Pergamon

Tetrahedron Letters, Vol. 35, No. 44, pp. 8197-8200, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01745-X

Ultrasonic Reaction of Triarylbismuthines and Triarylstibines with Iodosylbenzene. Mild Oxidizing Ability of the Organobismuth Oxide Function for Organic Substrates.

Hitomi Suzuki,* Tohru Ikegami and Yoshihiro Matano

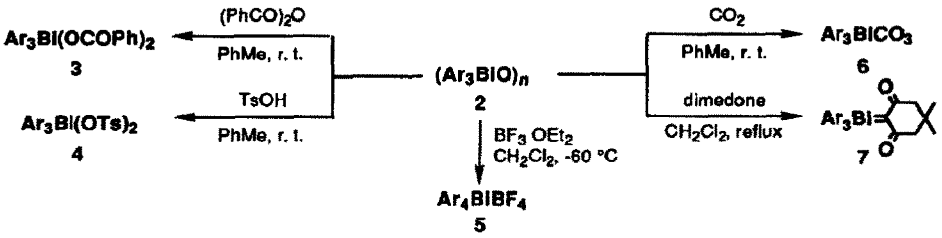
Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Abstract: Reaction of triarylbismuthines **1** with iodosylbenzene in dichloromethane under ultrasonic irradiation leads to the generation of triarylbismuthine oxides **2** as a bright yellow solution, in which activated alcohols are easily oxidized to carbonyl compounds, triphenylphosphine is converted into oxide and hydrazobenzene is rapidly dehydrogenated to azobenzene. Triphenylstibine **8** is similarly oxidized to give stibine oxide **9**, which lacks the corresponding oxidizing ability.

In contrast to extensive works on lighter organopnictogen oxides, little attention has hitherto been paid to the chemistry of organobismuth oxides. The first preparation of this class of compounds was claimed by Goel *et al.* in 1972,[1] who had carried out the metathesis reaction between triphenylbismuth dichloride and silver(I) oxide in benzene-water to obtain triphenylbismuthine oxide **2a** as a white polymeric powder melting at 155 °C.[2] Attempts to oxidize triarylbismuthines **1** direct to the corresponding oxides **2** with dinitrogen trioxide,[4] potassium permanganate,[5] hydrogen peroxide[6] and selenium dioxide[7] were all unsuccessful probably because of the instability of compound **2** as well as weakness of the bismuth-carbon bond. Oxidation of bismuthines **1** with ozone at low temperatures resulted in the unexpected formation of triarylbismuth diformates,[8] although this method has proven itself to be useful for converting lighter organopnictogens to the corresponding oxides.[9] We report herein a novel method for the *in situ* generation of *soluble* triarylbismuthine oxides **2** by the direct oxidation of triarylbismuthines **1** with iodosylbenzene under ultrasonic irradiation.[10] Also reported are our preliminary results on the reaction of bismuthine oxides **2** with some organic substrates. In marked contrast to the analogous oxides derived from lower pnictogen elements, which are devoid of the oxidizing ability for organic compounds, bismuthine oxides **2** have been found to oxidize activated alcohols to carbonyl compounds, convert triphenylphosphine to oxide, dehydrogenate hydrazobenzene to azobenzene, and cleave thioacetals to aldehydes.

$$\underset{\mathbf{1}}{Ar_3Bi} + PhIO \xrightarrow[CH_2Cl_2,\ ))),\ 35\ ^\circ C]{} \underset{\mathbf{2}}{(Ar_3BiO)_n} \qquad \begin{matrix} \mathbf{a}: Ar = C_6H_5 \\ \mathbf{b}: Ar = 4\text{-}MeC_6H_4 \end{matrix}$$

