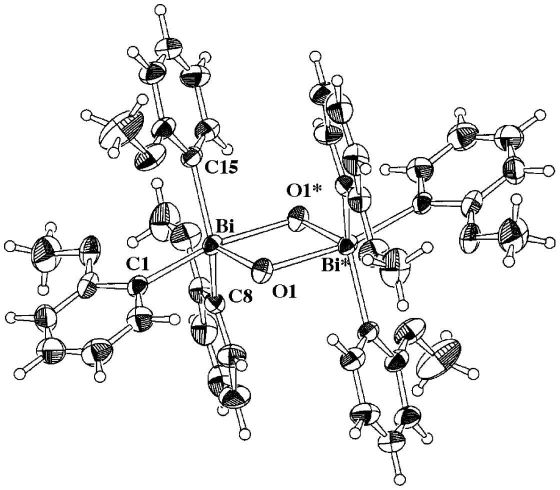


Figure 1. ORTEP diagram for **3a** (30% probability ellipsoids).

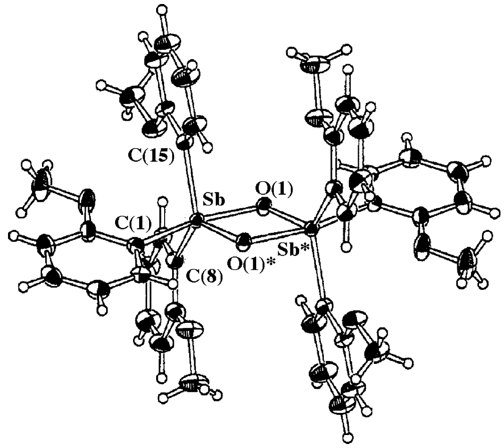


Figure 2. ORTEP diagram for **5** (30% probability ellipsoids).

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[21] Irrespective of the degree of oligomerization and hydration, compounds **3** are represented as triarylbismuthane oxides throughout this paper.

[22] The stibane oxide **5** was hydrated in the presence of water, and there was an equilibrium between the hydrate and the anhydride in solution. See the Experimental Section.

[23] Bi(V) compounds are detailed in the following. (a) $[Ph_3Bi(ClO_4)]_2O$ (2.065(15), 2.062(14) Å): March, F. C.; Ferguson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1291–1294. (b) $[Ph_3Bi(OTf)]_2O$ (2.091(8), 2.039(8) Å): Matano, Y.; Azuma, N.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1739–1747. (c) $[(4\text{-}Me_2NC_6H_4)_3BiCl]_2O$ (2.12(3), 2.02(3) Å): Hassan, A.; Breeze, S. R.; Courtenary, S.; Deslippe, C.; Wang, S. *Organometallics* **1996**, *15*, 5613–5621.

[24] Bi(III) compounds are detailed in the following. (a) $[(2,4,6\text{-}Me_3C_6H_2)_2Bi]_2O$ (2.075(8), 2.064(7) Å): Li, X.-W.; Lorberth, J.; Ebert, K. H.; Massa, W.; Wocadlo, S. *J. Organomet. Chem.* **1998**, *560*, 211–215. (b) $(TbtBiO)_2$; Tbt = 2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$ (2.101(10), 2.073(9) Å): Sasamori, T.; Arai, Y.; Takeda, M.; Okazaki, R.; Furukawa, Y.; Kimura, M.; Nagase, S.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 661–675.

Table 1. Crystallographic Data for 3a, 5, and 10

	3a	5	10
empirical formula	$C_{42}H_{42}Bi_2O_8$	$C_{42}H_{42}O_8Sb_2$	$C_{56}H_{56}Bi_4O_6$
formula wt	1092.75	918.29	1660.98
cryst size (cm)	0.20 × 0.05 × 0.05	0.10 × 0.04 × 0.03	0.20 × 0.15 × 0.10
cryst syst	triclinic	triclinic	triclinic
a (Å)	10.4018(6)	8.354(2)	11.270(2)
b (Å)	12.1622(8)	10.890(1)	11.367(2)
c (Å)	9.0988(6)	11.271(3)	12.355(2)
α (deg)	108.935(3)	85.78(1)	112.74(1)
β (deg)	104.073(3)	68.61(2)	91.34(1)
γ (deg)	104.779(2)	89.37(1)	113.96(1)
V (Å^3)	983.7(1)	952.1(4)	1303.0(4)
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	1	1	1
D_{calcd} (g cm^{-3})	1.845	1.601	2.117
radiation (*λ*, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 70)
μ (Mo Kα) (cm^{-1})	89.68	14.69	13.489
temp (°C)	23	27	−50
$2\theta_{max}$ (deg)	54.9	55.0	54.9
no. of rflns measd			
total	9056	4593	5082
unique	4446	3444	4126
no. of observns	4446 (all, $2\theta < 54.95°$)	4368 ($I > 2.00\sigma(I)$)	5082 ($I > -10.00\sigma(I)$)
no. of variables	235	257	326
R1, wR2	0.044, 0.103	0.032, 0.090	0.051, 0.133
goodness of fit	1.07	1.07	1.08

Table 2. Selected Bond Parameters of 3a and 5

M = Bi		M = Sb	
Bond Lengths (Å)			
Bi−O(1)	2.013(5)	Sb−O(1)	1.934(3)
Bi−O(1)*	2.309(6)	Sb−O(1)*	2.087(2)
Bi−C(1)	2.273(10)	Sb−C(1)	2.180(3)
Bi−C(8)	2.194(9)	Sb−C(8)	2.144(5)
Bi−C(15)	2.210(8)	Sb−C(15)	2.123(4)
Bond Angles (deg)			
Bi−O(1)−Bi*	102.0(2)	Sb−O(1)−Sb*	101.9(1)
O(1)−Bi−O(1)*	78.0(2)	O(1)−Sb−O(1)*	78.2(1)
O(1)−Bi−C(1)	92.3(3)	O(1)−Sb−C(1)	91.0(1)
O(1)−Bi−C(8)	109.9(3)	O(1)−Sb−C(8)	126.7(1)
O(1)−Bi−O(15)	121.3(3)	O(1)−Sb−O(15)	107.6(2)
O(1)*−Bi−C(1)	167.9(2)	O(1)*−Sb−C(1)	168.4(1)
O(1)*−Bi−C(8)	84.2(3)	O(1)*−Sb−C(8)	87.2(1)
O(1)*−Bi−C(15)	84.4(4)	O(1)*−Sb−C(15)	92.7(1)
C(1)−Bi−C(8)	92.4(3)	C(1)−Sb−C(8)	96.0(2)
C(1)−Bi−C(15)	107.1(3)	C(1)−Sb−C(15)	94.7(1)
C(8)−Bi−C(15)	123.5(3)	C(8)−Sb−C(15)	124.2(2)

would stabilize the positively charged bismuth center to prevent hydration and oligomerization of the $Bi^{+}{-}O^{-}$ bond (vide supra).

