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# FUNCTIONAL GROUP OXIDATION BY PENTAVALENT ORGANOBISMUTH REAGENTS†

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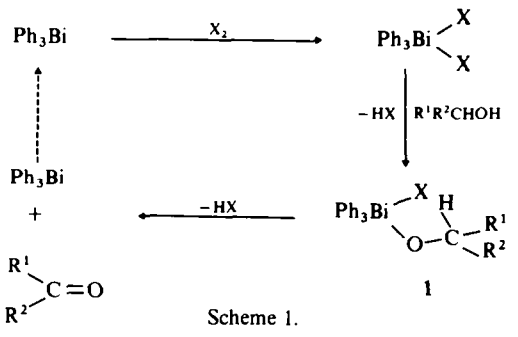
**Abstract**—Full experimental details are given for the oxidation of organic substrates by a variety of pentavalent organobismuth reagents. The remarkable selectivity of these reagents, particularly for oxidation of the allylic OH group under mild conditions, is exemplified. The mechanisms of alcohol oxidation and glycol cleavage are discussed.

The development of new methods for the selective oxidation of the OH group under neutral conditions continues to be a fundamental objective of modern organic synthesis. A major disadvantage of the numerous chromium based reagents lies in problems associated with their electrophilic nature and with the generation of intermediates formed by transfer of a single electron.[1] We conceived[2] that the inherent capability of the two electron bismuth (V)-bismuth (III) change should provide a convenient source of oxidising power (see (1)) and also afford the potential opportunity of developing a catalytic cycle based on trivalent bismuth (Scheme 1). Furthermore, we were attracted by the wide variety of crystalline pentavalent triaryl bismuth derivatives available.[3] Many of these substances are readily prepared, indefinitely stable, and reasonably soluble in organic solvents.

Examination of the literature revealed that very limited use had been made of bismuth (V) organic derivatives. Inorganic reagents, such as sodium bismuthate,[4] and bismuth trioxide[5] have been employed, normally under acidic conditions, to effect glycol cleavage and specific oxidation of acyloins to α-diketones. We were particularly encouraged by an isolated observation of Challenger and Richards[6] that oxidation of ethyl n- and iso-propyl alcohols with the unstable reagent, triphenylbismuth dihydroxide, led to the formation of the corresponding carbonyl compounds. These were isolated as their 2,4-dinitrophenyl-hydrazone derivatives in unspecified yield.

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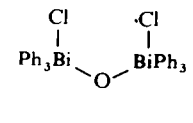
Scheme 1.

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Initially, we chose to investigate the properties of μ-oxobis (chlorotriphenylbismuth) (**2**), which is readily prepared by the action of alkali on triphenylbismuth dichloride.[7] The results obtained (Table 1) indicate that excellent yields of aldehydes and ketones can be obtained from a variety of hydroxy containing compounds under very mild conditions. We wish to emphasize that the oxidation of allylic alcohols by this method is a particularly facile process and that cleavage of 1,2-glycols also proceeds smoothly and in high yield. The selective oxidation of methyl hederagenin (**7**) to the ketone **8** without concomitant retroaldol reaction represents an improvement over the published method.[8]

We subsequently undertook a more detailed investigation of the reagent (**2**) and of its pentavalent congeners $Ar_3BiX_2$. As expected, introduction of electron withdrawing substituents on the aromatic ring led to an enhanced rate of reaction (*p*-tolyl: phenyl: *p*-chlorophenyl: *m*-nitrophenyl = 1:1.5:6: > 10). However, under the standard conditions which we had developed for the reagent **2** using carbonate or bicarbonate anion as the "base", it was initially surprising to observe that the rate of the reaction was unaltered by the nature of the leaving group in the series X = Cl, Br, $ONO_2$. In addition, replacement of carbonate or bicarbonate by pyridine or collidine led to sluggish reactions and substantial loss of oxidizing power. It was therefore reasonable to conclude that the active oxidant produced in all of these reactions involved the formation of a pentavalent triarylbismuth intermediate possessing a carbonate ligand.

Triphenylbismuth carbonate itself was simply prepared by reaction of triphenylbismuth dichloride with potassium carbonate in aqueous acetone.[9] In contrast to the previously described reagents this amorphous substance appears to have a limited

†Dedicated with respect to the memory of Robert Burns Woodward.

