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Bismuth derivatives for the oxidation of organic compounds [1]

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[1] Dedicated to Professor Dr. Kees Vrieze on the occasion of his 25th anniversary as professor of inorganic chemistry.

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Abstract

This review deals with the utilization of bismuth compounds in oxidation reactions of organic derivatives. Both the pentavalent and trivalent states of bismuth were found to display oxidizing power.

Inorganic bismuth reagents, such as sodium bismuthate, zinc bismuthate and bismuth trioxide, have been employed, normally under acidic conditions, to effect glycol cleavage and specific oxidations of alcohols to their carbonyl compounds.

Unlike these reagents, pentavalent triarylbismuth(V) is used under mild conditions of temperature and pH. Excellent yields of aldehydes and ketones were obtained from a variety of hydroxy containing compounds. Further, the oxidation of allylic alcohols by μ-oxobis(chlorotriphenylbismuth) was shown to be a particularly easy process. These transformations require stoechiometric amounts of the Bi(V) reagent and involve the Bi(V)/Bi(III) redox couple. This system could be made catalytic by using N-bromosuccinimide as the oxidant of $BiPh_3$ thus promoting the catalytic cleavage of α-glycols by Bi(V).

A new class of bismuth oxidation catalysts was described recently, based on functionalized bismuth(III) carboxylates (α-hydroxycarboxylates, pyridine- and pyrazine-carboxylates, salicylates, aminosalycilates). Thus, Bi(III) mandelate, $[(mand)_2Bi(\mu\text{-}O)Bi(mand)_2]$, was found to be an efficient catalyst for the oxidative C–C bond cleavage of epoxides and their transformation into carboxylic acids in anhydrous DMSO medium. Further, oxygen was found to be the oxidant in the Bi(III) carboxylate-catalyzed oxidative transformation of α-ketols to carboxylic acids and in the conversion of 1-octene in octanones by the Rh(III) or Pd(II)/$BiCl_3$/LiCl systems.

Keywords: Organic compounds; Bismuth derivatives

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1. Introduction

Bismuth is regarded as a relatively non-toxic heavy metal; it is noteworthy that bismuth is less toxic than antimony, which is unusual, since toxicity normally increases down a group [1]. On the other hand, bismuth holds a special position in the periodic table as the heaviest stable element, and bismuth compounds often show special behavior, both electronically and sterically. It thus appears that, although bismuth chemistry has been rather neglected until recently, it should find new and original applications in low-toxicity catalytic processes.

In the oxidation state III, bismuth possesses a lone pair of electrons which is predominantly s in character: as a consequence, bismuth(III) salts show a very 'soft' Lewis acidity. This has recently found applications (i) in the catalysis of Mukaiyama-cross aldol and -Michael reactions of enoxysilanes [2,3] and (ii) in the catalytic acylation reaction of enoxysilanes and allylsilanes [4]. Moreover, $BiCl_3$ itself is a catalyst of the Knoevenagel reaction [5] and a strong activator of the Si–Cl bond [6].

As one descends through group 15, the metal-carbon bond strength decreases and organobismuth(V) derivatives as arylating agents in organic synthesis have indeed shown a great selectivity toward a wide range of substrates [7]. There is also an increase in the stability of the lower oxidation state and this leads to the use of bismuth(V) and bismuth(III) compounds in oxidation reactions on which the present review focuses. Bismuth-salts oxidations have been reviewed in 1986 by J. P. Kitchin [8]. Previous reviews devoted to the chemistry of organobismuth, including oxidation reactions are by Barton et al. [7,9a], Finet [9b], Freedman and Doak [9c], and Wada and Ohki [9d].

This review is devoted to liquid phase oxidations of organic compounds in the presence of bismuth derivatives: the oxidation and ammoxidation of alkenes over heterogeneous bismuth-molybdate catalysts will not be considered.

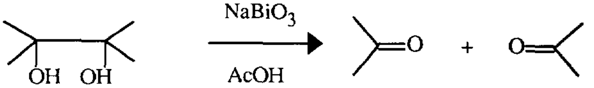
2. Bismuth(V) derivatives

2.1. Inorganic bismuthates

The synthetic potential of sodium bismuthate was first discovered in 1950 by Rigby when he demonstrated the cleavage of vicinal diols and the conversion of acyloins to α-diketones in high yields [10]. Sodium bismuthate is available commercially, is quite stable and can be used directly. Its reactivity in oxidation is comparable to that of lead tetraacetate. However, sodium bismuthate is an insoluble powder and a rather sluggish reagent in aprotic solvents: other bismuthates with various cations have been prepared and tried for the oxidation of alcohols in organic solvents. Among these, zinc bismuthate, which is easily prepared from sodium bismuthate and hydrated zinc chloride in water, prove to be an efficient and mild oxidant [11]. However, moderately stable solutions were obtained through digestion of sodium bismuthate in aqueous HF. The Bi(V) solution, which is likely to contain a mixture of $BiF_x(OH)_{6-x}^-$ complexes, is a powerful oxidizing agent and it was found to, typically, oxidize I^- to I_2, H_2O_2 to O_2 and NH_2NH_2 to N_2 [12].

2.1.1. Cleavage of 1,2-diols and related oxidations by sodium bismuthate

In glacial acetic acid medium, at or about room temperature, sodium bismuthate rapidly effects α,β-glycol fissions to aldehydes or ketones (Eq. 1); the carbonyl compounds are produced in good yields and there appears to be no tendency for aldehydes to be oxidized further. The rates of reaction are comparable with those of the corresponding lead tetraacetate oxidations [10].