Stibane oxide **5** also exists as a dimer with a flat, four-membered Sb_2O_2 core. The observed $Sb{-}O_{ap}$ and $Sb{-}O_{eq}$ bond lengths (2.087(3) and 1.933(3) Å) are comparable to the corresponding values ($Sb{-}O_{ap}$, 2.060(2)−2.080(4) Å; $Sb{-}O_{eq}$, 1.928(4)−1.943(3) Å) of known triarylstibane oxide dimers.[8,26] The $Sb{-}O_{eq}$ bond length lies close to the shorter end of the range of $Sb{-}O_{bridge}$ bond lengths (1.931(13)−2.004(7) Å) reported for oxo-bridged binuclear organoantimony compounds,[27,28] whereas the $Sb{-}O_{ap}$ bond length is slightly shorter than the $Sb{-}O_{ap}$ bond lengths observed for $Ph_3Sb(OR)_2$.[29]

The $Bi{-}O_{ap}/Bi{-}O_{eq}$ and the $Bi{-}O_{ap}/Bi{-}C_{ap}$ bond length ratios (1.15 and 1.02) of **3a** are larger than the $Sb{-}O_{ap}/Sb{-}O_{eq}$ and the $Sb{-}O_{ap}/Sb{-}C_{ap}$ ratios (1.07−1.08 and 0.96) of **5**, respectively. These suggest that the antimony center of **5** interacts more tightly with the apical oxygen than does the bismuth center of **3a**. Presumably, two molecules of the heavier pnictogen oxides with a polarized $Bi^{+}{-}O^{-}$ or $Sb^{+}{-}O^{-}$ bond aggregate to attain electrostatic stabilization.

To compare the relative stability between monomers and dimers of $Ph_3M{=}O$ (M = P, As, Sb, Bi), we carried out density functional theory calculations on their relative energies.[30] It was found that the dimers of $Ph_3Sb{=}O$ and $Ph_3Bi{=}O$ are more stable than the respective monomers, and the stabilization energies attained by dimerization were calculated to be 42−43 kcal mol^{-1}. This is in sharp contrast to the results calculated for $Ph_3P{=}O$ and $Ph_3As{=}O$, which are destabilized by dimerization. The main factors responsible for this difference would be the increasing polarity of the pnictogen−oxygen bond and the larger difference in orbital size between pnictogen and oxygen atoms for the heavier pnictogen oxides. The calculated results on the relative stabilities are in good accordance with the results obtained by X-ray analyses.[3,6,8,31]

Reactions. (a) Thermal Decomposition. In contrast to the lighter pnictogen counterparts, the bismuthane oxides **3** are thermally unstable. When stood in benzene at 80 °C, **3a**,**b**,**d**,**e** decomposed to give the corresponding triarylbismuthanes (**6a**,**b**,**d**,**e**) as the major products. The stability of **3** depends on the aryl ligands, and the ortho-substituted derivatives **3a**,**b** are less stable than the para-substituted and phenyl derivatives **3d**,**e**. After being heated for 0.5 h, **3a** decomposed to give **6a** in 64% yield,[32] whereas **3e** was mostly recovered unchanged (Table 3).

Although the mechanism is not fully understood at present, the present decomposition mode of **3** is of interest in that an active oxygen species might be generated with elimination of triarylbismuthane **6**.

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(25) For example, see the following. (a) $Ph_3Bi(OC_6F_5)_2$ (2.228(5), 2.212(5) Å), $Ph_3Bi(OC_6Cl_5)_2$ (2.250(7), 2.244(7) Å): Hoppe, S.; Whitmire, K. H. *Organometallics* **1998**, *17*, 1347−1354. (b) $Ph_3Bi(OCOCF_3)_2$ (2.309(7), 2.308(7) Å): Ferguson, G.; Kaitner, B.; Glidewell, C.; Smith, S. *J. Organomet. Chem.* **1991**, *419*, 283−291. (c) $Ph_3Bi[OCOC(OH)Ph_2]_2$ (2.292(2), 2.249(2) Å): Barucki, H.; Coles, S. J.; Costello, J. F.; Gelbrich, T.; Hursthouse, M. B. *Dalton* **2000**, 2319−2325. (d) $Ph_3Bi(OSO_2Ph)_2$ (2.280(4), 2.276(5) Å): Rüther, R.; Huber, F.; Preut, H. *Z. Anorg. Allg. Chem.* **1986**, *539*, 110−126.

(26) Breunig, H. J.; Probst, J.; Ebert, K. H.; Lork, E.; Cea-Olivares, R.; Alvarado-Rodríguez, J.-G. *Chem. Ber.* **1997**, *130*, 959−961.

(27) Sb(V) compounds are detailed as follows. (a) $[Ph_3Sb(N_3)]_2O$ (1.985(3) Å): Ferguson, G.; Ridley, D. R. *Acta Crystallogr.* **1973**, *B29*, 2221−2226. (b) $[Ph_3Sb(OTf)]_2O$ (1.963(4), 1.963(5) Å), $[Ph_3Sb(O_3SPh)]_2O$ (1.980(8), 1.937(10) Å): Preut, H.; Rüther, R.; Huber, F. *Acta Crystallogr.* **1986**, *C42*, 1154−1157. (c) $[Ph_3Sb(Cl)]_2O{\cdot}2C_6H_6$ (1.986(6), 1.980(6) Å): Tiekink, E. R. T. *J. Organomet. Chem.* **1987**, *333*, 199−204. (d) $[Ph_3Sb(Br)]_2O$ (1.958(13), 1.931(13) Å; 1.943(13), 1.943(13) Å): Ouchi, A.; Sato, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1806−1808.

(28) Sb(III) compounds are detailed as follows. (a) $(Ph_2Sb)_2O$ (1.975(5), 1.966(4) Å): Bordner, J.; Andrews, B. C.; Long, G. G. *Cryst. Struct. Commun.* **1974**, *3*, 53−56. (b) $(TbtSbO)_2$ (2.004(7), 1.990(6) Å): ref 24b.

(29) For example, see the following. (a) $Ph_3Sb(OAc)_2$ (2.130(3) Å): Sowerby, D. B. *J. Chem. Res., Synop.* **1979**, 80−81. (b) $Ph_3Sb(OCOCF_3)_2$ (2.153(9), 2.116(9) Å): ref 25b. (c) $Ph_3Sb[OCOC(OH)Ph_2]_2$ (2.145(2), 2.102(2) Å): ref 25c. (d) $Ph_3Sb(OSO_2Ph)_2$ (2.128(2), 2.106(3) Å): ref 25d. (e) $Ph_3Sb(OMe)_2$ (2.039(8), 2.027(8) Å): Shen, K.-W.; McEwen, W. E.; La Placa, S. J.; Hamilton, W. C.; Wolf, A. P. *J. Am. Chem. Soc.* **1968**, *90*, 1718−1723.