The representative procedure for the generation of *soluble* tris(4-methylphenyl)bismuthine oxide **2b** is as follows; tris(4-methylphenyl)bismuthine **1b** (482 mg, 1.0 mmol) was added to a suspension of freshly prepared iodosylbenzene (264 mg, 1.2 mmol) in dry dichloromethane (30 cm^3) and the resulting mixture was sonicated at 35 °C under argon on a commercial ultrasonic washing machine until bismuthine **1b** was completely consumed (checked by TLC).[11] After 2~3 h the chalky suspension turned into a bright yellow solution, which was quickly filtered through a Celite bed. When exposed to breath or air, this bright yellow solution gradually lost its characteristic colour, forming triarylbismuth carbonate **6b** as a powdery precipitate. Careful removal of the solvent together with iodobenzene under high vacuum left a glassy residue, which was soluble in benzene, acetone, tetrahydrofuran and dichloromethane, but insoluble in hexane. When scratched by a spatula in hexane, the residue was gradually transformed into an intractable powder, which, however, on stirring for 3 days with a half in weight of triphenylphosphine in benzene at ambient temperature, produced compound **1b** and phosphine oxide in 57 and 65 % yields, respectively, together with unchanged phosphine in 35 % yield, suggesting the polymeric composition largely consisted of a -Bi(Ar)$_3$-O- unit. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of compound **2b** at 25 °C exhibited a methyl signal at δ 2.38 and two broad signals due to aromatic protons at δ 7.4 and 8.2; the latters turned into a pair of doublets (δ 7.39 and 8.14; J = 7.6 Hz) at -75 °C. By the addition of acetic anhydride, the original NMR signals were completely replaced by those of tris(4-methylphenyl)bismuth diacetate. Toluene, benzene and dichloromethane were the solvents of choice; when the sonochemical oxidation reaction of bismuthine **1b** was carried out in chloroform or ethyl acetate, tris(4-methylphenyl)bismuth dichloride and diacetate were obtained as the respective side products.

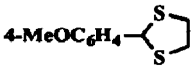


$$\underset{\mathbf{8}}{Ph_3Sb} + PhIO \xrightarrow[CH_2Cl_2,\ ))),\ r.t.]{} \underset{\mathbf{9}}{(Ph_3SbO)_2} \xleftarrow[xylene,\ 6\ d]{\Delta} \underset{\mathbf{10}}{Ph_4SbOMe}$$

Treatment of bismuthine oxide **2a** with benzoic anhydride or *p*-toluenesulfonic acid monohydrate in toluene afforded triphenylbismuth dibenzoate **3a** and bis(*p*-toluenesulfonate) **4a**, respectively, in 66 and 70 % isolated yields, while the action of boron trifluoride etherate on compound **2b** in dichloromethane resulted in the formation of tetraarylbismuthonium tetrafluoroborate **5b** in 24 % yield.[12] An attempt to isolate the presumed oxide **2a** by diluting the bright yellow solution with hexane under air led to a pale yellow precipitate, elemental analysis of which was inconsistent with the theoretical value for compound **2a**.[13] The reaction of this insoluble solid with 5,5-dimethylcyclohexane-1,3-dione (dimedone) in dichloromethane under reflux for 2 h led to the formation of a known bismuthonium ylide **7a** in 55 % yield.[15, 16]

The present sonochemical oxidation procedure was extended to the convenient preparation of triarylstibine oxides; a mixture of triphenylstibine **8** (353 mg, 1.0 mmol), iodosylbenzene (220 mg, 1.0 mmol) and dry dichloromethane (20 cm^3) was sonicated at ambient temperature for 1 h to give the expected stibine oxide **9**. Usual workup followed by recrystallization from hexane-dichloromethane (3:1; 20 cm^3) afforded compound **9** as colourless crystals (310 mg; 84 %), m.p. 219-221 °C (lit.[17] 220-222 °C). Crystalline stibine oxide **9** has previously been prepared by the thermal decomposition of methoxytetraphenylantimony **10**; heating of this compound at 60~70 °C in xylene for 6 days gave the oxide **9** in 31 % yield.[17] Direct oxidation of stibine **8** with hydrogen peroxide produced polymeric stibine oxide as an amorphous solid.[17] Interestingly, a

Table 1 Oxidation of selected organic compounds with bismuthine oxide **2b**[a]