(1)

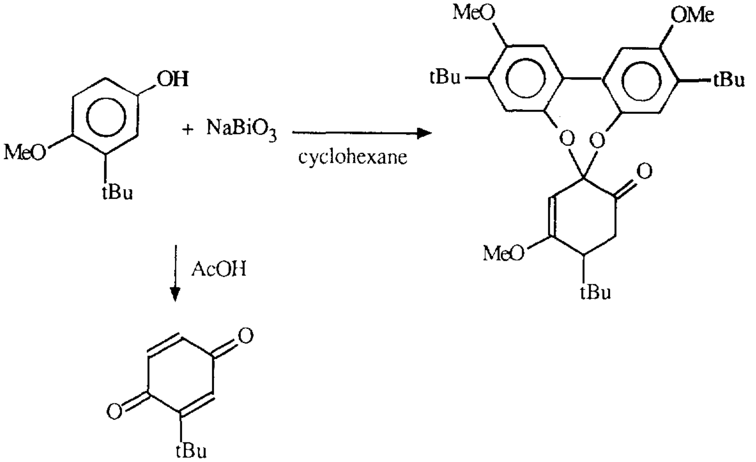
This reaction has been successfully applied to the determination of urinary corticosteroids [13]. 17-hydroxylated corticosteroids, upon oxidative cleavage of their side chain by sodium bismuthate, were converted to easily assayable 17-ketosteroïds.

This method allows the direct oxidation of urine and is well suited for routine estimations.

The closely related degradation of α-hydroxyacids to the corresponding carbonyl compounds was shown to occur with $NaBiO_3$: it is preferably performed in phosphoric acid as the solvent [10]. As typical examples, mandelic acid and lactic acid were converted at room temperature to, respectively, benzaldehyde (64%) and acetaldehyde (72%).

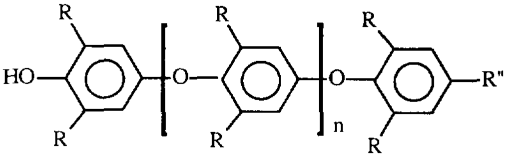
2.1.2. Oxidation of phenols by sodium bismuthate

Sodium bismuthate was also found to be a convenient oxidant of phenols [14–16]. The acidity of the solution has a decisive influence on the fate of the $NaBiO_3$ oxidation of *o*- or *p*-alkoxy-phenols. This is best illustrated in the 4-methoxy-3-t-butylphenol oxidation (Eq. 2): thus, in neutral cyclohexane solution, radical coupling occured, yielding 2,5′,10-trimethoxy-3,4′,9-tri-t-butyldibenzo[d,f]dioxepin-6-spiro-2′-cyclohexa-3′,5′-dienone, while, in acetic acid, the starting phenol was oxidatively demethylated and gave t-butyl-*p*-benzoquinone [14]. In the case of t-butylphenols, phenols bearing both methoxy and bromo groups in *o*- or *p*-positions, demethylation was preferred to debromination independent on the *ortho* or *para* position of the methoxy to the hydroxy group [15].



(2)

The potential of sodium bismuthate, as an heterogeneous one-electron oxidant for phenols in acidic medium, was utilized for the oxidative polymerization of 2,6-xylenol, durenol or 2,6-dimethoxyphenol to the corresponding polyphenylene oxides (I) [16].



(I)

The stoichiometry of the bismuthate oxidation was shown to be:

$$2NaBiO_3+4(H) \rightarrow H_2O+Bi_2O_3+2NaOH.$$

2.1.3. *Oxidation of olefins by sodium bismuthate*

$NaBiO_3$ in acetic acid oxidizes olefins to vicinal hydroxy acetates [17]. The yields are highest when a tertiary center is present in the olefin, e.g. α-methylstyrene (62% of 1-acetoxy-2-phenyl-2-propanol), while mono- and 1,2-disubstitued olefins react sluggishly and only afford low yields of hydroxy acetates.

2.1.4. *Oxidation by zinc bismuthate*

Zinc bismuthate was more recently introduced as an attractive oxidant for a number of synthetically important oxidations [11]. Primary and secondary saturated, allylic and benzylic alcohols in refluxing toluene were converted to their corresponding aldehydes and ketones in high yields (>90%). Further oxidation of the aldehydes to their carboxylic acids was not observed. Under the same conditions, α-hydroxy ketones, such as benzoïn and furoïn, were oxidized to diketones, respectively benzil (97%; 0.7 h reaction time) and furil (95%; 0.3 h reaction time). Oxidation of thiols afforded disulfides in excellent yields while thioethers were converted into sulfoxides.

2.2. *Organobismuth(V) reagents*

The oxidizing capability of arylbismuth(V) reagents has been known for many years [18], but their application for the oxidation of organic substrates was only developped from 1978 on, mainly by Barton et al.

Oxidation reactions have been performed with three types of organobismuth(V) reagents: triaryl Ar_3BiX_2, tetraaryl Ar_4BiX, and pentaaryl Ar_5Bi. The most general method for the synthesis of Ar_3BiX_2 is through oxidation of triarylbismuthine compounds which are themselves easily accessible from the reaction of Grignard reagents with bismuth trihalides (Eq. 3) [19]. Tetraphenylbismuth trifluoroacetate is readily prepared by addition (at 0 °C) of trifluoroacetic acid to a solution of pentaphenylbismuth in benzene [20], which is obtained by reacting phenyllithium with triphenylbismuth dichloride [21].

$$BiX_3+3ArMgX \rightarrow Ar_3Bi \xrightarrow{X_2} Ar_3BiX_2$$

$$Ar_3BiX_2 \xrightarrow{ArLi} AR_5Bi \xrightarrow{HA} Ar_4BiA \qquad (3)$$

2.2.1. *Oxidation reactions with Ar_3BiX_2*

2.2.1.1. *$(Ph_3BiCl)_2O/Ph_3BiCO_3$*. Oxobis(triphenylbismuth) dichloride, in the presence of an excess of potassium carbonate or sodium bicarbonate, has been found to be a mild but effective reagent for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively [22]. The reagent is easily prepared by the alkaline hydrolysis of triphenylbismuth dichloride (Eq. 4).