(30) The optimized geometries of pnictogen centers in the $Ph_3Sb{=}O$ and $Ph_3Bi{=}O$ dimers are close to the observed geometries of **3a** and **5**.

(31) Howell, J. A. S.; Palin, M. G.; Yates, P. C.; McArdle, P.; Cunningham, D.; Goldschmidt, Z.; Gottlieb, H. E.; Hezroni-Langerman, D. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1769−1775.

(32) Although we reported the highest yield of 93% in our previous communication,[19] the average isolated yield of **6a** after repeated experiments was ca. 70%.

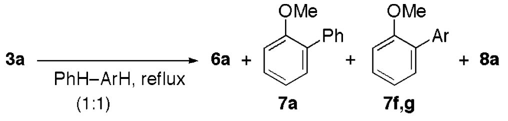
Table 3. Thermal Decomposition of 3

$$\mathbf{3} \xrightarrow[\text{PhH, reflux}]{} \underset{\mathbf{6}}{Ar_3Bi} + \underset{\mathbf{7}}{ArPh} + \underset{\mathbf{8}}{ArOAr} + \underset{\mathbf{9}}{ArH} + \text{insol solid}$$

entry	3	time/h	product[a] (yield/%[b])			insol solid[c]
1	**3a**	0.5	**6a** (64)	**7a** (16)	**8a** (8)	nm[d]
2	**3a**	4	**6a** (74)	**7a** (18)	**8a** (6)	14
3	**3b**	0.5	**6b** (63)	**7b** (18)	**8b** (7)	18
4	**3d**	0.5	**6d** (7)	**7d** (trace)	**8d** (trace)	nm
5	**3d**	4	**6d** (35)	**7d** (5)	**8d** (trace)	nm
6	**3d**	15	**6d** (65)	**7d** (12)	**8d** (3)	nm
7	**3e**	0.5[e]	**6e** (10)	**7e** (nm)	**8e** (nm)	nm

[a] Legend: **a**, Ar = 2-$MeOC_6H_4$; **b**, Ar = 2-MeC_6H_4; **d**, Ar = 4-MeC_6H_4; **e**, Ar = Ph. [b] Based on **3**. The yield of **9** was not determined. [c] Weight percent of insoluble solid vs **3**. [d] Not measured. [e] **3e** was recovered in ca. 80% yield.

Scheme 2



Solvent	Product ratio
PhH–$MeOC_6H_5$	**7a**/**7g** = 1±0.2
PhH–MeC_6H_5	**7a**/**7g** = 1±0.2

7f; Ar = $MeOC_6H_4$ (*o*/*m*/*p* = 58/18/24)
7g; Ar = MeC_6H_4 (*o*/*m*/*p* = 63/14/23)

Challenger and Richards proposed in their report that triphenylbismuth dihydroxide (**3e**, $n = 0$) decomposed by heat to produce triphenylbismuthane (**6e**) and an O_2 gas.[13] Nagase and co-workers determined the reaction energy of the formation of $H_3M{=}O$ from H_3M and $^1/_2$ O_2 (M = N, P, As, Sb, Bi) by ab initio molecular orbital calculations, where $H_3Bi{=}O$ was thermodynamically less stable than a combination of H_3Bi and $^1/_2$ O_2 over 18.9 kcal mol^{-1}.[33] To probe the fate of the oxygen atoms originally attached to the bismuth(V) center of **3**, we carefully characterized the byproducts formed by the thermolysis. However, we could not detect O_2 gas evolution by GC or GCMS analyses. This result indicated that active oxygen species such as singlet oxygen were not generated in a detectable amount. In fact, when the thermolysis of **3a** was carried out in the presence of an excess of 1,4-cyclohexadiene, 1,3-cyclooctadiene, *trans*-stilbene, or 9,10-dihydroanthracene, no singlet oxygen derived products such as peroxides, epoxides, and dehydrogenated arenes could be determined by GC, GCMS, or ^1H NMR. Instead, biaryls (**7**), diaryl ethers (**8**), and arenes (**9**) were detected in all cases. The formation of **7** suggested the involvement of an aryl radical or aryl cation intermediate. When **3a** was heated in a mixture of benzene/toluene or benzene/anisole, an ortho/meta/para mixture of biaryls **7f**,**g** was also formed together with **7a** in almost the same ratio (Scheme 2). This result strongly suggests that the 2-methoxyphenyl radical or its equivalent is generated during decomposition of **3a**.[34]

In the thermolysis of **3**, a small amount of bismuth-derived insoluble solid was also formed. The IR spectrum of this solid showed a broad absorption at around 550–600 cm^{-1}, attributable to a composite of several Bi–O–Bi stretching modes. Elemental analyses of the solids revealed that they contained only 10–15% carbon. These data implied that the insoluble solids consist of both organic and inorganic bismuth oxides with an oligomeric or polymeric Bi–O–Bi linkage. The oxygen atom of **3** may be included as a significant part of these byproducts.

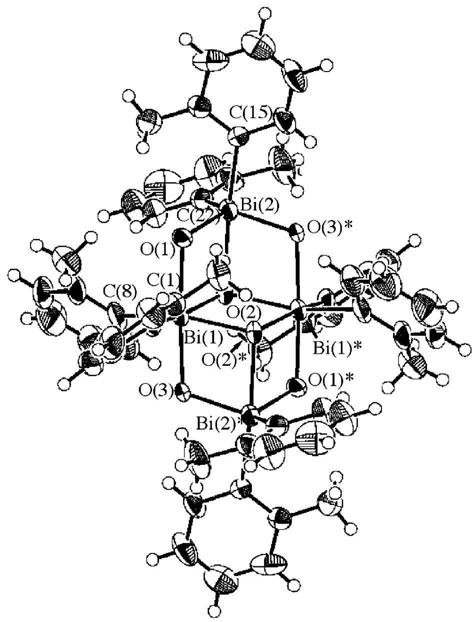


Figure 3. ORTEP diagram for **10** (30% probability ellipsoids).