Table 1. Oxidation of the hydroxyl group, by $\mu$-oxo-bis-(chlorotriphenylbismuth)

| ALCOHOL | TIME (h) | TEMP. °C | BASE | PRODUCT | YIELD % |
|---|---|---|---|---|---|
| PRIMARY | | | | | |
| 1-PENTANOL | 6 | 60 | A | PENTANAL[a] | 79 |
| SECONDARY | | | | | |
| CHOLESTANOL | 30 | 21 | B | CHOLESTANONE | 75 |
| TIGOGENIN (3) | 4 | 60 | A | TIGOGENONE | 80 |
| $\alpha$-AMYRIN (4) | 15 | 21 | B | $\alpha$-AMYRONE | 86 |
| TESTOSTERONE (5) | 4 | 60 | A | ANDROST-4-ENE-3,17-DIONE | 98 |
| CHOLESTAN-3$\beta$,6$\beta$-DIOL (6) | 15 | 21 | B | CHOLESTAN-3$\beta$-OL-6-ONE | 50 |
| | | | | CHOLESTAN-3,6-DIONE | 25 |
| PRIMARY v. SECONDARY | | | | | |
| METHYL-HEDERAGENIN (7) | 24 | 21 | B | METHYLHEDERAGONATE (8) | 30 |
| BENZYLIC | | | | | |
| BENZYL ALCOHOL | 15 | 21 | B | BENZALDEHYDE[a] | 82 |
| P-NITROBENZYL ALCOHOL | 1 | 60 | A | P-NITROBENZALDEHYDE[a] | 97 |
| ANISYL ALCOHOL | 1 | 60 | A | ANISALDEHYDE[a] | 75 |
| ALLYLIC | | | | | |
| CHOLEST-1-EN-3$\beta$-OL (9) | 6 | 21 | B | CHOLEST-1-EN-3-ONE | 85 |
| CHOLEST-4-EN-3$\beta$-OL | 6 | 21 | B | CHOLEST-4-EN-3-ONE | 89 |
| (-)-CARVEOL | 6 | 21 | B | CARVONE[a] | 34 |
| CROTYL ALCOHOL | 5 | 60 | A | CROTONALDEHYDE[a] | 76 |
| CINNAMYL ALCOHOL | 15 | 21 | B | CINNAMALDEHYDE[a] | 83 |
| GERANIOL | 15 | 21 | B | GERANIAL[a] | 95 |
| 3-METHYL-BUT-2-EN-1-OL | 2 | 60 | A | 3-METHYL-BUT-2-EN-AL[a] | 90 |
| VITAMIN A ALCOHOL | 15 | 21 | A | VITAMIN A ALDEHYDE[a] | 68 |
| $\alpha$-GLYCOL CLEAVAGE | | | | | |
| MESO-HYDROBENZOIN | 3 | 21 | B | BENZALDEHYDE[a] | 82 |
| 1,2:5,6-DI-O-ISOPROPYLIDENE-D-MANNITOL | 0.25 | 60 | A | 2,3-ISOPROPYLIDENE-D-GLYCERALDEHYDE | 76 |

(a) isolated as the 2,4-dinitrophenylhydrazone derivative.