$$2Ar_3BiX_2 + NaOH \rightarrow (Ar_3BiCl)_2O \tag{4}$$

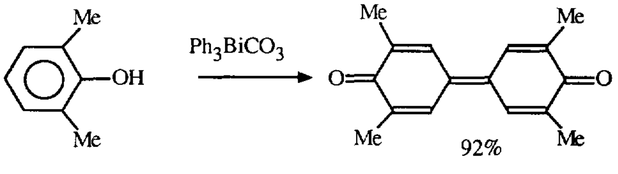
The oxidations are conveniently carried out in dichloromethane in which the reagent is readily soluble. It is particularly useful for the oxidation of allylic alcohols to the corresponding aldehydes and it can also be employed for the cleavage of 1,2-glycols. The aldehydes or ketones formed in these reactions are easily separated from the triphenylbismuth produced by the reduction of the reagent.

It was noted that oxobis(triphenylbismuth) dichloride suffers a loss of oxidizing power if the carbonate or bicarbonate used in the above process is replaced by pyridine or collidine. Further investigation led to the conclusion that a pentavalent triarylbismuth intermediate possessing a carbonate ligand is actually the active oxidant [23]. This compound is easily obtained by a metathetical reaction in aqueous acetone (Eq. 5).

$$Ar_3BiX_2 + K_2CO_3 \rightarrow Ar_3BiCO_3 + 2KX \tag{5}$$

Triphenylbismuth carbonate revealed as a useful heterogeneous oxidant for a number of functional groups. Thus, alcohols are oxidized to aldehydes or ketones, hydrazones to diazocompounds and hydrazines to azo compounds; allylic oxidation and glycol cleavage occur rapidly and in high yield. Thiols are oxidized to disulfides but the rate is much slower than that of alcohol oxidation. This results in a remarkable selectivity in the competitive oxidation of an allylic alcohol in the presence of a thiol function. This has been applied for the selective oxidation of highly functionalized natural products [24–28].

Pentavalent organobismuth derivatives were found to react with phenols essentially as efficient, regioselective O- and C-arylating reagents [20,29–31]. However, oxidative dimerisation has been observed with 2,6-dialkyl phenols. The first example was observed in the reaction of 2,6-dimethylphenol with triphenylbismuth carbonate which gave 2,2′,6,6′-tetramethylbiphenoquinone in 92% yield (Eq. 6) [20]. The more sterically hindered phenol, 2,6-di-t-butylphenol, was also oxidized to diphenoquinone (40%–50%) by Ph_3BiCO_3 or Ph_3BiCl_2 in the presence of N-t-butyl-N′,N′,N″,N″-tetramethylguanidine (BTMG) [30,31].



(6)

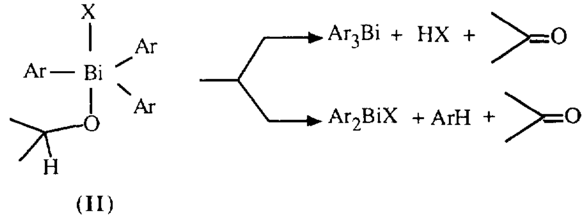
2.2.1.2. *$Ph_3Bi(OCOR)_2$*. Completely homogeneous oxidation conditions can be realized by employing triphenylbismuth diesters (acetate, benzoate, trifluoroacetate) in the presence of strong bases such as tetramethylguanidine or 1,5-diazobicyclo-[5.4.0]undec-5-ene [27]. It should be noted that $Ph_3Bi(OAc)_2$ was found to oxidize primary and secondary alcohols in an evacuated ampule to give the corresponding aldehydes and ketones [32].

2.2.1.3. Bismuth alkylperoxides: $Ph_3Bi(OOCMe_3)_2$. Bis(t-butylperoxy)triphenylbismuth, $Ph_3Bi(OOCMe_3)_2$, was recently isolated in good yield (80%) by reaction of triphenylbismuth with t-butylhydroperoxide in benzene [33]. It was found to oxidize alcohols and aromatic hydrocarbons to carbonyl compounds: thus, $PhCH_2OH$ gave PhCHO whereas $PhCH_2CH_3$ gave $PhC(O)CH_3$ [34]. Saturated linear hydrocarbons are oxidized at room temperature by the Ph_3Bi/t-BuOOH system to afford α-diketones which, under the reaction conditions, undergo further transformation to carboxylic acid anhydrides [35].

2.2.1.4. Organobismuth oxides: $(Ar_3BiO)n$. Little attention has been paid to the chemistry of organobismuth oxides. The first preparation of this class of compounds was reported in 1972 [36] through metathesis reaction between Ph_3BiCl_2 and Ag_2O to afford triphenylbismuth oxide as a white polymeric powder. While all previous attempts to oxidize triarylbismuth to the corresponding oxides, by various reagents such as hydrogen peroxide, ozone, permanganate *a.s.o.*, had been unsuccessfull, the reaction of Ar_3Bi with iodosylbenzene under ultrasonic irradiation in dichloromethane was very recently shown to generate soluble $(Ar_3BiO)_n$ [37].

In marked contrast with the analogous oxides of the lower pnictogen elements which have no oxidizing ability for organic compounds, the soluble triarylbismuth oxides were found to be mild oxidizing reagents under neutral conditions [37]. They easily converted alcohols to aldehydes, and benzoin to benzil. Hydrazobenzene was rapidly dehydrogenated to azobenzene, and triphenylphosphine was oxidized to triphenylphosphine oxide. In contrast, thiols and organic sulfides such as thioanisole and methyl-octyl-sulfide remained intact even after 6 days contact at ambient temperature.

