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Dimeric Triarylbismuthane Oxide: A Novel Efficient Oxidant for the Conversion of Alcohols to Carbonyl Compounds

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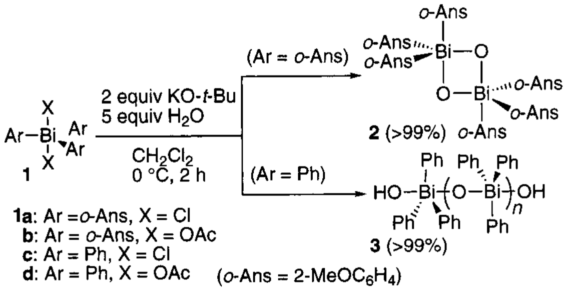
The oxidation of organic compounds by metal−oxo or heteroatom−oxo species has received much attention because of its importance in organic synthesis, biological systems, and industrial processes.[1] Such oxidants exist in monomeric, dimeric, or oligomeric forms, and their oxidizing abilities differ considerably, depending on the central elements as well as on the attached ligands. Triorganylbismuthane oxides ($R_3Bi{=}O$), formally bearing a Bi(V)═O bond, are attractive oxidants due to the potent oxidizing ability of the pentavalent bismuth[2] and also because of the low toxicity of bismuth.[3] Despite this interest, however, the chemistry of bismuthane oxides has been much less explored than that of lighter pnictogen counterparts, probably due to the limited access to this class of compounds.[4] All bismuthane oxides prepared thus far have been polymeric substances in the solid state,[5,6] and there are no well-characterized examples. We report herein the first synthesis of a dimeric bismuthane oxide that was structurally characterized by X-ray crystallography. In marked contrast to the lighter pnictogen counterparts, this bismuthane oxide readily oxidizes alcohols to aldehydes or ketones with high efficiency under mild conditions.

Treatment of tris(2-methoxyphenyl)bismuth dichloride[7] (**1a**) or diacetate[8] (**1b**) with 2 equiv of KO-*t*-Bu in the presence of 5 equiv of water in CH_2Cl_2 at 0 °C afforded tris(2-methoxyphenyl)bismuthane oxide (**2**) as a pale yellow solid (Scheme 1).[9] The present method is simple and efficient for obtaining **2**, which is otherwise difficult to prepare.[10] Compound **2** is soluble in $CHCl_3$ and CH_2Cl_2 but insoluble in acetonitrile, diethyl ether, and benzene. Its structure was characterized by NMR, IR, and FAB mass spectrometry as well as by a chemical transformation. The FAB mass spectrum of **2** showed a strong fragment ion peak at *m*/*z* 969, attributable to a cation with a dimeric framework ($Ar_5Bi_2O^+$). When treated with 0.5 equiv of acetic anhydride, **2** was converted to μ-oxobis[tris(2-methoxyphenyl)bismuth] diacetate in a ca. 80% yield. These findings suggest that bismuthane oxide **2** would exist for the most part in dimeric form. When triphenylbismuth dichloride (**1c**) or diacetate (**1d**) was used instead of **1a**, triphenylbismuth dihydroxide[4b] or its μ-oxo-bridged dimer (**3**, $n = 0$ or 1) was formed as the initial product. As in a previous finding,[4b] **3** was dehydrated in vacuo to give an amorphous powder, insoluble in most organic solvents. On the basis of the spectral and analytical data, we have characterized this powder as polymeric triphenylbismuthane oxide.[11] Thus, the *o*-methoxy groups in **2** are likely to prevent both hydration and polymerization of the Bi(V)═O bond.

Scheme 1



The structure of **2** was further determined by X-ray crystallography.[12] As shown in Figure 1, oxide **2** exists, at least in the solid state, in a dimeric form with a four-membered Bi_2O_2 ring. Each bismuth center adopts a distorted trigonal bipyramidal geometry with two *ipso* carbon and one oxygen atom at the equatorial sites and one *ipso* carbon and one oxygen at the apical sites. The $Bi−O_{ap}$ bond is longer than the $Bi−O_{eq}$ bond over 0.3 Å, and the $Bi−O_{ap}/Bi−O_{eq}$ bond length ratio (1.147) is slightly larger than the $Sb−O_{ap}/Sb−O_{eq}$ ratio (1.074−1.078) observed for an analogous triphenylstibane oxide dimer.[13] The $Bi−O_{bridge}$ single bond lengths of known μ-oxo-bridged dinuclear organobismuth compounds range from 2.02(3) to 2.12(3) Å.[14,15] Thus, the $Bi−O_{eq}$ bond length of 2.013(5) Å is at the shorter end of this range and would be best represented as a Bi−O single bond. It is likely that two molecules of the oxide monomer with a polarized $Bi^+−O^-$ bond aggregate to attain electrostatic stabilization.