A Sodium Bicarbonate

B Potassium Carbonate

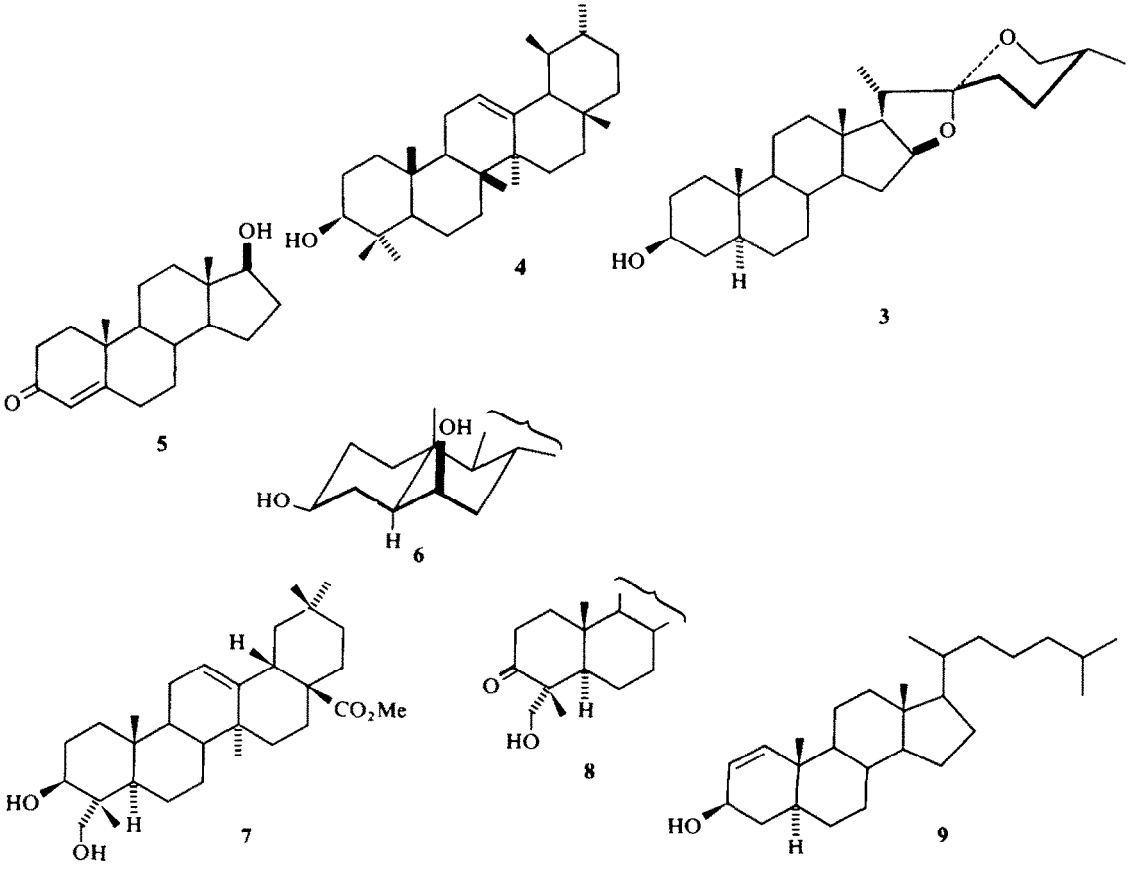


Table 2. Functional group selectivity in oxidation with triphenylbismuth carbonate.

| SUBSTRATE | TIME (H) | TEMP. °C | PRODUCT | YIELD % |
|---|---|---|---|---|
| SECONDARY ALCOHOL | | | | |
| t-BUTYLPHENYLMETHANOL ≠ | 18 | 40 | t-BUTYLPHENYL KETONE | 90 |
| ALLYLIC ALCOHOL | | | | |
| (-)-CARVEOL | 1.5 | 40 | (-)-CARVONE | 84 |
| CHOLEST-4-EN-3 -OL | 18 | 20 | CHOLEST-4-EN-3-ONE | 97 |
| GERANIOL | 2.5 | 40 | GERANIAL[a] | 95 |
| SELECTIVITY | | | | |
| ANDROST-4-EN-3β,17β-DIOL | 43 | 20 | TESTOSTERONE[b] | 51 |
| | | | ANDROST-4-EN-3,17 DIONE | 15 |
| | | | ANDROST-4-EN-3β,17β-DIOL | 22 |
| CHOLESTAN-3β-OL (1 EQUIV.) + CHOLEST-4-EN-3 -OL (1 EQUIV.) | 5.5 | 40 | CHOLESTAN-3β-OL | 80 |
| | | | CHOLEST-4-EN-3-ONE | 89 |
| THIOPHENOL (1 EQUIV.) + CHOLEST-4-EN-3β-OL (1 EQ.) | 24 | 20 | CHOLEST-4-EN-3-ONE | 76 |
| ISO-BUTYLTHIOL (1 EQUIV.) + CHOLEST-4-EN-3β-OL (1 EQUIV.) | 23 | 40 | CHOLEST-4-EN-3-ONE | 95 |
| PYROLLIDINE (1 EQUIV.) + (-)-CARVEOL (1 EQUIV.) | 18 | 20 | (-)-CARVONE | 87 |
| INDOLE (1 EQUIV.) + (-)-CARVEOL (1 EQUIV.) | 24 | 24 | (-)-CARVONE | 80 |
| 8-METHYLSELENOTETRADECAN-7-OL (10) | 48 | 40 | 8-METHYLSELENOTETRADECAN-7-ONE | 85 |
| N-ACETYLEPHEDRINE | 18 | 40 | N-ACETYL-α-METHLAMINO-PROPIOPHENONE | 75 |
| EPHEDRINE (11) | 1.5 | 40 | BENZALDEHYDE[a] | 100 |
| THIOLS | | | | |
| THIOPHENOL | 18 | 20 | DIPHENYLDISULPHIDE | 70 |
| ORTHO-THIOCRESOL | 3 | 20 | DI-ORTHO-TOLYLDISULPHIDE | 90 |
| PARA-THIOCRESOL | 3 | 20 | DI-PARA-TOLYLDISULPHIDE | 89 |
| MISCELLANEOUS | | | | |
| 5-α-CHOLESTAN-3-ONE OXIME | 15 | 20 | 5-α-CHOLESTAN-3-ONE | 80 |
| BENZOPHENONE HYDRAZONE | 5 | 20 | DIPHENYLDIAZOMETHANE | 97 |
| HYDRAZOBENZENE | 1.5 | 20 | AZOBENZENE | 90 |
| PHENYLHYDRAZOTRIPHENYL-METHANE | 4 | 20 | PHENYLAZOTRIPHENYLMETHANE | 80 |
| 1,2,5,6-DI-O-ISOPROPYLIDENE-3(N-4-NITROPHENYLTHIONO-CARBAMATO)-α-D-GLUCOFURA-NOSE (12) | 17 | 40 | DISULPHIDE (13) | 91 |
| 2,3,4,6-TETRA-O-BENZYL-α-D-GLUCOPYRANOSE (14) ≠ | 4 | 40 | 2,3,4,5-TETRA-O-BENZYL-GLUCONIC ACID δ LACTONE | 89 |
| GLYCOL CLEAVAGE | | | | |
| CIS-CYCLOHEXANE 1,2 DIOL | 2 | 40 | 1,6-HEXANEDIAL | 100 |
| MESO-HYDROBENZOIN | 1.5 | 40 | BENZALDEHYDE | 97 |
| 1,2,5,6-DI-O-ISOPROPYLI-DENE D-MANNITOL | 2 | 40 | 2,3-O-ISOPROPYLIDENE-D-GLYCERALDEHYDE | 80 |