2.2.1.5. Mechanistic aspects. The oxidation of alcohols by pentavalent derivatives of triarylbismuth was proposed to proceed through the alcoxy intermediate (**II**), which decomposes into the carbonyl derivative and triarylbismuth(III) (Eq. 7) [27].



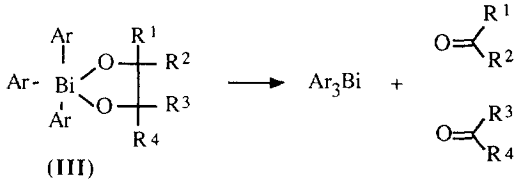
(7)

(7 bis)

(II)

The yield of recovered triarylbismuth should, if the above mechanism is operative, be comparable with the yield of the oxidized organic substrate. However, in the oxidation of (-)-carveol by either triphenylbismuth diacetate, ditrifluoroacetate or carbonate, the recovered yields of triphenylbismuth were 32%, 0% and 50% respectively, when the yields of (-)-carvone were 87%, 64% and 84% respectively. Further, NMR monitoring during the reaction of (-)-α-deuteriocarveol with tri-p-methoxyphenylbismuth carbonate in deuteriochloroform, clearly indicated the formation of p-deuterioanisole [38]. These results demonstrated that the facile cleavage of the bismuth-aryl bond [9b] results in two competitive pathways for the breakdown of the bismuth alcoxy intermediate, leading either to triarylbismuth or to a diarylbismuth derivative with ArH acting as a leaving group (Eq. 7 bis) [39]. The aryl group thus cleaved may be transferred to oxygen, nitrogen, sulfur or carbon and thus constitutes a new arylation process with a number of synthetically useful applications [9b].

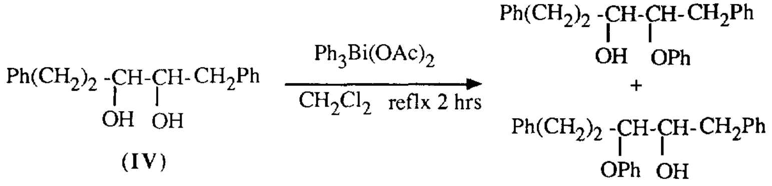
Oxidation of 1,2-glycols with triphenylbismuth carbonate is entirely different: 1,2-glycols are cleaved into the corresponding carbonyl derivatives and triphenylbismuth is quantitatively recovered in most cases [27]. In this reaction, a cyclic intermediate (**III**) was postulated to break down with exclusive formation of triphenylbismuth (Eq. 8). A catalytic bismuth system–triphenylbismuth, N-bromosuccinimide as the oxidant, K_2CO_3 — was then conceptually possible and indeed shown to be effective for the cleavage of α-glycols [39] (vide infra).



(8)

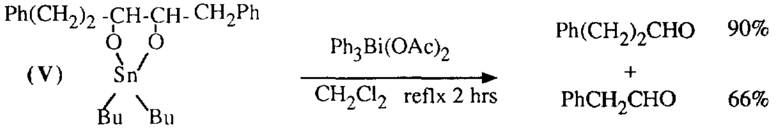
It is noteworthy that, in the molecular structure of $Ph_3Bi(OAc)_2$ determined by X-ray diffraction [40], the coordination at bismuth is intermediate between trigonal bipyramidal with apical monodentate CF_3COO groups, and pentagonal bipyramidal with equatorial bidentate CF_3COO groups. This is consistent with the intermediates (**II**) and (**III**) proposed in the above mechanisms.

The ability of organobismuth(V) reagents to function as phenylating agents not only for carbonyl compounds but also for diols has been illustrated by the reaction of 1,2-*trans*-cyclohexanediol with one equivalent of $Ph_3Bi(OAc)_2$ without added base: this resulted in 88% isolated yield of *trans*-2-phenoxycyclohexanol, i.e. in the conversion of one hydroxy group of the diol to a phenyl ether [41] and no oxidative α-diol cleavage. Similarly, the reaction of $Ph_3Bi(OAc)_2$ on diol (IV) afforded an equimolar mixture of the two possible monophenylethers (Eq. 9).



$$\underset{\text{(IV)}}{Ph(CH_2)_2\text{-}\underset{OH}{CH}\text{-}\underset{OH}{CH}\text{-}CH_2Ph} \xrightarrow[CH_2Cl_2\ \text{reflx 2 hrs}]{Ph_3Bi(OAc)_2} Ph(CH_2)_2\text{-}\underset{OH}{CH}\text{-}\underset{OPh}{CH}\text{-}CH_2Ph + Ph(CH_2)_2\text{-}\underset{OPh}{CH}\text{-}\underset{OH}{CH}\text{-}CH_2Ph \qquad (9)$$

In marked contrast, the covalent Sn derivative of diol (V), afforded $PhCH_2CHO$ and $PhCH_2CH_2CHO$ (Eq. 10) [42] thus recalling the oxidative cleavage of a free diol with Ph_3BiCO_3 in the presence of a base [27].

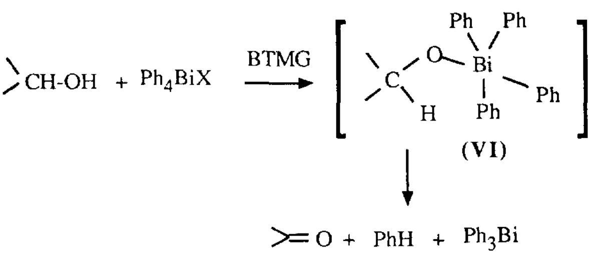


(10)

2.2.2. Oxidations with Ar_4BiX

Tetraphenylbismuth mono(trifluoroacetate) was obtained in high yields (90%) by reacting trifluoroacetic acid with pentaphenylbismuth in benzene under an argon atmosphere at 15 °C [43]. Under neutral or slightly acidic conditions, $Ph_4Bi(OCOCF_3)$ O-phenylates primary alcohols. In contrast, under basic conditions, the reaction of the Bi(V) reagent with alcohols gives exclusively oxidation [44]. Thus, in the presence of N-t-butyl-N′,N′,N″,N″-tetramethylguanidine (BTMG), neopentyl alcohol was oxidized to the aldehyde in good yields (78%); similarly, 3β-cholestanol was oxidized to 3β-cholestanone by tetraphenylbismuth ester in 92% yield in 12 h at room temperature.

