Observations on the Cleavage of the Bismuth–carbon bond in Bi$^{\text{V}}$ Compounds: a New Arylation Reaction

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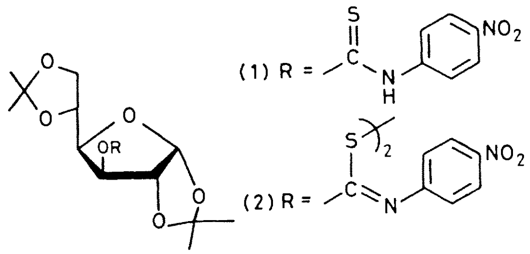
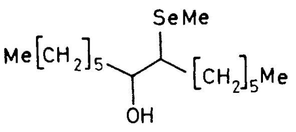
Summary. Further examples of the selectivity of pentavalent triaryl-organobismuth oxidants are presented; deuterium labelling studies have established that the mechanism of oxidation of allylic alcohols by these reagents involves, to some extent, cleavage of the bismuth–aryl bond; several reactions involving the synthetically useful transfer of an aryl group from bismuth to nitrogen and to carbon are described.

WE have recently shown that several pentavalent triaryl-organobismuth reagents are efficient oxidants of exceptional selectivity.[1,2] In continuation of these studies we now report that triphenylbismuth carbonate does not oxidize the thiocarbonyl group in xanthates, dialkylamino-thionocarbamates, or in di-t-butyl thioketone.[3] However, oxidation of the monoalkyl thionoamide (**1**) gave smoothly the disulphide (**2**) (81%). A striking example is the selective oxidation of the hydroxy selenide (**3**) to the corresponding carbonyl compound[4] (86%).

We have also indicated[2] that, whereas glycol cleavage with triphenylbismuth carbonate gives a virtually quantitative yield of recovered triphenylbismuth, oxidation of an allylic alcohol results in a recovery which is without exception, less than the yield of the derived enone. This observation is incompatible with exclusive regeneration of triarylbismuth from intermediate (**4**) (Path A, Scheme). In order to realise a catalytic cycle based on trivalent bismuth, it was important to examine the course of a typical oxidation in detail.





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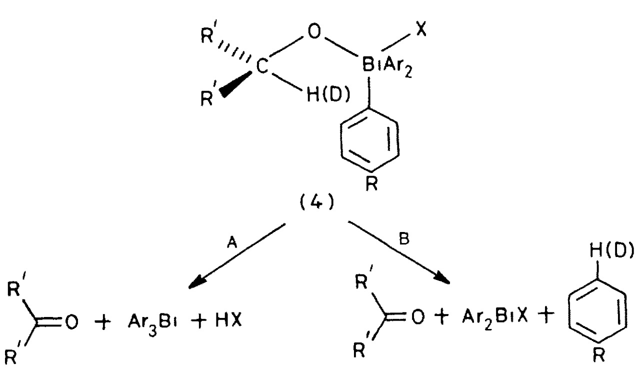
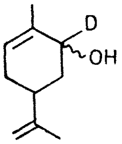


SCHEME

The reaction of (−)-carveol with triphenylbismuth diacetate in deuteriochloroform containing tetramethylguanidine was monitored by n.m.r. spectroscopy. The growth of an aromatic singlet at δ 7.24 was strongly indicative of benzene formation. By choosing tetralin as solvent and 1,5-diazabicyclo[5,4.0]undec-5-ene (DBU) as base, it was possible to isolate the toluene produced in the oxidation of (−)-carveol with tri-*p*-tolylbismuth dibenzoate. Moreover, oxidation of the (−)-deuteriocarveol (**5**) prepared by lithium aluminium deuteride reduction of (−)-carvone, furnished monodeuteriotoluene (mass spectrum). In an analogous experiment the position of the deuterium atom was unambiguously established. Oxidation of (**5**) with tri-*p*-methoxyphenylbismuth carbonate gave *p*-deuterioanisole as the sole isomer, as evidenced by 400 MHz n.m.r. and mass spectroscopy. All attempts to trap free aryl radicals by the addition of nitrosobenzene or nitrosomesitylene even in molecular excess, have been uniformly unsuccessful. Thus, the easy cleavage of the bismuth–carbon bond[5] provides a second competitive pathway for the oxidation of allylic alcohols (Path B, Scheme).