The following compounds were not oxidised by the reagent, (compound, temp., time). Benzophenone phenylhydrazone, 40, 24 ; Benzophenone 2,4 dinitrophenylhydrazone, 40, 24 . Benzophenone semicarbazone, 20, 72 , 5α-cholestan-3-one tosylhydrazone, 20, 24 ; Tri-O-acetyl glucal, 20 , 24 ; Aniline, 20, 18 ; N,N-dimethylaniline, 20 , 24 ; 3-pyrollidino-cholesta-3,5 diene, 20, 24 ; Di-t-butyl thionoketone, 40, 16 , 3β-cholestanyl-S-methyl xanthate, 40, 24 ; 3β-cholestanyl-N,N diethyl thionocarbamate 40, 24,

(a) Isolated as the 2,4 dinitrophenylhydrazone derivative

(b) The reagent was prepared in situ by reaction of $Ph_3BiCl_2$ and $K_2CO_3$.

≠ Experiment performed by Mlle. B. Charpiot

solubility in common organic solvents. Nevertheless, it is a highly selective non-electrophilic oxidant for a variety of functional groups (Table 2). Once again, allylic oxidation and glycol cleavage occur rapidly and in high yield. The selective oxidation of an allylic alcohol in the presence of a secondary alcohol is noteworthy, as is the oxidation of the hydroxy selenide (**10**). The thiocarbonyl group in xanthates, dialkylaminothionocarbamates, or in di-t-butyl thionoketone is unaffected, but oxidation of the monoarylthionocarbamate (**12**) gave the disulphide (**13**). Although C–C bond cleavage with formation of benzaldehyde was observed on attempted oxidation of ephedrine (**11**), oxidation of the derived acetamide gave the corresponding ketone. Treatment of the carbohydrate hemiacetal (**14**) gave the known lactone which was further characterised by formation of a crystalline hydroxy amide.[10] The competitive oxidation of an allylic alcohol in the presence of a thiol is without precedent. Since aniline, dimethylaniline, pyrollidine, indole and 3-pyrollidino-cholesta 3,5-diene are inert under standard conditions the reagent should find application in complex natural product synthesis.

We have also discovered that homogeneous oxidation of allylic alcohols can be accomplished by employing triphenylbismuth diesters (X = acetate, benzoate and trifluoroacetate) in the presence of

strong bases such as tetramethyl-guanidine (TMG) and 1,5 diazabicyclo |5,4,0| undec-5-ene (DBU).

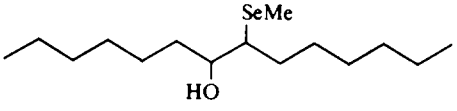
Several features of mechanistic interest deserve some comment. The selective oxidation of the more hindered 6β-OH group in cholestan-3β,6β-diol (**6**) would suggest that the normal rate determining step involves breakdown of an intermediate of type **1**. However, there was no observable difference in rate between the oxidation of benzyl alcohol and *p*-nitrobenzyl alcohol nor between benzyl alcohol and anisyl alcohol when a mixture of the two alcohols was allowed to compete for a deficiency of oxidant. In the oxidation of t-butylphenylmethanol by chromium trioxide the intermediate chromate (IV) ester is known to undergo electron transfer with elimination of the t-Bu radical and formation of benzaldehyde.[11] However, oxidation with triphenylbismuth carbonate proceeds cleanly to give the corresponding ketone.

We have consistently monitored the yield of recovered triarylbismuth after oxidation with the objective of developing a catalytic cycle based on bismuth (III). This yield should, if the above mechanism is operative, be comparable with the yield of the oxidised organic substrate, since we have shown that triphenylbismuth itself is stable under the conditions of the reaction. In the event, however, significant variation has been observed according to the nature of the leaving group X. Thus, in the oxidation of (−)-carveol by triphenylbismuth diacetate, ditrifluoroacetate and carbonate the recovered yields of triphenylbismuth are 32%, 0% and 50% respectively. Accordingly, it was of interest to examine the reaction mixture directly by NMR spectroscopy. Oxidation of (−)-carveol with triphenylbismuth dibenzoate in deuterochloroform containing tetramethylguanidine resulted in the growth of an aromatic singlet (δ 7.24) whose chemical shift was identical with benzene. Moreover, it was possible to isolate toluene by repetition of the experiment using tri-*p*-tolyl-bismuth dibenzoate in tetralin as solvent. Finally, oxidation of deuteriocarveol (**5**) with tri-*p*-methoxyphenyl bismuth carbonate furnished exclusively *p*-deuterioanisole as established by 400 MHz NMR spectra. It is thus apparent that the facile cleavage of the bismuth-aryl bond results in two competitive pathways for the breakdown of the organobismuth ester intermediate **1** (Scheme 2).