Under basic conditions, it thus appears that the ester function behaves as a good leaving group: a covalent intermediate (VI) is proposed to be formed and to decompose in a second step to the carbonyl derivative, tripenylbismuth and benzene (Eq. 11). These could be identified after the 2 days reaction of 3β-cholestanol with tetraphenylbismuth ester in 1,2-dimethoxyethane and distillation of the solvent: benzene was easily detected, while chromatography of the residue afforded cholestanone and triphenylbismuth (75%). Further, ^1H NMR monitoring during the oxidation of neopentyl alcohol by $Ph_4Bi(OCOCF_3)$ in the presence of BTMG, allowed the detection of intermediate (VI), i.e. $Ph_4Bi(OCH_2tBu)$.



(11)

2.2.3. Oxidations with Ar_5Bi

Pentaphenylbismuth is readily prepared by the reaction of triphenylbismuth dichloride with phenyllithium; it is not very stable in air at room temperature but it can be stored for months at −20 °C [45]. It should be noted that Ph_5Bi being quite sensitive, all reactions are to be performed in an inert solvent like benzene at room temperature under an argon atmosphere.

Ph_5Bi was found to oxidize benzylic alcohol to benzaldehyde (45%), 3β-cholestanol to 3β-cholestanone (46%): these results show that Ph_5Bi is a much poorer oxidizing reagent than Ph_3BiCO_3 for which much higher yields in oxidized products, respectively 93% and 84%, are obtained under the same conditions.

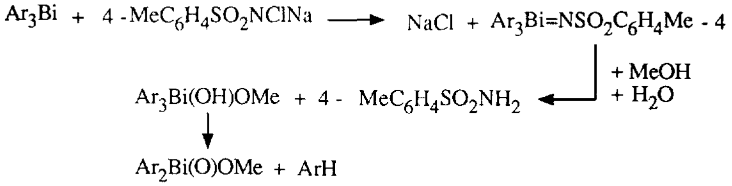
In 1975, Razuvaev et al. [46] showed that Ph_5Bi undergoes easy Bi–C bond cleavage in the presence of water, pyridine, isopropyl alcohol or phenol. Isopropyl alcohol is simultaneously oxidized to acetone (Eq. 12).

$$Ph_5Bi + (CH_3)_2CHOH \rightarrow Ph_3Bi + PhH + (CH_3)_2CO \qquad (12)$$

When reacted with PhOH, Ph_5Bi was in fact demonstrated to be a useful reagent for specific *ortho*-phenylation [45].

2.2.4. Oxidations with $Ar_2Bi(O)OR$

The esters of diarylbismuthinic acids, $Ar_2Bi(O)OR$, can be obtained by heating Ar_3Bi with sodium N-chloro-4-toluenesulfonamide in a mixture of benzene and methanol (Eq. 13) [47]. Surprisingly, all previous attempts to prepare organobismuth(V) compounds containing two organic groups had failed: the authors attributed their successfull results to the prior formation of highly reactive bismuthonium imines.



$$\begin{tikzcd} Ar_3Bi + 4\text{-}MeC_6H_4SO_2NClNa \arrow[r] & NaCl + Ar_3Bi{=}NSO_2C_6H_4Me\text{-}4 \arrow[dl, "+MeOH\ +H_2O"] \\ Ar_3Bi(OH)OMe + 4\text{-}MeC_6H_4SO_2NH_2 \arrow[d] & \\ Ar_2Bi(O)OMe + ArH & \end{tikzcd}$$

(13)

Methyl bis(1-naphtyl)bismuthinate was selected because of its stability and easy accessibility and examined for its oxidizing ability. When heated with benzoïn in benzene for 2 h, benzil was obtained together with naphtalene and metallic bismuth. 1,1,2,2-Tetraphenylethanediol gave benzophenone, hydrazobenzene gave azobenzene, both in quantitative yields. However, cyclohexane-1,2-diol and 1-phenylethane-1,2-diol were found to not react with methyl bis(1-naphtyl)bismuthinate [47].

The alkoxyl group attached to bismuth in alkyl diarylbismuthinates was found to be very labile and to allow ester exchange reaction with alcohols to occur with unusual ease [47]. This has been applied for the mild acetylation of amides, thioamides, ureas and thioureas with acetic acid [48]: simple stirring of these compounds in acetic acid in the presence of methyl bis(1-naphtyl)bismuthinate at room temperature afforded the corresponding N-acetyl derivatives in high yields.

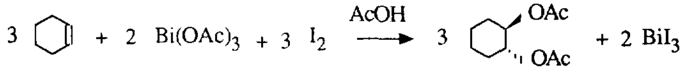
3. Bismuth(III) derivatives

3.1. Bismuth trioxide and related reagents

The oxidizing potential of bismuth(III) was first observed as a side-reaction in benzoin oxidation by sodium bismuthate: metallic bismuth was precipitated and was taken to indicate that some compound of tervalent bismuth had been further reduced [49]. It was indeed found that acyloins are readily oxidized to 1,2-diketones by warming them in media containing acetic acid with bismuth oxide, Bi_2O_3, which is reduced to bismuth (0). This bismuth trioxide oxidising method is best applied to sensitive acyloins: benzil (96%), anisil (95%), piperil (97%) or furil (92%) could be produced in very high yields. The reaction appears to be specific of α-hydroxyketones and was utilized as a convenient qualitative test for acyloins [48], e.g. in alkaloid structure assignments [50]. Further, Djerassi et al. took advantage of the specificity of bismuth oxide for acyloins in the conversion of a steroïdal sapogenin, hecogenin, to cortisone [51].

