

## **Oxidation of Organic Substrates by Pentavalent Organobismuth Reagents**

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**Summary** Five-valent bismuth reagents, especially tri-phenylbismuth carbonate, show remarkable functional group selectivity, permitting alcohol oxidation even in the presence of benzenethiol, indole, and pyrrole.

WE have recently shown that  $\mu$ -oxo-bis(chlorotriphenylbismuth) is a very effective reagent for the oxidation of the hydroxy-group, especially in allylic and benzylic alcohols.<sup>1</sup> In order to exploit the oxidation potential inherent in the bismuth(V)-bismuth(III) change, we have made a more detailed investigation of readily prepared organobismuth derivatives.<sup>2</sup>

aniline, dimethylaniline, pyrrolidine, and 3-pyrrolidinocholesta-2,5-diene is noteworthy. The virtually quantitative formation of diphenyldiazomethane provides a useful alternative to established methods for the oxidation of hydrazones. It was of mechanistic interest to note that the glycol cleavage of *cis*-cyclohexane-1,2-diol was appreciably faster than that of the *trans*-isomer.

TABLE 1  
Functional group oxidation by triphenylbismuth carbonate<sup>a</sup>

Substrate	Temp./°C	Time/h	Product	Yield/%
(-)-Carveol	40	1.5	(-)-Carvone	84
Cholest-4-en-3-ol	Room temp.	18	Cholest-4-en-3-one	97
Geraniol	40	2.5	Geranial <sup>b</sup>	95
<i>cis</i> -Cyclohexane-1,2-diol	40	2	Hexane-1,6-dial <sup>b</sup>	100
<i>meso</i> -Hydrobenzoin	"	1.5	Benzaldehyde <sup>b</sup>	97
1,2:5,6-Di- <i>O</i> -isopropylidene-D-mannitol	"	2	2,3- <i>O</i> -Isopropylidene-glyceraldehyde <sup>b</sup>	89
Ph <sub>3</sub> C=NNH <sub>2</sub>	Room temp	5	Ph <sub>3</sub> CN <sub>2</sub>	97
PhNHNHPh	"	1.5	PhN=NPh	90
PhNHNHCPH <sub>3</sub>	"	4	PhN=NCPH <sub>3</sub>	95
5 $\alpha$ -Cholestan-3-one oxime	"	15	5 $\alpha$ -Cholestan-3-one	60
PhSH	"	18	PhSSPh	70
PhSH (1 equiv.) + Cholest-4-en-3 $\beta$ -ol (1 equiv.)	"	24	Cholest-4-en-3-one	76
Pyrrolidine (1 equiv.) + (-)carveol (1 equiv.)	"	18	(-)-Carvone	87
Indole (1 equiv.) + (-)carveol (1 equiv.)	"	24	(-)-Carvone	80

<sup>a</sup> All reactions were carried out in dichloromethane as solvent using 1.1--2 equiv. of triphenylbismuth carbonate. The following compounds were not oxidized by the reagent (compound, temp./°C, time/h): benzophenone phenylhydrazone, 40, 24; benzophenone 2,4-dinitrophenylhydrazone, 40, 24; benzophenone semicarbazone, room temp., 72; 5 $\alpha$ -cholestan-3-one tosylhydrazone, room temp., 24; diphenyl disulphide, room temp., 24; diphenyl diselenide, room temp., 24; tri-*O*-acetyl glucal, room temp., 24; aniline, room temp., 18; 3-pyrrolidinocholesta-3,5-diene, room temp., 24; *NN*-dimethylaniline, room temp., 24. <sup>b</sup> Isolated as the 2,4-dinitrophenylhydrazone derivative.

By allowing a 1:1 mixture of Ar<sup>1</sup><sub>3</sub>BiCl<sub>2</sub> and Ar<sup>2</sup><sub>3</sub>BiCl<sub>2</sub> to compete for a deficiency of allylic alcohol and determining the resultant ratio of isolated triaryl bismuths it was possible to construct a series of relative rate values which demonstrated, as expected, that electron-withdrawing substituents on the aromatic ring led to enhanced rates of reaction (*p*-tolyl:phenyl:*p*-chlorophenyl = *ca.* 1:1.5:6).

We also studied the effect of the leaving group, X, in the pentavalent derivatives Ph<sub>3</sub>BiX<sub>2</sub>. Under our standard conditions using carbonate or hydrogen carbonate anion as the 'base,' the rate of the reaction was unaltered in the series, X = Cl, Br, ONO<sub>2</sub>. Moreover, replacement of carbonate or hydrogen carbonate by pyridine or collidine led to loss of oxidizing power. We conclude that a common reagent, triaryl bismuth carbonate, was the active oxidant.

An analytically pure sample of triphenylbismuth carbonate<sup>3</sup> (Ph<sub>3</sub>BiCO<sub>3</sub>) was accordingly prepared (98%) by reaction of the pentavalent dichloride with potassium carbonate in aqueous acetone. It is a very useful heterogeneous oxidant for a variety of functional groups (Table 1).

Examination of the data in Table 1 serves to highlight the exceptional selectivity of the reagent. In addition to the previously reported oxidation of allylic alcohols, the competitive oxidation of an allylic alcohol in the presence of a thiol is without precedent. The lack of reactivity of

Homogeneous conditions for oxidation can be realised by employing triphenylbismuth diesters<sup>2</sup> in the presence of relatively strong bases such as tetramethylguanidine (TMG) and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) (Table 2). We have also noted that the addition of these bases accelerates the oxidation of cinnamyl alcohol by triphenylbismuth carbonate.

TABLE 2

Oxidation of (-)-carveol by the triphenylbismuth diesters Ph<sub>3</sub>BiX<sub>2</sub>.<sup>a</sup>

X	Base	Time/h	Yield/%
OAc	TMG	18	87
OAc	DBU	4	89
OCOPh	TMG	18	81
OCOCF <sub>3</sub>	TMG	1.5	64

<sup>a</sup> All reactions were carried out at room temperature in dichloromethane as solvent using 1 equiv. of bismuth reagent and 2 equiv. of base.

Throughout our investigation, we have constantly monitored the yield of recovered triaryl bismuth, with the ultimate objective of developing an oxidative catalytic cycle based on bismuth. The yield varies according to the

nature of the substrate. Thus, in oxidations with triphenylbismuth carbonate, glycol cleavage of hydrobenzoin yields 97% recovered triphenylbismuth whereas oxidation of (–)-carveol yields only 50%. Since triphenylbismuth itself is stable to the reaction conditions, this may be a reflection of the operation of different mechanisms.

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<sup>1</sup> D. H. R. Barton, J. P. Kitchin, and W. B. Motherwell, *J.C.S. Chem. Comm.*, 1978, 1099.

<sup>2</sup> 'Gmelin Handbuch der Anorganischen Chemie,' Band 47, Bismut-organische Verbindungen, Springer Verlag, Berlin, Heidelberg, New York, 1977.

<sup>3</sup> R. G. Goel and H. S. Prasad, *Canad. J. Chem.*, 1971, **49**, 2529.