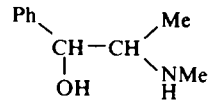
The addition of nitrosomesitylene or nitrosobenzene does not alter the course of a typical oxidation reaction and we do not consider that free radicals are involved in normal Bi(V) reactions.

The mechanism of glycol cleavage is entirely different. The cleavage of *cis*-1,2-cyclohexanediol is considerably faster than that of the *trans*-isomer and yields of recovered triphenylbismuth are essentially quantitative in all cases so far studied. These results provide strong presumptive evidence for the preferential formation of a cyclic organobismuth intermediate (**17**) which breaks down with exclusive formation of triphenylbismuth. A catalytic cycle for glycol cleavage is therefore a practical possibility. Preliminary studies (Table 3) indicate that cleavage of hydrobenzoin by hydrogen peroxide in the presence of sodium bicarbonate, or by tertiary butyl hydroperoxide can be catalysed by triphenylbismuth. Attempts to extend this reaction to other glycols have so far been unsuccessful.

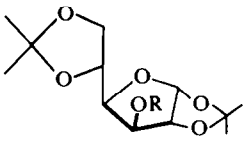
In summary, pentavalent organobismuth reagents are mild, nonelectrophilic and highly selective



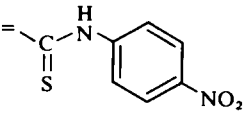

**10**




**11**




**12**: R =

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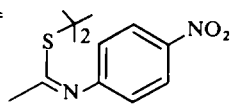
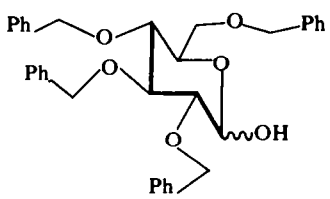
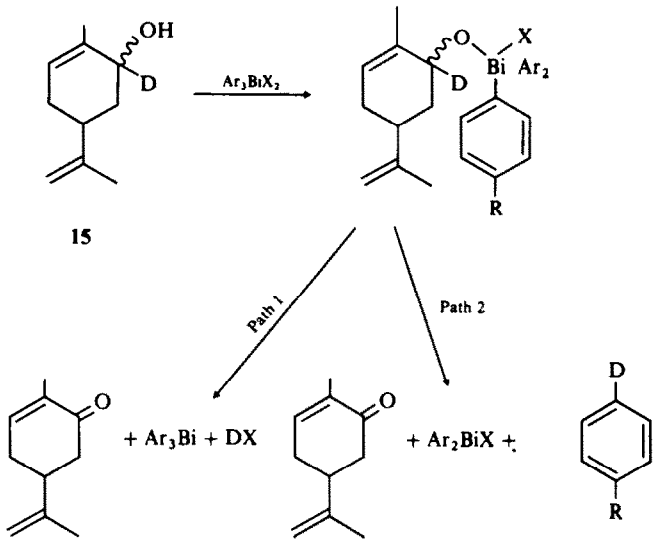



**14**




Scheme 2.

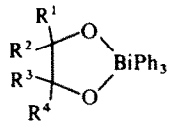



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Table 3. Cleavage of *meso*-hydrobenzoin catalysed by triphenylbismuth

| TRIPHENYLBISMUTH | BENZALDEHYDE YIELD % | | | |
|---|---|---|---|---|
| N° OF EQUIV. | HYDROGEN PEROXIDE (3 EQ.) + $NaHCO_3$ (9 EQ.) | TIME H. | T-BUTYL HYDROPEROXIDE (3 EQ.) | TIME H. |
| 1.0 | 98 | 1 | 93 | 2.5 |
| 0.5 | - | - | 93 | 2.5 |
| 0.25 | 94 | 1 | 90 | 16 |
| 0.1 | 73 | 2 | 84 | 16 |
| 0.05 | 70 | 16 | - | |

oxidants. From the practical standpoint, anhydrous conditions are not necessary, and unlike manganese dioxide,[12] chromium trioxide-pyridine[13] and silver carbonate on celite,[14] a large excess of reagent is not required.

## EXPERIMENTAL

M.ps were determined with a Kofler hot stage apparatus and are uncorrected. NMR spectra were determined for solns in ($^2$H) chloroform with TMS as internal standard on Varian T-60 and Varian E.M. 360 instruments. IR spectra were recorded on a Perkin Elmer 257 instrument. Optical rotations were measured on a Perkin Elmer 141 polarimeter and mass spectra were recorded with an AEI M.S 9 instrument. Organic extracts were dried over $Na_2SO_4$ and evaporated at reduced pressure. All solvents and reagents were purified and dried by standard techniques.