Bismuth triacetate, which is initially formed in the reaction medium, is the actual compound reduced: bismuth triacetate can be used directly but was reported to offer no advantage over the mixture of Bi_2O_3 and acetic acid [49].

More recently, bismuth triacetate in acetic acid and in the presence of iodine, was reported to achieve olefin diacetylation with very high stereoselectivity in both 'wet' and 'dry' reactions [52]: yields of *trans*-diacetates from dry reactions were in the range 60%–70% (Eq. 14) while yields of *cis*-diacetates from wet reactions were 70%–90% (Eq. 15). It is important to note that, in these reactions, the actual oxidant is iodine.



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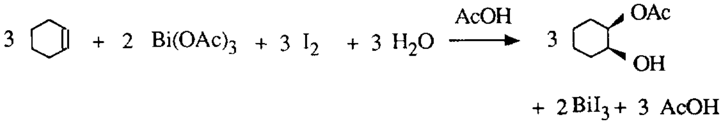
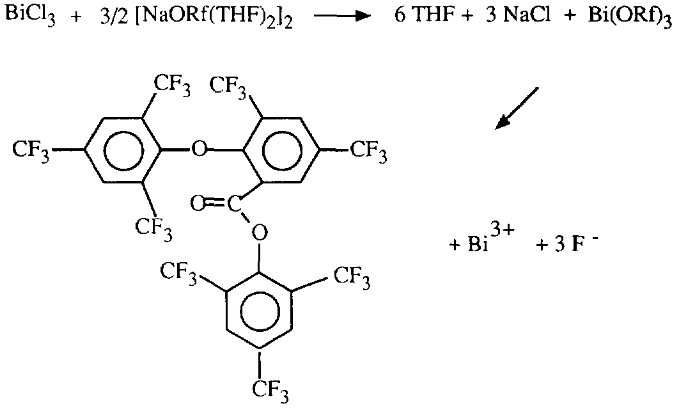


(15)

3.2. *Miscellaneous Bi(III) reagents*

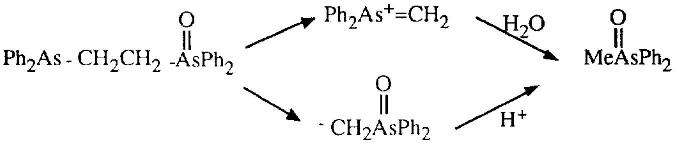
$BiCl_3$ reacts with sodium 2,4,6-tris(trifluoromethyl)phenoxide (NaORf) to produce an unusual condensation product: $RfOC_6H_2(CF_3)_2C(O)ORf$ (Eq. 16) [53]. It is believed that the formation of this condensation product proceeds through the unstable $Bi(ORf)_3$ intermediate, in which activation of the benzylic C–F bonds occurs because of the presence of bismuth(III). The mechanism of this peculiar coupling/rearrangement process remains unclear [54].



(16)

Arylthiolato complexes of bismuth(III) are easily accessible via protonolysis of a $Bi(NR_2)_3$ metal amide with the corresponding thiol or, alternatively, through reaction of lithium thiolate with $BiCl_3$. The resulting $Bi(SAr)_3$ complexes are stable in the solid state. However, heating $Bi(SPh)_3$ in toluene under reflux in air rapidly yields 84% of $(PhS)_2$ [55]. Similarly, the solutions of the sterically more hindered trimethyl-, triisopropyl- or even tri-t-butyl-benzenethiolates of bismuth(III) are prone to air oxidation with formation of the corresponding diaryl disulfides [56].

Air oxidation of the ligand L has been reported for several $BiX_3 \cdot L$ complexes. Thus, the reaction between $BiBr_3$ and dimethylphenylphosphine $PhPMe_2$ led to the isolation of $[Bi_2Br_6(PMe_2Ph)_2(OPMe_2Ph)_2]$ which contains two phosphane and two phosphane oxide ligands [57]. An other elegant example of specious ligand rearrangement was provided when $BiCl_3$ was allowed to react with tris(dimethylamino)phosphane selenide, $[(Me_2N)_3PSe]$: the bismuth(III) salt $[(Me_2N)_3PSeSeP(NMe_2)_3][BiCl_4]_2$ was formed rather than the anticipated $BiCl_3 \cdot 2SeP(NMe_2)_3$ adduct [58]. This ligand coupling was supposed to follow from air oxidation in the presence of Bi(III) chloride. Perharps the most surprising aspect reported so far, among these in situ ligand oxidation, is the C–C cleavage of diarsinoethane by serendipitous introduction of air/water molecules in conjunction with bismuth(III) chloride [59]. Direct treatment of $BiCl_3$ with dpae, $Ph_2AsCH_2CH_2AsPh_2$, provides the 1:1 molecular adduct $BiCl_3 \cdot$dpae which, in attempting to grow crystals, afforded pale needles of $[BiCl_3(As(O)MePh_2)(Ph_2As(O)CH_2CH_2As(O)Ph_2)]_n$where all As(III) have been oxidized to As(V)=O and where one C–C bond has been cleaved. This has been rationalized by considering that the 'half-oxidized' As(III)-As(V) ligand undergoes the cleavage (Eq. 17). The role of bismuth in this cleavage remains unclear.