Table 4. Selected Bond Parameters of 10

Bond Lengths (Å)			
Bi(1)–O(1)	2.192(9)	Bi(1)–O(2)	2.183(8)
Bi(1)–O(2*)	2.195(8)	Bi(1)–O(3)	2.17(1)
Bi(1)–C(1)	2.24(1)	Bi(1)–C(8)	2.30(2)
Bi(2)–O(1)	2.011(8)	Bi(2)–O(2)	2.38(1)
Bi(2)–O(3*)	2.034(8)	Bi(2)–C(15)	2.22(1)
Bi(2)–C(22)	2.19(1)		

Bond Angles (deg)			
O(1)–Bi(1)–O(2)	77.2(3)	O(1)–Bi(1)–O(2)*	99.5(4)
O(1)–Bi(1)–O(3)	176.5(3)	O(1)–Bi(1)–C(1)	90.3(4)
O(1)–Bi(1)–C(8)	95.2(5)	O(2)–Bi(1)–O(2)*	74.7(3)
O(2)–Bi(1)–O(3)	99.5(3)	O(2)–Bi(1)–C(1)	160.3(5)
O(2)–Bi(1)–C(8)	86.7(4)	O(2)*–Bi(1)–O(3)	78.2(4)
O(2)*-Bi(1)–C(1)	92.8(4)	O(2)*–Bi(1)–C(8)	153.0(5)
O(3)–Bi(1)–C(1)	92.5(4)	O(3)–Bi(1)–C(8)	85.9(5)
C(1)–Bi(1)–C(8)	109.8(5)	O(1)–Bi(2)–O(2)	76.4(3)
O(1)–Bi(2)–O(3)*	111.8(3)	O(1)–Bi(2)–C(15)	99.1(4)
O(1)–Bi(2)–C(22)	117.0(5)	O(2)–Bi(2)–O(3)*	76.8(4)
O(2)–Bi(2)–C(15)	169.4(3)	O(2)–Bi(2)–C(22)	84.0(4)
O(3)*–Bi(2)–C(15)	96.4(4)	O(3)*–Bi(2)–C(22)	120.8(4)
C(15)–Bi(2)–C(22)	106.6(5)	Bi(1)–O(2)–Bi(2)	97.0(3)
Bi(1)–O(1)–Bi(2)	108.8(4)	Bi(1)*–O(2)–Bi(2)	96.3(4)
Bi(1)–O(2)–Bi(1)*	105.3(3)	Bi(1)–O(3)–Bi(2)*	108.3(5)

It should be noted here that the insoluble solid obtained from **3b** contained a small amount of bis(2-methylphenyl)bismuthinic acid anhydride (**10**). Compound **10** is a colorless, air-stable solid and is insoluble in organic solvents and water. The structure of **10** was determined by X-ray crystallography: data collection parameters are summarized in Table 1, the ORTEP diagram is shown in Figure 3, and selected bond parameters are listed in Table 4. Although the preparation method has not been established yet, compound **10** is a new class of bismuth(V)–oxo species that has been

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(33) Naito, T.; Nagase, S.; Yamataka, H. *J. Am. Chem. Soc.* **1994**, *116*, 10080–10088.

(34) Hey, D. H. In *Advances in Free-Radical Chemistry*; Williams, G. H., Ed.; Logos Press: London, 1967; Vol. 2, Chapter 2, pp 47–86.

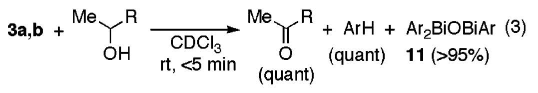
structurally characterized.[35] The cluster **10** contains a Bi_4O_6 cage with two kinds of bismuth centers: one adopts a distorted-trigonal-bipyramidal geometry, and the other adopts a distorted-octahedral geometry. The pentacoordinate bismuth center Bi(2) possesses two shorter $Bi-O_{eq}$ bonds (2.010(8)–2.033(9) Å) and one longer $Bi-O_{ap}$ bond (2.39(1) Å), the lengths of which match well with the equatorial and apical Bi–O bonds of **3a**. The hexacoordinate bismuth center Bi(1) possesses four Bi–O bonds of almost identical lengths (2.17(1)–2.193(9) Å). The core of **10** consists of a flat, diamond-shaped Bi_2O_2 ring with a wide Bi(1)–O(2)–Bi(1)* angle of 105.3(3)° and a narrow O(2)–Bi(1)–O(2)* bond angle of 74.7(3)°. The other four Bi_2O_2 rings are also flat, with wide Bi–O–Bi angles of 96.3(4)–108.8(4)° and narrow O–Bi–O angles of 76.4(3)–78.2(4)°. These structural features strongly indicate that the Bi=O bonds of the monomeric bismuthinic acid anhydride are highly polarized and dimerize to attain electronic stabilization.

The present decomposition mode of **3** is in marked contrast to that of $Ph_3Sb{=}O$, which decomposes under very severe conditions to yield a stibinic acid anhydride, $(Ph_2SbO)_2O$, as the major product.[36] The characteristic reactivity of **3** is undoubtedly derived from the good leaving ability of the triarylbismuthonio moiety.[37] In fact, **3a** transferred the oxo group to the lighter triphenylpnictogens (Ph_3M, M = P, As, Sb) within 1 min, giving **6a** and $Ph_3M{=}O$ quantitatively (eq 2).

$$\mathbf{3a} + Ph_3M \xrightarrow[CDCl_3,\ r.t.,\ <5\ min]{} \underset{(quant)}{\mathbf{6a}} + \underset{(quant)}{Ph_3M{=}O} \qquad (2)$$

(M = P, As, Sb)

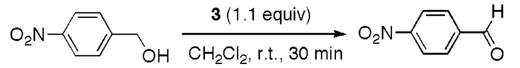
(b) Oxidation of Alcohols. Compounds **3a**,**b** were found to possess a remarkable oxidizing ability. Ethanol and 2-propanol were oxidized by **3a**,**b** within 5 min at room temperature to acetaldehyde and acetone, respectively, in quantitative yields (eq 3). In these oxidations, equimolar amounts of arene and $Ar_2BiOBiAr_2$ (**11**) were formed as byproducts,[38] indicating that an α-hydrogen was abstracted by the aryl group bound to the Bi(V) center. In fact, when C_2D_5OH was used as the substrate in the oxidation using **3a**, *o*-deuterioanisole was produced quantitatively.



(3)

(R = H, Me; Ar = 2-MeOC$_6$H$_4$; 2-MeC$_6$H$_4$)

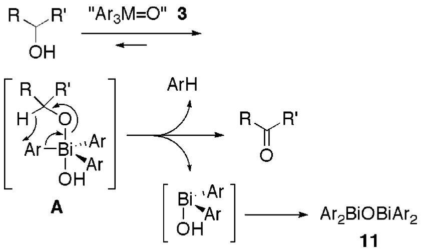
Table 5. Comparison of the Oxidizing Ability of 3



entry	**3**	conversn/%[a]	yield/%[b]
1	**3a**	99	91
2	**3b**	99	97
3	**3c**	25	17
4	**3d**	34	34
5	**3e**	50	47

[a] Conversion of *p*-nitrobenzyl alcohol, determined by ^{1}H NMR. [b] Isolated yield of *p*-nitrobenzaldehyde.

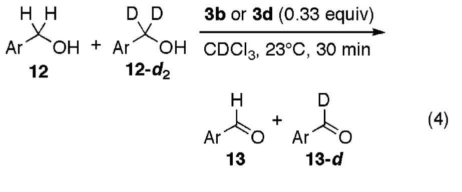
Scheme 3



To examine the effect of aryl ligands, we performed the oxidation of *p*-nitrobenzyl alcohol with **3a**–**e** under the same reaction conditions. As shown in Table 5, the ortho-substituted derivatives **3a**,**b** oxidized the alcohol much more rapidly than the para-substituted and phenyl derivatives **3c**–**e**.[39] Thus, the reaction rate strongly depends on the structure of the aryl ligands of **3**.