*Preparation of organobismuth reagents*

Triphenylbismuth was prepared by reaction of bismuth trichloride with phenylmagnesium bromide.[15] Tri(*p*-tolyl)bismuth, [16]tri(*p*-methoxyphenyl) bismuth[17] and tri(*p*-chlorophenyl) bismuth[18] were prepared in an analogous manner. Triphenylbismuth dibromide,[19] triphenylbismuth dichloride,[20] tri(*p*-tolyl)bismuth dichloride,[21] tri(*p*-methoxy phenyl)bismuth dibromide[22] and tri(*p*-chlorophenyl)bismuth dichloride[23] were prepared by the action of the halogen with the triarylbismuth. Triphenylbismuth diacetate[24] and triphenylbismuth di(trifluoroacetate)[25] were prepared by the reaction of triphenylbismuth carbonate[9] with the acid. Triphenylbismuth dibenzoate[26] was prepared by reaction of triphenylbismuth with dibenzoyl peroxide. Trephenylbismuth dinitrate[27] and tri(*p*-tolylbismuth) dinitrate[28] were prepared from the corresponding dichlorides by reaction with silver nitrate. Nitration of triphenylbismuth dinitrate with fuming nitric acid gave tri (*m*-nitrophenyl) bismuth

dinitrate.[29] μ-oxo-bis(chlorotriphenylbismuth) was prepared by reaction of the dichloride with alkali.[7]

*Improved preparation of triphenylbismuth carbonate*[9]

To a well stirred soln of triphenylbismuth dichloride (13 g) in acetone (100 ml) was added a soln of $K_2CO_3$ (3.6 g) in water (20 ml). After 5 min, the precipitated triphenylbismuth carbonate was filtered off, washed with acetone, and dried, yield 12.7 g (100%) m.p. 155 (dec), lit.[9] 164 . (Found: C, 45.31; H, 3.17. Calc. for $C_{19}H_{15}BiO_3$: C, 45.61; H, 2.94%).

*General procedure for oxidation with μ-oxobis(chlorotriphenylbismuth)* (**2**) (Table 1).

μ-oxobis(chlorotriphenylbismuth) is soluble in dichloromethane, chloroform, tetrahydrofuran and hot benzene. In a typical oxidation procedure, the alcohol (0.25 mmole) and the reagent **2** (0.20 mmole) in dichloromethane or chloroform (2 ml) are stirred with an excess of $K_2CO_3$ or $NaHCO_3$ (200 mg) until reaction is complete by aliquot monitoring. The mixture is filtered and the solvent evaporated. Chromatography on silica gel separates the product from non-polar triphenylbismuth. Alternatively, acid stable oxidation products may be isolated by heating the entire mixture on a steam bath for 30 min with glacial AcOH to destroy triphenylbismuth The resulting soln is then poured into water and thoroughly extracted with ether. The combined ethereal extracts are washed successively with $NaHCO_3$ aq and then brine, dried, and the crude product purified by crystallisation. Reaction conditions and yields for a variety of alcohols are given in Table 1.

*General procedure for oxidation by triphenylbismuth carbonate* (Table 2)

Triphenylbismuth carbonate (1·1–2 equiv.) is added all in one portion to a well stirred soln of the substrate (1 equiv) in dichloromethane as solvent. As reaction proceeds the soln becomes homogeneous. When all starting material has been consumed, the mixture is filtered, the solvent removed and the product purified by chromatography (or as described above). Reaction conditions and yields for a variety of functional groups are tabulated (Table 2).

*Oxidation of* 1,2,5,6-*Di-O-isopropylidene*-3-(N-4′-*nitrophenylthionocarbamato*)-α-*D-glucofuranose* (**12**) *with triphenylbismuth carbonate*

Oxidation of **13**[30] as described above led to the isolation of the disulphide **14**) 81%. Recrystallisation from hexane gave a white solid, m.p. 83–85 $[\alpha]_D^{20} - 87.7$ (*c* 0.22, $CHCl_3$); $\nu_{max}$ ($CHCl_3$) 1640, 1590, 1340 $cm^{-1}$; *m/e* (chemical ionisation, isobutane) 863 ($M^+ - CH_3$); (Found: C, 52.24; H, 5.19; N, 6.14; S, 7.05. Calc. for $C_{38}H_{46}O_{16}N_4S_2$: C, 51.95; H, 5.28; N, 6.38; S, 7.30%).

*Homogeneous oxidation of* (−)-*carveol by triphenylbismuth diesters in the presence of base*

To a soln of (−)-carveol (31.2 mg, 0.2 mmol) in chloroform (2 ml) was added the base (0.5 mmole) and the triphenylbismuth diester (0.2 mmole). The mixture was stirred at room temp until reaction was complete. Purification of (−)-carvone was achieved by preparative thick layer chromatography. The following results were obtained (ester, base, time h., (−)-carvone %). Diacetate, TMG 18, 87; diacetate, DBU 4, 89; dibenzoate, TMG 18, 81; ditrifluoroacetate, TMG, 1.5, 64.