Bismuthane oxide **2** was found to possess remarkable oxidizing ability (Scheme 2). Primary and secondary alcohols are oxidized by **2** (1.0−1.2 equiv) *within 10 min* at room temperature to aldehydes and ketones, respectively, in excellent yields (Table

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[6] Oxygenation of Ar_3Bi (Ar = Ph, *p*-Tol) with iodosylbenzene: Suzuki, H.; Ikegami, T.; Matano, Y. *Tetrahedron Lett.* **1994**, *35*, 8197−8200.

[7] Matano, Y.; Nomura, H.; Shiro, M.; Suzuki, H. *Organometallics* **1999**, *18*, 2580−2582.

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

[9] For details, see Supporting Information.

[10] An attempt to prepare **2** 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.

[11] This insoluble powder was reversibly converted to **3** on treatment with water in CH_2Cl_2.

[12] Space group $P\bar{1}$, $a = 10.4018(6)$ Å, $b = 12.1622(8)$ Å, $c = 9.0988(6)$ Å, $\alpha = 108.935(3)°$, $\beta = 104.073(3)°$, $\gamma = 104.779(2)°$, $V = 983.7(1)$ Å^3, $Z = 1$, $D_c = 1.845$ g cm^{-3}, $T = 23$ °C.; 9056 collected and 4446 observed reflections ($I > -10.00\sigma(I)$) refined to $R = 0.072$, $R_1 = 0.044$, GOF = 1.07.

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[14] Bi(V) compounds: (a) $Ph_3BiOBiPh_3(ClO_4)_2$ [2.065(15), 2.062(14) Å]: March, F. C.; Ferguson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1291−1294. (b) $Ph_3BiOBiPh_3(OTf)_2$ [2.091(8), 2.039(8) Å]: Matano, Y.; Azuma, N.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1739−1747. (c) $Ar_3BiOBiAr_3Cl_2$; Ar = 4-$Me_2NC_6H_4$, [2.12(3), 2.02(3) Å]: Hassan, A.; Breeze, S. R.; Courtenary, S.; Deslippe, C.; Wang, S. *Organometallics* **1996**, *15*, 5613−5621.

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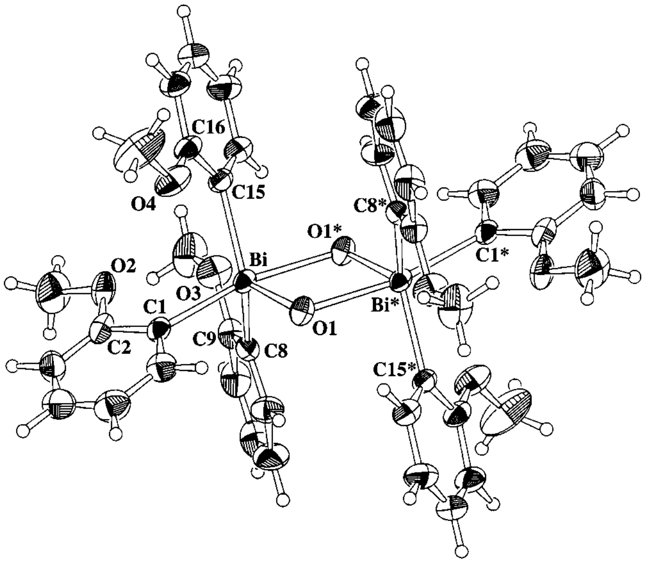

Figure 1. Bi−O(1), 2.013(5); Bi−O(1)*, 2.309(6); Bi−C(1), 2.273(10); Bi−C(8), 2.194(9); Bi−C(15), 2.210(8); Bi−O(1)−Bi*, 102.0(2); O(1)−Bi−O(1)*, 78.0(2); O(1)−Bi−C(1), 92.3(3); O(1)−Bi−C(8), 109.9(3); O(1)−Bi−C(15), 121.3(3); O(1)*−Bi−C(1), 167.9(2); O(1)*−Bi−C(8), 84.2(3); O(1)*−Bi−C(15), 84.4(3); C(1)−Bi−C(8), 92.4(3); C(1)−Bi−C(15), 107.1(3); C(8)−Bi−C(15), 123.5(3).

Scheme 2

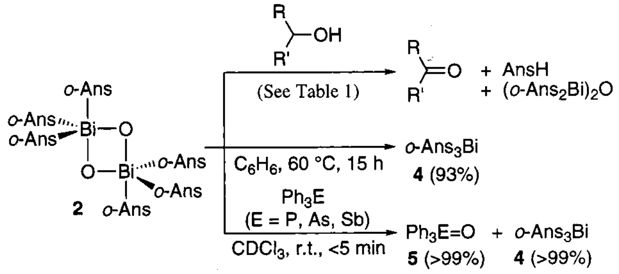

Table 1. Oxidation of Alcohols by Organobismuth(V) Compounds[a]