A plausible mechanism of the present oxidation is depicted in Scheme 3. The first step is formation of the alkoxybismuth(V) intermediate **A**, and the second step is α-hydrogen abstraction, affording equimolar amounts of carbonyl compound, arene, and **11**. A similar intermediate was proposed by Barton and co-workers for the Ph_3BiX_2-based oxidation of alcohols.[18]

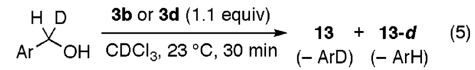
To probe the nature of the rate-determining step, the H/D kinetic isotope effects were examined by competitive oxidations using *p*-bromobenzyl alcohol (**12**) and its α-deuterio derivatives **12**-*d* and **12**-d_2 (eqs 4 and 5). The k_H/k_D values were determined from ratios of the aldehydes **13** and **13**-*d* produced. In the oxidations with **3b**,**d** the intermolecular k_H/k_D values of 3.0–3.7 were close to the intramolecular k_H/k_D values of 3.3–3.7, which are much larger than the values of the secondary isotope



(4)

(Ar = 4-BrC$_6$H$_4$)

	13/13-*d*
3b	3.0±0.1
3d	3.7±0.5



(5)

	13-*d*/13
3b	3.3±0.2
3d	3.7±0.2

(Ar = 4-BrC$_6$H$_4$)

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[35] Ogawa et al. reported the synthesis of bis(2-methylphenyl)bismuthinic acid, the acid form of **10**, by treatment of **6b** with Chloramin-T in boiling benzene/methanol. See: Ogawa, T.; Murafuji, T.; Iwata, K.; Suzuki, H. *Chem. Lett.* **1988**, 2021–2024. Despite many attempts to prepare the authentic sample, however, we were not able to reproduce their result: the major products formed by their method were found to be *o*-Tol_2BiX (X = OBi(*o*-Tol)$_2$, OMe) and toluene.

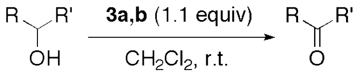
[36] The stibinic acid anhydride was formed in 45% yield by refluxing a xylene solution of $Ph_3Sb{=}O$ for 4 days.[7e,8] The anhydride was alternatively prepared by oxidation of Ph_4Sb_2. See: Breunig, H. J.; Krüger, T.; Lork, E. *J. Organomet. Chem.* **2002**, *648*, 209–213.

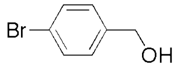
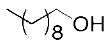
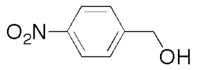
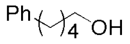
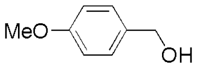
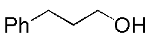
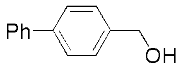
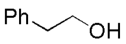
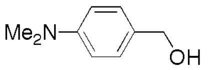
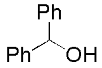
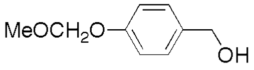
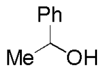
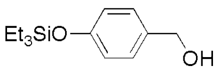
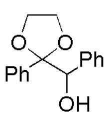
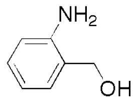
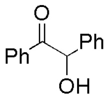
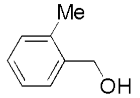
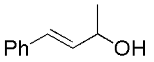
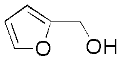
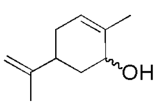
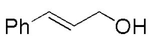
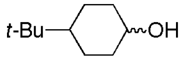
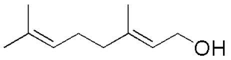
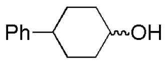
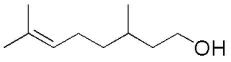
[37] Matano, Y. *Organometallics* **2000**, *19*, 2258–2263.

[38] Compound **11** gradually disproportionated in solution to give **6** and an insoluble solid.

[39] The ortho effect on the reactivity was also observed for the Ar_3BiCl_2–DBU oxidation system.[18d]

Table 6. Oxidation of Alcohols Using 3a,b



Entry	Alcohol	Yield/%[a] **3b** (**3a**)	Entry	Alcohol	Yield/%[a] **3b** (**3a**)
1		91	14		92 (96)[d]
2		97 (91)	15		89
3		92	16		53[g]
4		99 (89)	17		–[h]
5		99	18		99
6		78[b]	19		99 (99)[d]
7		28[c]	20		96
8		88	21		86
9		99	22		90
10		99[d]	23		96
11		97 (99)	24		98 (98)[d]
12		94[e]	25		81
13		97 (90)[f]			

[a] Isolated yield unless otherwise noted. [b] 93% NMR yield. [c] 4-Hydroxybenzaldehyde was also obtained in 70% yield. [d] NMR yield. [e] Geranial was obtained as a sole product. [f] Citronellal was obtained. [g] The alcohol was recovered in 35% yield. [h] A complex mixture was formed with recovery of the alcohol (ca. 60%).

effect. This indicates that the rate-determining step involves the α-hydrogen abstraction process.[40] It is most likely that the ortho substituents cause steric congestion around the bismuth center to weaken the Bi–C bonds of the intermediate **A**.

With new efficient oxidants **3a**,**b** in hand, we examined oxidations of various primary and secondary alcohols (Table 6). In most cases, the reactions were complete within 5–30 min at room temperature, and aldehydes and ketones were isolated in good yields by silica gel column chromatography. In our system, the aldehydes produced were not oxidized further to carboxylic acids, in either the presence or absence of KCl and water. This is in sharp contrast to the reaction mode of iodosylbenzene, which oxidizes primary alcohols, in the presence of KBr and water, to carboxylic acids.[41] It should also be noted that the bismuthane oxides **3** do not require any additives, which are necessary for activating diorganyl sulfoxide in the Swern oxidation.[42]

Benzylic and allylic alcohols were oxidized efficiently by **3a**,**b** to aromatic and α,β-unsaturated carbonyl

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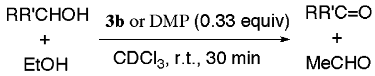
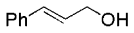
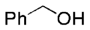
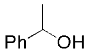
(40) If the first step in Scheme 3 is irreversible or consists of a slow equilibrium as compared to the second step, the intermolecular k_H/k_D value should be close to that of the secondary isotope effect.

(41) Tohma, H.; Takizawa, S.; Maegawa, T.; Kita, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 1306–1308.

(42) (a) Omura, K.; Sharma, A. K.; Swern, D. *J. Org. Chem.* **1976**, *41*, 957–962. (b) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651–1660.