*Competition experiments for the oxidation of allylic alcohols by triphenylbismuth dihalides*

A 1:1 mixture of two triarylbismuth dichlorides $Ar^1_3BiCl_2$ and $Ar^2_3BiCl_2$ was allowed to compete for a deficiency of an allylic alcohol (typically cholest-1-en-3-ol or cholest-4-en-3-ol) in dichloromethane soln with $K_2CO_3$ as base. The mixture of triarylbismuths $Ar^1_3Bi$ and $Ar^2_3Bi$ formed in the reaction was isolated by preparative tlc and the resultant ratio of the two compounds was determined by NMR. In this way it was possible to construct a series of relative rate values which showed *p*-tolyl: phenyl: *p*-chlorophenyl: *m*-nitrophenyl = 1:1.5:6: > 10.

Repetition of the above experiments with $Ar^1_3BiX_2$ and $Ar^2_3BiY_2$ and subsequently with $Ar^1_3BiY_2$ and $Ar^2_3BiX_2$ showed that, after correction for the effect of the aryl group, the ratio of triarylbismuths $Ar^1_3Bi$ and $Ar^2_3Bi$ was unaffected by the nature of X and Y. (X, Y = Cl, Br, $ONO_2$).

*Competition experiments for oxidation of benzylic alcohols*

To a mixture of benzyl alcohol (0.2 mmole) and *p*-nitrobenzyl alcohol (0.2 mmole) in chloroform (4 ml) containing μ-oxobis(chlorotriphenylbismuth) (0.1 mmole) was added $K_2CO_3$ (200 mg), and the mixture was stirred and heated at 60 for 1 hr. The cooled mixture was filtered and the solvent evaporated. After purification by plc the ratio of the two resultant aldehydes was determined by NMR. No preferential oxidation was observed. The above experiment was repeated with *p*-anisyl alcohol and benzyl alcohol and the same result was obtained. By using deuterochloroform as solvent, it was possible to determine the ratio of the two aldehydes directly in the crude reaction mixture by NMR.

*Oxidation of* (−)-*carveol with tri*-p-*tolylbismuth dibenzoate*

*Isolation of toluene.* Tri-*p*-tolylbismuth dibenzoate (2.76 g) was added all in one portion to a stirred soln of (−)-carveol (0.35 g) and DBU (0.4 g) in tetralin (10 ml) as solvent. After 20 hr at room temp, the volatile portion of the reaction was isolated by high vacuum trap to trap distillation at room temp and shown by NMR to contain toluene. Addition of further toluene to the NMR sample led only to signal enhancement. Repetition of the experiment using (−)-α-deuteriocarveol (**16**), prepared by lithium aluminum deuteride reduction of (−)-carvone, led to the isolation of a mono-deuterio-toluene. τ 2.6 (4 H, unresolved multiplet), 7.5 (3 H, s) *m/e* 93 ($M^+$ for $C_7H_7D$).

*Oxidation of* (−)-α-*deuteriocarveol* (**15**) *with tri*-p-*methoxyphenylbismuth carbonate*

*Isolation of* p-*deuteroanisole.* To a soln of (−)-carveol (30.2 mg, 0.2 mmole) in dichloromethane (2 ml) was added tri-*p*-methoxyphenylbismuth carbonate (118 mg, 0.2 mmole) and the stirred suspension was heated to reflux. Aliquot monitoring by tlc indicated that reaction was complete after 2 days. Purification by preparative tlc afforded anisole (19,7 mg), (−)-carvone (27.0 mg, 89%) and tri-*p*-methoxyphenyl bismuth (21.3 mg), all products being identical with authentic samples. Repetition of the experiment using (−)-α-deuteriocarveol (**16**) led to the isolation of *para*-deuterioanisole. *m/e* 109. ($M^+$), 79, 66 (of anisole $M^+$ 108, 78, 65), τ (400 MHz) 2.82 and 3.21 (4 H, ABq, J = 8 Hz), 6.24 (3 H, s, OMe).

*Oxidation of* (−)-*Carveol by triphenylbismuth dibenzoate in the presence of nitrosomesitylene and nitrosobenzene*

To a soln of (−)-carveol (31.2 mg, 0.2 mmole) in dichloromethane (1 ml) was added nitrosomesitylene (30 mg, 0.2 mmole), triphenylbismuth dibenzoate (160 mg, 0.2 mmole) and DBU (30 mg). The mixture was stirred at room temp for 30 min. Purification by preparative tlc afforded nitrosomesitylene (21 9 mg, 73%), (−)-carvone (20.0 mg, 64%) and triphenylbismuth (17.2 mg, 20%). Repetition of the experiment in the presence of a two molar excess of nitrosobenzene led to the same result. Diphenylnitroxide was not detected in the reaction mixture by tlc comparison with an authentic sample.

*Glycol cleavage catalysed by triphenylbismuth. Typical experimental procedure*

(a) *With Hydrogen peroxide and sodium bicarbonate.* To a stirred soln of hydrobenzoin (107 mg, 0.5 mmol) and triphenylbismuth (220 mg, 0.5 mmol) in acetone (2 ml) containing $NaHCO_3$ (378 mg) was added dropwise at room temp a soln of $H_2O_2$ (1.5 mmol) in aqueous acetone (0.9 ml).