entry	substrate	Bi(V) compound	reaction conditions	yield[b] (%)
1	*n*-C$_{10}$H$_{21}$OH	**2**	rt, 5 min	96[c]
2	citronellol	**2**	rt, 10 min	90[d]
3	4-PhC$_6$H$_4$CH$_2$OH	**2**	rt, 10 min	89
4	4-O$_2$NC$_6$H$_4$CH$_2$OH	**2**	rt, 10 min	87
5[e]	4-O$_2$NC$_6$H$_4$CH$_2$OH	(Ph$_3$BiCl)$_2$O[f]	60 °C, 1 h	87
6	PhCH═CHCH$_2$OH	**2**	rt, 5 min	>99[c]
7[e]	PhCH═CHCH$_2$OH	(Ph$_3$BiCl)$_2$O[g]	21 °C, 15 h	83
8[h]	PhCH═CHCH$_2$OH	(*p*-Tol$_3$BiO)$_n$	rt, 2 h	80
9	Me$_2$CHOH	**2**	rt, 5 min	>99[c]
10[i]	Me$_2$CHOH	Ph$_3$Bi(OAc)$_2$[g]	60 °C, 26.5 h	98
11	PhCH(OH)Me	**2**	rt, 5 min	>99[c]
12	*trans*−4-*tert*-butylcyclohexanol	**2**	rt, 5 min	92[c]

[a] Substrates were treated with Bi(V) compound in CDCl$_3$ (CHCl$_3$) or CH$_2$Cl$_2$. [b] Isolated yield unless otherwise indicated. [c] NMR yield. [d] Citronellal was obtained. [e] Data from ref 17b. [f] NaHCO$_3$ was added. [g] K$_2$CO$_3$ was added. [h] Data from ref 6. Toluene was used as a solvent. [i] Data from ref 17c.

1). During this oxidation process, anisole and a Bi(III) compound are formed as the byproducts.[16] These findings indicate that the α-hydrogen of the alcohol is abstracted by the anisyl group attached to the Bi(V) center. Triarylbismuth(V) compounds of the type Ar$_3$BiX$_2$,[17] as well as a polymeric triarylbismuthane oxide,[6] have been reported to oxidize alcohols to carbonyl compounds. However, compound **2** oxidizes the substrates more rapidly and under milder conditions (entries 4 vs 5; 6 vs 7, 8; 9 vs 10). The remarkable efficiency of this oxidation system may reflect the highly basic character of the oxo group of **2**. Under the present reaction conditions, the aldehydes produced were not oxidized further to carboxylic acids, indicating the potential utility of **2** as a selective oxidant. This selectivity is in contrast to that of iodosylbenzene, which oxidizes primary alcohols, in the presence of water, to carboxylic acids.[18] On the basis of the results obtained here, bismuthane oxide **2** qualifies as a reliable addition to the existing methods[19] for oxidizing alcohols to aldehydes or ketones under neutral conditions. Such oxidizing ability has not been observed for the phosphorus(V), arsenic(V), and antimony(V) oxo-species of this type.

In contrast to the lighter pnictogen counterparts, bismuthane oxide **2** is thermally unstable. When heated in benzene for 15 h at 60 °C, **2** decomposed to produce tris(2-methoxyphenyl)bismuthane (**4**) in a 93% yield.[20] Although the mechanism is not clear at present, this mode of decomposition is of interest in that an active oxygen species might be generated via elimination of **4**.[21] Compound **2** transferred the oxo group to triphenylphosphane, triphenylarsane, and triphenylstibane to give the corresponding pnictogen(V) oxides **5**, with a quantitative recovery of bismuthane **4**. The oxygen transfer was complete within a few minutes, suggesting that **2** is thermodynamically much less stable than **5**.

In summary, we have synthesized and characterized for the first time a dimeric bismuthane oxide. The observed remarkable oxidizing ability demonstrates the high utility of the bismuthane oxide in oxidation reactions. Further studies of the use of triarylbismuthane oxide for organic synthesis are currently in progress.

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Supporting Information Available: Experimental details on the synthesis, the X-ray crystallographic analysis, and the reactions of **2** (PDF). An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) We tentatively assigned the Bi(III) product as (*o*-Ans$_2$Bi)$_2$O on the basis of the ^{1}H NMR spectrum. This species gradually disproportionates to give **4** and an insoluble substance.

(17) Synthetic as well as mechanistic studies on the oxidation of alcohols by organobismuth(V) compounds have been reported by Barton et al. and by Dodonov et al.: (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) Barton, D. H. R.; Kitchin, J. P.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1978**, 1099−1100. (c) Dodonov, V. A.; Gushchin, A. V.; Brilkina, T. G. *J. Gen. Chem. USSR* **1985**, *55*, 63−68 (*Zh. Obsh. Khim.* **1985**, *55*, 73−80) and references therein.

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

(19) Larock, R. C. *Comprehensive Organic Transformations*; Wiley: New York, 1999; pp 1234−1249.

(20) Compound **2** gradually decomposed in a refrigerator (at 4 °C).

(21) When **2** was allowed to stand in excess 1,1-diphenylethene or α-methylstyrene, the olefinic double bond was cleaved to afford benzophenone or acetophenone in a 22−36% yield.