Table 7. Competitive Oxidations of Alcohols by 3b and Dess–Martin Periodinane (DMP)

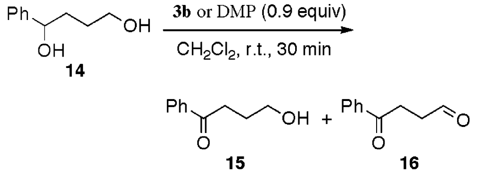


RR'CHOH	RR'C=O/MeCHO	
	3b	DMP
	>99/<1	91/9
	96/4	90/10
	95/5	75/25

compounds, respectively (Table 6, entries 1–12 and 18–23). The nitro, amino, and *O*-methoxymethyl groups remained intact during the reaction (entries 2, 5, 6, and 8), whereas the phenolic *O*-triethylsilyl group was partially deprotected (entry 7). Nonconjugated aliphatic alcohols were converted to the corresponding carbonyl compounds in moderate to good yields (entries 13–16, 24, and 25). On the other hand, treatment of 2-phenylethanol with **3b** resulted in the formation of a complex mixture including the unconsumed alcohol (entry 17).[43] It is probable that the acidic α-proton of the initially formed phenylacetaldehyde was abstracted by remaining **3b** to generate a bismuth(V) enolate, which subsequently underwent side reactions to afford α-functionalized aldehydes.[44] The newly developed oxidants **3a**,**b** oxidize the alcohols more rapidly and under milder conditions than the previously reported organobismuth(V) oxidants.[18]

To estimate the relative reactivities of allylic, benzylic, and nonconjugated alcohols toward **3b**, intermolecular competitive oxidations were carried out using ethanol as a reference (Table 7). Both allylic and benzylic alcohols were oxidized much more rapidly than ethanol. Under the reaction conditions employed, the chemoselectivities observed for **3b** were better than those observed for the Dess–Martin periodinane (DMP).[45]

High chemoselectivity was also observed in the intramolecular competitive oxidation of 1-phenyl-1,4-butanediol (**14**) with **3b**, where 4-hydroxy-1-phenylbutan-1-one (**15**) and 4-oxo-4-phenylbutyraldehyde (**16**) were obtained in 81% and 7% yields, respectively, based on **3b** (eq 6). When DMP was used in place of **3b**, **15** and **16** were formed with low selectivity. These results show the usefulness of **3b** as a chemoselective oxidant.



(6)

	15	**16**
3b	81%	7%
DMP	47%	24%

On the basis of the results presented here, **3a**,**b** qualify as reliable additions to the existing oxidants for converting alcohols selectively to aldehydes or ketones.[46] Such oxidizing ability has not been observed for the phosphorus(V), arsenic(V), or antimony(V) oxo species of this type and is characteristic of bismuth(V).

Conclusions. We established a simple and efficient method for the preparation of triarylbismuthane oxides and compared their structures and reactivities with those of the phosphorus, arsenic, and antimony counterparts for the first time. X-ray structure analyses of tris(2-methoxyphenyl)bismuthane oxide and bis(2-methylphenyl)bismuthinic acid anhydride revealed that these bismuth(V)–oxo compounds exist in crystalline form as dimers. The observed results clearly show that the Bi=O bonds of their monomers are highly polarized as $Bi^+–O^-$ and aggregate to attain electronic stabilization. In sharp contrast to the lighter pnictogen counterparts, bismuthane oxides readily undergo thermal decomposition to afford triarylbismuthanes as the major products. More importantly, the bismuthane oxides convert primary and secondary alcohols to aldehydes and ketones, respectively, under mild conditions. The remarkably high oxidizing ability of triarylbismuthane oxides, specifically those bearing ortho substituents, contrasts well with the lighter pnictogen counterparts, which do not exhibit such oxidizing ability, and represents their potential utility in organic synthesis.

Experimental Section

General Considerations. All melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^1H NMR spectra were recorded on a JEOL FX-400 (400 MHz) or a JEOL AL300 (300 MHz) spectrometer using $CDCl_3$ as the solvent unless otherwise noted. Chemical shifts are reported as the relative value vs tetramethylsilane. $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL FX-400 (100 MHz) spectrometer with a complete proton decoupling mode. IR spectra were observed as KBr pellets on a Shimadzu FTIR-8100S or FTIR-8200A spectrophotometer. GCMS spectra were recorded on a Shimadzu QP5000 mass spectrometer. FABMS spectra were measured on a JEOL JMS-HS100 spectrometer using 3-nitrophenyl *n*-octyl ether as a matrix. GC was performed on a Shimadzu GC-8A fitted with a 5 Å molecular sieve packed column or a Shimadzu GC-14A fitted with a silica gel capillary column. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University. Column chromatography was performed on silica gel (Wakogel C200). Dichloromethane (CH_2Cl_2) was distilled from CaH_2 before use. Hexane, acetonitrile, and $CDCl_3$ were distilled from CaH_2 and stored over 4 Å molecular sieves. Benzene and toluene were distilled from sodium and stored over sodium metal. Triarylbismuth dichlorides **1a**–**e**[17b] were prepared from the corresponding triarylbismuthanes and sulfuryl chloride according to Barton's procedure.[47] Tris(2-methoxyphenyl)antimony dichloride (**4**) was prepared similarly.[17b] Triarylbismuth diacetates **2a**–**e** were prepared according to Finet's method.[48] Trapping agents such as 1,4-cyclohexadiene, 1,3-cyclooctadiene, *trans*-stilbene, and 9,10-dihydroanthracene were purified according to the standard procedures. 4-Bromobenzyl alcohol-*d* (**12**-*d*),[49]

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[43] The ^1H NMR spectrum of the reaction mixture exhibited the presence of small amounts of phenyl(2-methylphenyl)acetaldehyde and phenylbis(2-methylphenyl)acetaldehyde.

[44] Treatment of **3b** with phenylacetaldehyde gave a complex mixture including the α-arylated aldehydes.

[45] (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155–4156. (b) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277–7287.

[46] Larock, R. C. *Comprehensive Organic Transformations,* 2nd ed.; Wiley: New York, 1999; pp 1234–1249.

[47] Barton, D. H. R.; Bhatnagar, N. Y.; Finet, J.-P.; Motherwell, W. B. *Tetrahedron* **1986**, *42*, 3111–3122.

[48] Combes, S.; Finet, J.-P. *Synth. Commun.* **1996**, *26*, 4569–4575.

[49] Corey, E. J.; Link, J. O. *Tetrahedron Lett.* **1989**, *30*, 6275–6278. In the present study, **12**-*d* was prepared by the reduction of *p*-bromobenzaldehyde with $NaBD_4$.

4-bromobenzyl alcohol-d_2 (**12**-d_2),[50] 1-phenyl-1,4-butanediol,[51] 2,2′-dimethoxydiphenyl ether (**8a**),[52] and 2,2′-dimethyldiphenyl ether (**8b**)[53] were prepared according to the known procedures. Other reagents were used as commercially received.