The mixture was heated at 40 until reaction was complete (tlc; 1 hr), filtered, and solvent removed *in vacuo*. Benzaldehyde was isolated in the form of its 2,4-dinitrophenylhydrazone dirivative (98%) m.p. 238 .

(b) *With t-butyl hydroperoxide.* To a stirred soln of hydrobenzoin (107 mg, 0.5 mmol) and triphenylbismuth (220 mg, 0.5 mmol) in acetone (3 ml) was added dropwise at room temp t-butylhydroperoxide (1.5 mmole, 0.15 ml) in acetone (0.5 ml) and the mixture was then heated at 40 until reaction was complete. Removal of solvent followed by treatment with 2,4-dinitrophenylhydrazine in the usual manner led to benzaldehyde 2,4-dinitrophenylhydrazone (93%), m.p 238 .

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## REFERENCES

[1]J. Roček and A. E. Radkowski, *J. Am. Chem. Soc.* **90,** 2986 (1968). P. M. Nave and W. S. Trahanovsky, *Ibid.* **92,** 1120 (1970).
[2]D. H. R. Barton, J. P. Kitchin and W. B. Motherwell, *J. Chem. Soc.* Chem. Comm. 1099 (1978); D. H. R. Barton, D. J. Lester, W. B. Motherwell and M. T. B. Papoula, *Ibid.* Chem. Comm. 705 (1979), *Ibid.* Chem. Comm 246 (1980).
[3]*Gmelin Handbuch der Anorganischen Chemie.* Band 47, Bismut-organische Verbindungen, Springer Verlag, Berlin, Heidelberg, New York (1977).
[4]W. Rigby, *J. Chem. Soc.* 1907 (1950); C. J. W. Brooks and J. K. Norymberski, *Biochem. J.* **55,** 371 (1953).
[5]W. Rigby, *J. Chem. Soc.* 793 (1951).
[6]F. Challenger and O. V. Richards, *Ibid.* 405 (1934).
[7]R. G. Goel and H. S. Prasad, *J. Organometal. Chem.* **36,** 323 (1972).
[8]W. A. Jacobs, *J. Biol. Chem.* **63,** 631 (1925).
[9]R. G. Goel and H. S. Prasad, *Canad. J. Chem.* **49,** 2529 (1971).
[10]H. Kuzuhara and H. G. Fletcher Jr., *J. Org. Chem.* **32,** 2531 (1967).
[11]P. Müller and J. Blanc, *Helv. Chim. Acta* **62,** 1980 (1979).
[12]J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen and T. Walker, *J. Chem. Soc.* 1094 (1952).
[13]G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Am. Chem. Soc.* **75,** 422 (1953).
[14]M. Fétizon and M. Golfier, *C.R. Acad. Sci., Paris,* **267,** 900 (1968); M. Fétizon, M. Golfier and J.-M. Louis, *J. Chem. Soc.* Chem. Comm. 1102, 1118 (1969).
[15]F. F. Blicke, U. O. Oakdale and F. S. Smith, *J. Am. Chem. Soc.* **53,** 1925 (1931).
[16]H. Gilman and H. L. Yablunky, *Ibid.* **63,** 949 (1941).
[17]J. Supniewski and R. Adams, *Ibid.* **48,** 507 (1926).
[18]H. Gilman and A. C. Svigoon, *Ibid.* **61,** 3586 (1939).
[19]G. Wittig and K. Clauss, *Liebigs Ann.* **578,** 136 (1952).
[20]F. Challenger, *J. Chem. Soc.* **105,** 2210 (1914); C. Heitz and J.-P. Adloff, *J. Organometal. Chem.* **2,** 59 (1964).
[21]F. Challenger and C. F. Allpress, *J. Chem. Soc.* **119,** 913 (1921).
[22]A. Gillmeister, *Ber. Deutsch. Chem. Ges.* **30,** 2843 (1897); *cf* also Ref. 17. This unstable substance was converted to the corresponding carbonate and used immediately.
[23]F. Challenger and L. R. Ridgway, *J. Chem. Soc.* **121,** 104 (1922).
[24]F. Challenger and A. E. Gooddard, *Ibid.* **117,** 762 (1920).
[25]R. G. Goel and H. S. Prasad, *Can. J. Chem.* **48,** 2488 (1970).
[26]H. Gilman and H. L. Yale, *J. Am. Chem. Soc.* **73,** 4470 (1951).
[27]F. Challenger and J. F. Wilkinson, *J. Chem. Soc.* **125,** 854 (1925).
[28]J. V. Supniewski, *Roczniki Chem.* **5,** 298 (1925)
[29]D. Vorländer, *Ber. Deutsch. Chem. Ges.* **B 58,** 1893 (1925).
[30]D. H. R. Barton and S. W. McCombie, unpublished observations (1974).
[31]J. Lucchetti and A. Krief, *C.R. Acad. Sci. Paris, C,* 537 (1979).