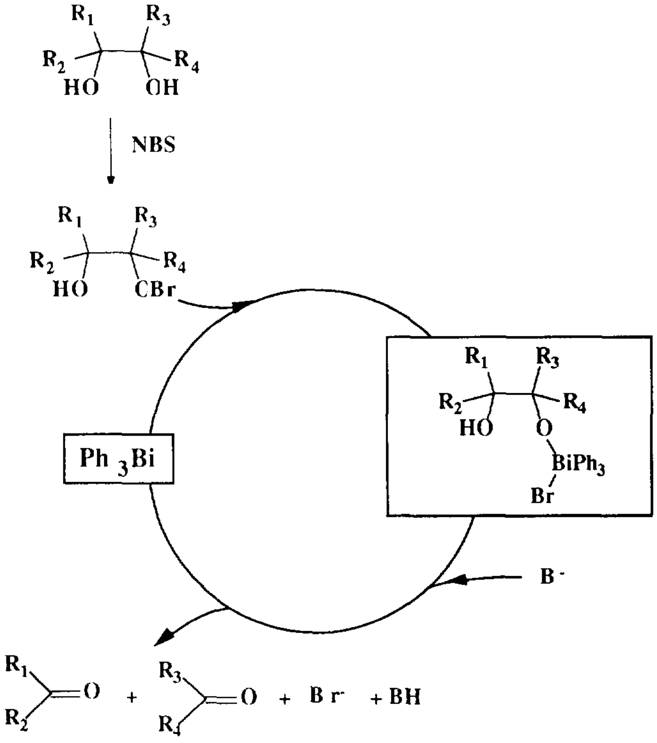


(17)

3.3. *Catalytic cleavage of α-glycols by the Ph₃Bi/NBS system*

That Ph_3Bi could be quantitatively recovered after the oxidation of 1,2-glycols by Ph_3BiCO_3 (see Section 2.2.1.5., Ref. [38]) led to the conception of a Bi(V)/Bi(III)/oxidant catalytic system for the cleavage of α-glycols. Hydrogen peroxide in the presence of sodium hydrogenocarbonate, or t-butylhydroperoxide, were first used as oxidant for Ph_3Bi: they indeed allow catalytic cleavage of hydrobenzoin to benzaldehyde by triphenylbismuth [38], but this system was found to be restricted to hydrobenzoïn.

A more general system was realised by use of N-bromosuccinimide (NBS) as oxidant for Ph_3Bi [39]. The presence of potassium carbonate and a small amount of water are essential. Preparative useful yields of aldehydes and ketones were obtained with only 1% of triphenylbismuth. The reaction is rapid and yields are



Scheme 1

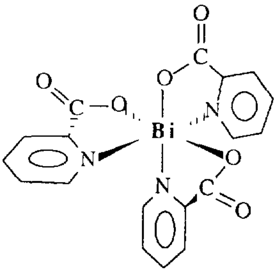
comparable with, or superior to those obtained in the presence of lead tetraacetate or sodium periodate.

This catalytic system was found to have a different mechanism from the process observed with the stoichiometric $Ph_3Bi(V)$ reagents previously studied: the catalytic system cleaves *cis*- and *trans*-decalin-9,10-diols at nearly the same rate, whereas the stoichiometric reagents do not cleave the *trans*-9,10-diol. This was explained by the mechanism depicted in Scheme 1. In the first step, NBS oxidises the α-glycol to a glycol monohypobromite and succinimide: isolation of the pure glycolhypobromite was not possible but its presence was evidenced by spectroscopy. In the following steps, insertion of triphenylbismuth into a hypobromite bond is followed by fragmentation of the resulting Bi(V) intermediate. The role of the base is essential as a trap for any acid formed or as a catalyst for the cleavage of the bismuth intermediate. The role of water is also important: it can catalyse the formation of a hypobromite species or solubilise K_2CO_3.

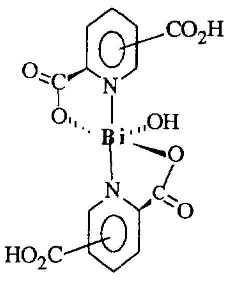
3.4. *Oxidative carbon-carbon bond cleavage catalyzed by Bi(III) carboxylates*

A new class of bismuth oxidation catalysts was recently described based on oxobismuth(III) carboxylates.

The reaction of Bi_2O_3 with a series of pyridine (py) and pyrazine (pz) monocarboxylic acids afforded tris-carboxylates, e.g. $[py(COO)]_3Bi$, (**VII**), whereas hydroxo-bis-carboxylates, e.g. $[py(COO)(COOH)]_2Bi(OH)$, (**VIII**), were isolated with pyridine dicarboxylic acids [60].



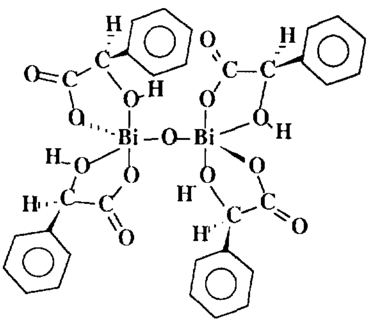
(VII)



(VIII)

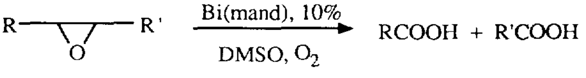
These latter compounds were found to act as rather poor activators of dimethylsulfoxide (DMSO) in oxidation reactions [61]. The molecular structure, determined by X-ray diffraction for the dimeric bismuth-DMSO adduct, $\{[py(COO)_2][py(COO)(COOH)]Bi(DMSO)\}_2$, which was isolated in the presence of DMSO, showed only little lenghthening of the S—O bond with respect to the free ligand [62].

In a search for a better environment for Bi, α-hydroxycarboxylates were prepared [63]. The reaction of bismuth trioxide with mandelic acid ($mandH_2$) resulted in the 2:1 $[(mandH)_2Bi]_2(\mu\text{-}O)$ complex, Bi(mand), (**IX**), where only the carboxylato group of the ligand is deprotonated.