Synthesis of Triarylbismuthane Oxides 3. General Procedure. Water (50 μL, 2.8 mmol) was added to a mixture of triarylbismuth dichloride **1** (0.50 mmol), KO-*t*-Bu (123 mg, 1.10 mmol), and CH_2Cl_2 (10 mL), and the resulting mixture was stirred for 2 h at 0 °C. The mixture was then passed quickly through a plastic filter (Nacalai, Cosmo Nicefilter S), and acetonitrile (1 mL) was added to the filtrate. The resulting solution was concentrated under reduced pressure at 0−10 °C to give **3** as a pale yellow or colorless solid. The ^1H NMR analysis of the solid showed that **3** was formed quantitatively in a high state of purity (>99%). Triarylbismuth diacetates **2a**−**e** also reacted with H_2O/KO-*t*-Bu to give **3** quantitatively. Compounds **3a**−**c**,**e** did not show definite melting points.

3a: ^1H NMR δ 3.84 (s, 18H), 7.13−7.19 (m, 12H), 7.43−7.47 (m, 6H), 8.02 (br-*d*, 6H); IR ν_{max} 1580, 1566, 1471, 1431, 1302, 1275, 1244, 1231, 1182, 1175, 1156, 1117, 1051, 1020, 937, 851, 789, 756, 748, 710, 638, 588, 574, 565, 534, 473, 436 cm^{-1}; FABMS *m/z* (%) 1831 (7), 1301 (14), 969 (63), 879 (8), 755 (24), 637 (100), 423 (32), 316 (20), 209 (28). Weak fragment ion peaks due to the tetramer (*m/z* 1831) and trimer (*m/z* 1301) were also detected. Due to the thermal and chemical instability of **3a**, we have not been successful in obtaining satisfactory analytical data of an accuracy within ±0.4%.

3b (n = 1): ^1H NMR δ 1.07 (s, ca. 2H, O*H*), 2.68 (s, 18H), 7.35−7.52 (m, 18H), 7.86 (d, 6H, J = 7.2 Hz); IR ν_{max} 1582, 1559, 1509, 1472, 1458, 1442, 1377, 1272, 1206, 1157, 1115, 1007, 920, 797, 739, 642, 548, 532, 471, 424 cm^{-1}; FABMS *m/z* 889. Anal. Calcd for $C_{42}H_{44}Bi_2O_3$: C, 49.71; H, 4.37. Found: C, 49.39; H, 4.49.

3c (n = 0): mp 96−105 °C dec; ^1H NMR δ 0.56 (s, ca. 2H, O*H*), 3.83 (s, 9H), 7.09 (d, 6H, J = 8.8 Hz), 8.19 (d, 6H, J = 8.8 Hz); $^{13}C\{^1H\}$ NMR δ 55.4, 116.0, 135.4, 144.2, 161.6; IR ν_{max} 1580, 1487, 1460, 1441, 1396, 1294, 1248, 1175, 1117, 1101, 1026, 997, 824, 785, 611, 584, 511, 475 cm^{-1}. Anal. Calcd for $C_{21}H_{23}BiO_5$: C, 44.69; H, 4.11. Found: C, 44.55; H, 3.90.

3d (n = 0): ^1H NMR δ 0.56 (s, ca. 2H, O*H*), 2.39 (s, 9H), 7.39 (d, 6H, J = 8.0 Hz), 8.14 (d, 6H, J = 8.0 Hz); $^{13}C\{^1H\}$ NMR δ 21.3, 131.4, 134.0, 141.4, 150.3; IR ν_{max} 1481, 1445, 1389, 1306, 1205, 1178, 1113, 1095, 1045, 1007, 844, 804, 694, 595, 475, 428 cm^{-1}; FABMS *m/z* (%) 1205 (14), 1023 (12), 997 (28), 889 (100), 707 (54), 499 (25), 391 (58). Anal. Calcd for $C_{21}H_{23}BiO_2$: C, 48.84; H, 4.49. Found: C, 48.84; H, 4.28.

3e (n = 0): ^1H NMR δ 0.65 (s, ca. 2H, O*H*), 7.47 (t, 3H, J = 7.6 Hz), 7.60 (t, 6H, J = 7.6 Hz), 8.29 (d, 6H, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR δ 130.9, 131.1, 134.2, 153.6; IR ν_{max} 1566, 1472, 1433, 1372, 1325, 1300, 1173, 1051, 1013, 993, 968, 912, 833, 737, 725, 689, 573, 527, 449, 432 cm^{-1}; FABMS *m/z* (%) 1275 (17), 1121 (15), 913 (12), 835 (32), 819 (100), 759 (28), 665 (48), 457 (20), 363 (20). The peak at δ 0.65 disappeared in the presence of D_2O. When allowed to stand in vacuo for 6 h, **3e** was converted to an amorphous substance, insoluble in most organic solvents. We have characterized this insoluble substance as a polymeric triphenylbismuthane oxide. Anal. Calcd for $C_{18}H_{15}BiO$: C, 47.38; H, 3.31. Found: C, 47.56; H, 3.35. The polymeric oxide was reversibly converted to the dihydroxide **3e** by treatment with an excess of water in CH_2Cl_2.

Synthesis of Tris(2-methoxyphenyl)stibane Oxide (5).[17b,20] This compound was prepared from tris(2-methoxyphenyl)antimony dichloride (**4**), H_2O, and KO-*t*-Bu according to a procedure similar to that described for the synthesis of **3**. After several hours in vacuo, **5** was obtained in an anhydrous, dimeric form. ^1H NMR: δ 3.24 (s, 18H), 6.94 (d, 6H, J = 8.0 Hz), 7.01 (t, 6H, J = 7.6 Hz), 7.48 (ddd, 6H, J = 8.0, 7.6, 1.5 Hz), 7.65 (dd, 6H, J = 7.6, 1.5 Hz). In the presence of a suitable amount of water, the hydrated species was observed together with the anhydride. ^1H NMR: δ 1.87 (s, ca. 1.5H), 3.78 (s, 9H), 6.70 (d, 3H, J = 8.0 Hz), 7.13 (t, 3H, J = 7.6 Hz), 7.45 (ddd, 3H, J = 8.0, 7.6, 1.5 Hz), 7.88 (dd, 3H, J = 7.6, 1.5 Hz).

Thermal Decomposition of 3. **Typical Procedure.** Compound **3** (0.3 mmol) was heated for 0.5−15 h in 10 mL of refluxing benzene. The insoluble substance that formed was removed by filtration. The formation of biphenyl **7**, diaryl ether **8**, and arene **9** was confirmed by GC and GCMS spectrometry. The filtrate was concentrated under reduced pressure to leave an oily residue, which was chromatographed on a silica gel column (hexane/EtOAc = 50/1) to give bismuthane **6**. The eluted compounds **7** and **8** were characterized by comparison with authentic specimens. During the thermal decomposition of **3a**, both the vapor phase and the liquid phase of the reaction mixture were analyzed at several intervals by GC fitted with a 5 Å molecular sieves column, but O_2 gas could not be detected in all cases examined. When the thermolysis of **3a** was carried out in the presence of an excess (>5 equiv) of a trapping agent or a hydrogen source such as 1,4-cyclohexadiene, 1,3-cyclooctadiene, *trans*-stilbene, or 9,10-dihydroanthracene, **6a** was obtained and the trapped products were not detected by GCMS or ^1H NMR. In the competition experiments, a 1/1 (v/v) benzene/toluene or benzene/anisole mixture was used as the solvent.