At the same time, we have discovered that the cleavage of the bismuth–aryl bond may be used to advantage in organic synthesis. Thus, oxidation of phenylhydroxylamine with triphenylbismuth carbonate led, not only to the anticipated nitrosobenzene (22%), but also to the persistant free radical diphenyl nitroxide (64%). Reaction with tri-*p*-tolylbismuth carbonate gave the corresponding phenyl-*p*-tolyl nitroxide (50%), thus obviating the problems of over reduction encountered in the reaction of nitroso compounds with Grignard reagents.[6] Nitrosobenzene itself was not affected by triphenylbismuth carbonate.

A second arylation reaction, in which the aromatic ring attached to bismuth is transferred to carbon, was discovered during the course of our studies on alcohol oxidation. The classical problem[7] posed by the oxidation of quinine to the corresponding ketone quininone (**6**) was considered to be an excellent test of the selectivity of pentavalent organobismuth oxidants. Quininone was formed as an isolable intermediate in the oxidation of quinine by triphenylbismuth carbonate, but in low yield (34%). The final product, which could be prepared independently from quininone itself, was a diastereoisomeric mixture of the α-arylated ketones (**7**) (75%). Oxidation of quininone with tri-*p*-tolylbismuth carbonate gave the analogous α-tolyl ketones (**8**) (90%). From the mechanistic viewpoint, it seems reasonable to postulate that the reaction proceeds *via* the formation of an enolic derivative (**9**), which can subsequently undergo intramolecular arylation. The reaction of ethyl acetoacetate with triphenylbismuth carbonate leads, in like manner to the formation of ethyl α-phenylacetoacetate[8] (59%). By using an excess of reagent, it was also



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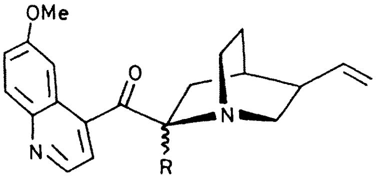
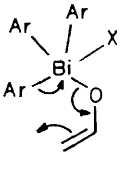


(6) R = *endo*-H
(7) R = phenyl
(8) R = tolyl



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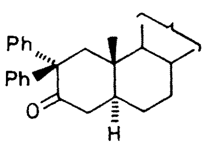

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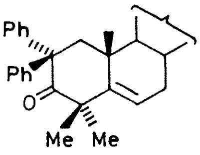

(11)

possible to prepare ethyl 2,2-diphenylacetoacetate (55%), which was also accompanied by minor amounts of ethyl diphenylacetate (21%). As a logical extension of this reaction, we investigated the behaviour of potassium enolates. Thus, sequential treatment of cholestan-3-one with potassium hydride and the carbonate gave 2,2-diphenylcholestan-3-one (**10**) (64%). The assigned structure is supported by ^{13}C n.m.r. data. Similar treatment of 4,4-dimethylcholest-5-en-3-one afforded the highly hindered ketone (**11**) (80%).

We have also carried out a preliminary investigation of the behaviour of phenols. Treatment of β-naphthol with triphenylbismuth carbonate at room temperature in the presence of tetramethylguanidine (TMG) gave 1-phenyl-2-naphthol[9] in 76% yield.

One of us (M.T.B.P.) thanks the Instituto Nacional Investigaçao Cientifica and the Instituto Universitario Evora, Portugal, for sabbatical leave. We thank Professor A. Krief (Namur) for compound (**3**).

(*Received, 3rd December* 1979; *Com.* 1259.)

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