Bi(mand), (**IX**)

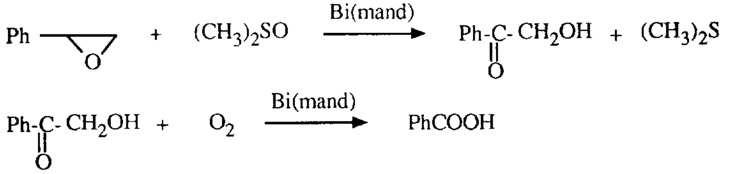
Bi(III)-mandelate constitutes an efficient catalyst for the oxidative C–C cleavage of epoxides into carboxylic acids in DMSO (Eq. 18), a transformation which was unprecedented. It is noteworthy that no reaction occured with Bi_2O_3 and that only traces of acids were detected in the presence of bismuth acetate [64].



$$R\text{-epoxide-}R' \xrightarrow[\text{DMSO, } O_2]{\text{Bi(mand), 10\%}} RCOOH + R'COOH \quad (18)$$

The catalytic effect of bismuth(III)-mandelate was studied towards styrene oxide, taken as a typical aryl epoxide. The reaction was found to be not only faster but to yield a different product distribution under oxygen. It was shown that phenacyl alcohol is in fact the product from the DMSO oxidation and that oxygen is necessary in the C–C cleavage of phenacyl alcohol to benzoic acid (Eq. 19). Bismuth mandelate acts as a catalyst in both steps [65].

The process was applied to the oxidative C–C cleavage of a series of styrene epoxides; the reaction is accelerated in the presence of electron-donating groups substituting the aryl ring [65].

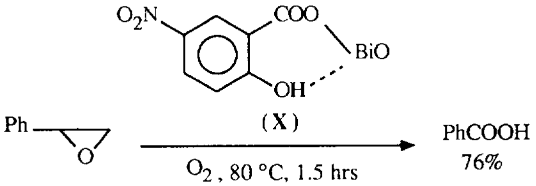


(19)

As expected from Eq. (20), Bi(mand) catalyses the oxidative C–C cleavage by molecular oxygen of a series of α-ketols into the corresponding acids. The catalysis proceeds in DMSO or DMF, under mild conditions, with linear or cyclic, aliphatic or aromatic α-ketols which are converted in carboxylic acids in medium to good yields (40% to 80%) [66].

$$R_2COCHOHR_2 \xrightarrow[O_2]{\mathrm{Bi(III)mandelate(5\%molar)}} R_1COOH + R_2COOH \qquad (20)$$

A series of Bi(III) oxo-carboxylates has recently been obtained with monocarboxylic acids HL derived from salicylic acid: these ligands were chosen because they should be more resistant in oxidizing conditions and, therefore, bring up long life catalysts [67]. The LBiO oxo salicylates do catalyze the C–C oxidative cleavage of epoxides and α-hydroxyketones: both the rate of the reaction and the selectivity in carboxylic acid compare well with the results obtained in the presence of Bi(mand) as a catalyst. It is noticeable that the presence of an electron-releasing substituent on the aromatic ring of the salicylato ligand retards the oxidation process whereas electron-attracting groups, such as NO_2 in complex (**X**), accelerates the reaction: total epoxide consumption required 2 h at 80 °C in the presence of 5% of (X) as a catalyst, and afforded 76% yield of benzoic acid. (Eq. 21) [68].



(21)

3.5. *Oxidation of alkenes in the presence of heterobimetallic systems including bismuth*

Various systems have recently been proposed as alternatives to the Pd/Cu-cocatalyzed Wacker process for the ketonisation of alkenes. Thus, rhodium chloro complexes in association with bismuth trichloride and lithium chloride were found to be effective in the oxidation of terminal olefins to methylketones by dioxygen [69]. The proposed key intermediates are a hydroxo- ($HRhCl_xL_y$) and a hydroperoxo- ($HOORhCl_xL_y$) rhodium complexes. Later, Bregeault reported new catalytic systems, based on palladium(II) chloro complexes and bismuth trichloride in anhydrous alcoholic solvents: these activate molecular oxygen and terminal alkenes to yield the corresponding ketones [70]. One atom of oxygen is incorporated into the olefinic substrate while the other is involved in a cooxidation process of the solvent: with oct-1-ene in ethanol, acetaldehyde and diethyl acetate were found to be the main cooxidation products beside the three possible ketones, in which octan-2-one represents 65%. It is suggested that, in this catalysis, the key Pd-H and Pd-OOH intermediates are stabilized by $BiCl_3$ in the mixed $[HPdCl_x(BiCl_3)_{3-x}]^{(x-1)-}$ and $[HOOPd(BiCl_3)_{3-x}]^{(x-1)-}$ complexes.

It should be noted that the autoxidation of cyclohexene catalyzed by insoluble bismuth sulfate in acidic solvents was reported to selectively afford 1-cyclopentene-1-carboxaldehyde [71].

4. Conclusions

The oxidizing potential of bismuth(V) and bismuth(III) had already been shown in the early fifties for inorganic derivatives. Later on, the utility of organobismuth(V) compounds as mild and selective stoechiometric oxidants in organic sysnthesis was demonstrated. However, due to the weakness of the Bi–C bond, arylation reactions frequently compete with oxidation and have in fact found numerous applications in synthesis as arylating agents.

The originality and the advantages of the recently developped Bi(III) oxo-carboxylate/O_2 system can be highlighted with the following characteristics: (i) the reactions are catalytic in bismuth(III); (ii) the system presents a very interesting functional group selectivity; (ii) the use of molecular oxygen at atmospheric pressure as the oxidant is of particular interest, as a simple, cheap and clean reagent and (iv) bismuth oxo-carboxylates are stable complexes, easy to prepare. They should find a range of applications as catalysts for the selective oxidation of organic compounds by molecular oxygen.

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