Compound	Reaction time / h	Product	Yield / %[b]
$PhCH(OH)Me$	2	$PhCOMe$	86
$PhCH{=}CHCH_2OH$	2	$PhCH{=}CHCHO$	80
$4\text{-}MeOC_6H_4CH_2OH$	2	$4\text{-}MeOC_6H_4CHO$	100
$PhCOCH(OH)Ph$	2	$PhCOCOPh$	95
$Ph_2C(OH)C(OH)Ph_2$	2	$PhCOPh$	75
$PhNHNHPh$	1	$PhN{=}NPh$	52
Ph_3P	2	$Ph_3P{=}O$	100
	6	$4\text{-}MeOC_6H_4CHO$	33[c]

[a] All reactions were carried out at ambient temperature under argon, using a mixture of the given substrate (0.8 mmol), bismuthine oxide **2b** (1.0 mmol) and toluene (40 cm^3).
[b] Yields refer to the isolated compounds and were not optimized. The other product was unchanged starting material. [c] Boron trifluoride etherate (1.0 mmol) was added, in the absence of which no aldehyde was obtained.

similar reaction of tris(2, 4, 6-trimethylphenyl)stibine with iodosylbenzene led to the known stibine dihydroxide.[18] In contrast to triphenylphosphine oxide and triphenylarsine oxide which occur in monomeric form, the crystalline form of compound 9 has been shown by X-ray analysis to exist in a dimeric state.[17]

The *soluble* triarylbismuthine oxides 2 proved themselves to be a mild oxidizing agent for some organic compounds under neutral conditions (Table 1). They easily converted secondary alcohols to ketones, allylic and benzylic alcohols to aldehydes, benzoin to benzil, and benzopinacol to benzophenone. Hydrazobenzene was rapidly dehydrogenated to azobenzene, and triphenylphosphine was oxidized to phosphine oxide. Organic sulfides such as thioanisole and methyl *n*-octyl sulfide remained intact even after stirring for 6 days at ambient temperature. In the presence of an equimolar boron trifluoride etherate, 2-(4-methoxyphenyl)-1,3-dithiolane was cleaved to form 4-methoxybenzaldehyde. In contrast, triphenylstibine oxide 9 has been found to exhibit only a limited ability as oxidant for organic substrates; stirring of an equimolar mixture of stibine oxide 9 and a given substrate in dichloromethane at ambient temperature under argon resulted in most cases in the recovery of starting materials. Exceptions are benzoin and benzopinacol, which were oxidized to benzil and benzophenone, respectively. These results clearly show the different chemical nature of the "Bi=O" bond compared with the other pnictogen-oxygen double bonds P=O, As=O and Sb=O.

Attempts to find out a stable organobismuthine oxide and isolate it in a crystalline form appropriate for X-ray analysis are under way, and the results will be published elsewhere in due course.

We acknowledge financial support of this work by a Grant-in-Aid for Special Project Research No. 05236101 from the Ministry of Education, Science and Culture of Japan.

References and Notes

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10. For a survey of synthetic uses of ultrasonic waves, see C. Einhorn, J. Einhorn and J. L. Luche, *Synthesis*, 1989, 787.
11. For convenience of ^{1}H NMR monitoring, bismuthine **1b** was employed as substrate.
12. Compound **5b**: Colourless crystals, m.p. 205~207 °C; δ_H (CDCl$_3$) 2.44 (s, 12H), 7.49 (d, 8H, J_{AB} = 8.0 Hz) and 7.63 (d, 8H, J_{AB} = 8.0 Hz); ν_{max}(KBr)/cm^{-1} 1487, 1446, 1391, 1312, 1281, 1209, 1188, 1121, 1061, 1005, 799, 519 and 475; m/z (FAB) 573 (^{p}Tol$_4$Bi), 391 (^{p}Tol$_2$Bi) and 300 (^{p}TolBi). Found: C, 50.73; H, 4.15. $C_{28}H_{28}BBiF_4$ requires C, 50.93; H, 4.27 %.
13. This precipitate decomposed above 150 °C without showing a definite melting range, and was analyzed for C, 31.1 and H, 2.3 %. $(C_6H_5)_3BiO$ requires C, 47.4; H, 3.3 %. A similar degradation product was obtained from the autooxidation of trialkylbismuthines.[14] Soluble bismuthine oxide **2a** is likely to exist in oligomeric form, but its molecular weight determination was not successful because of its facile conversion into an insoluble substance.
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(*Received in Japan* 24 *May* 1994; *accepted* 20 *August* 1994)