Reaction of 3a with Ph_3M (M = P, As, Sb). Ph_3M (M = P, As, Sb; 0.5 mmol) was added to a CH_2Cl_2 solution (10 mL) of **3a** (273 mg, 0.25 mmol) at room temperature. After 30 min, the reaction was concentrated under reduced pressure and examined by ^1H NMR spectroscopy. Bismuthane **6a** and the oxide $Ph_3M{=}O$ were formed quantitatively. The ^1H NMR monitoring of the same reaction in $CDCl_3$ did not show any intermediates.

Oxidation of Ethanol and 2-Propanol: NMR Experiments. Compounds **3a**,**b** (1.1−1.2 equiv) were added in one portion to a $CDCl_3$ solution of alcohol at room temperature. After 5 min, the reaction mixture was measured by ^1H NMR (9,10-dihydroanthracene as an internal standard). In these oxidations, anisole (from **3a**) or toluene (from **3b**) was formed quantitatively with $Ar_2BiOBiAr_2$ (**11a**,**b**). Compounds **11a**,**b** were characterized by comparison with authentic samples independently prepared from Ar_2BiOTf and aqueous NaOH. Compounds **11a**,**b** gradually underwent disproportionation in solution to give triarylbismuthanes **6a**,**b** and insoluble solids.

Bis[bis(2-methoxyphenyl)bismuth] Oxide (11a).[17b] ^1H NMR δ 3.63 (s, 12H), 7.01 (d, 4H, J = 8.0 Hz), 7.12−7.16 (m, 4H), 7.27−7.32 (m, 4H), 8.15 (dd, 4H, J = 7.0, 1.4 Hz).

Bis[bis(2-methylphenyl)bismuth] Oxide (11b).[17b] ^1H NMR δ 2.15 (s, 12H), 7.22−7.32 (m, 8H), 7.38−7.42 (m, 4H), 8.20 (d, 4H, J = 7.2 Hz). IR ν_{max} 1578, 1560, 1458, 1447, 1375, 1267, 1200, 1155, 1113, 1043, 1028, 752, 746, 617, 588 cm^{-1}.

Oxidation of Alcohols: General Procedure. Alcohol (0.45 mmol) was added to a CH_2Cl_2 solution (10 mL) of **3** (0.5 mmol) at room temperature. Thin-layer chromatography indicated that the reaction was complete within a few minutes at room temperature. After 5−30 min, the reaction mixture was concentrated under reduced pressure to leave an oily residue, which was then chromatographed on a silica gel column (hexane/EtOAc = 20/1) to give a carbonyl product.

Competitive Oxidation of Alcohols. A $CDCl_3$ solution (0.5 mL) containing **12** (0.06 mmol) and **12**-d_2 (0.06 mmol) was added to a solution of **3b**,**d** (0.02 mmol) in $CDCl_3$ (0.5 mL) at 23 ± 1 °C. After a few minutes, the resulting mixture was measured by ^1H NMR. The intramolecular competition experiment was carried out using **12**-*d* (0.02 mmol), **3b**,**d** (0.02 mmol), and $CDCl_3$ (1.0 mL). Both intermolecular and intra-

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(50) Pollack, S. K.; Raine, B. C.; Hehre, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 6308−6313.

(51) Klement, I.; Lütjens, H.; Knochel, P. *Tetrahedron* **1997**, *53*, 9135−9144.

(52) Kime, D. E.; Norymberski, J. K. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1048−1052.

(53) Barton, D. H. R.; Finet, J.-P.; Khamsi, J.; Pichon, C. *Tetrahedron Lett.* **1986**, *27*, 3619−3622.

molecular H/D kinetic isotope effects (k_H/k_D) were estimated on the basis of the integral ratios of **13** and **13**-*d* formed. The same reactions were carried out three times, and the average values are shown in eqs 4 and 5.

X-ray Crystallographic Analyses of 3a, 5, and 10. Single crystals of compounds **3a** and **5** were grown from CH_2Cl_2/hexane at 4 °C. Single crystals of **10** were obtained from the reaction mixture of thermolysis of **3b**. All attempts to grow single crystals of **3b**−**e** were unsuccessful. Data were recorded on a Rigaku RAXIS-RAPID imaging-plate diffractometer (for **3a**), a Rigaku AFC7S diffractometer (for **5**), or a Rigaku RAXIS-IV imaging-plate diffractometer (for **10**), with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. The structures were solved by heavy-atom Patterson methods (for **3a** and **5**)[54] or direct methods (for **10**)[55] and were expanded using Fourier techniques.[56] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[57] Anomalous dispersion effects were included in F_c;[58] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[59] The values for the mass-attenuation coefficients are those of Creagh and Hubbel.[60] All calculations were performed using a teXsan[61] crystallographic software package from Molecular Structure Corp. CIF files are provided in the Supporting Information of the previous communication[19] (for **3a**) and the present paper (for **5** and **10**).

Density Functional Theory (DFT) Calculations on the Structures of Monomers and Dimers of $Ph_3M{=}O$ (M = P, As, Sb, Bi). The structures and relative energies between $Ph_3M{=}O$ (M = P, As, Sb, Bi) and their dimers were calculated using DFT. The basis set used was LanL2DZ, which uses valence double-ζ functions for the first-row elements (D95V)[62] and an effective core potential for inner electrons and double-ζ quality valence functions for the heavier elements.[63] For pnictogens and oxygen, this basis set was augmented with a d polarization function (the exponents of d functions were 0.961 (O), 0.364 (P), 0.286 (As), 0.207 (Sb), and 0.192 (Bi)).[64] The functionals of DFT were the Becke 1988 exchange and Lee−Yang−Parr correlation functionals (B3LYP).[65,66] All the calculations were carried out using the Gaussian 03 suite of programs.[67]

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Supporting Information Available: CIF files giving X-ray crystallographic data for **5** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(54) PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Cranda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1992.

(55) SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(56) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

(57) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(58) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(59) Creagh, D. C.; McAuley, W. J. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Boston, 1992; Vol. C, Table 4.2.6.8, pp 219−222.

(60) Creagh, D. C.; Hubbell, J. H. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Boston, 1992; Vol. C, Table 4.2.4.3, pp 200−206.

(61) teXsan: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985 and 1999.

(62) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 3, pp 1−27.

(63) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−98.

(64) Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. *J. Phys. Chem. A* **2001**, *105*, 8111−8116.

(65) Becke, A. D. *J. Chem. Phys.* **1988**, *98*, 5648−5652.

(66) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(67) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.3; Gaussian, Inc.: Pittsburgh, PA, 2003.