Bismuth(III) Acetate: A Cheap, Efficient, and Environmentally Acceptable Reagent for 'Wet' and 'Dry' Prevost Reactions

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cis- and *trans-*Diol derivatives can be prepared from alkenes by reaction with bismuth(III) acetate in 'wet' and 'dry' acetic acid respectively.

Bismuth(III) acetate can be used in both the 'wet' and 'dry' Prevost[1,2] reactions as shown in Scheme 1.

Bismuth(III) acetate was prepared either by literature methods from bismuth(III) nitrate[3] or *in situ* from cheap and readily available bismuth(III) oxycarbonate, $(BiO)_2CO_3$. It is also commercially available. In a typical 'dry' reaction, bismuth oxycarbonate (12.3 mmol) was heated under reflux for 1 h with freshly dried acetic acid (40 cm^3) containing acetic anhydride (*ca.* 17%). Cyclohexene (36.6 mmol) and iodine (37.0 mmol) were added to the cooled solution and the mixture was refluxed for 17.5 h. *trans*-1,2-Diacetoxycyclohexane was obtained in good yield (80%, after distillation) and no trace of the *cis*-diacetate could be detected by high-field ^1H n.m.r. spectroscopy (200 MHz).

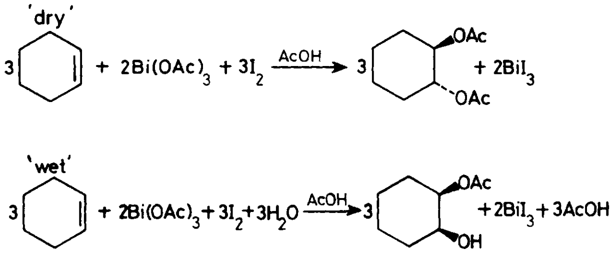
A typical 'wet' reaction used similar quantities of reagents except that Laboratory Reagent grade acetic acid (containing *ca.* 0.6% w/w water) was used and sufficient water (2.5 cm^3) was added to the freshly prepared solution of bismuth(III) acetate in acetic anhydride–acetic acid to convert the remaining acetic anhydride into acetic acid. The product was a mixture of hydroxyacetate and diacetate and on acetylation with acetic anhydride/pyridine gave *cis*-1,2-diacetoxycyclohexane (93%) with no trace of the *trans*-isomer indicated by ^1H n.m.r. spectroscopy. A similar reaction of 1-methylcyclohexene but under milder reaction conditions (90 °C, 2.5 h) gave *cis*-2-acetoxy-1-methylcyclohexanol (95%) whose stereochemistry was confirmed by reduction to the *cis*-diol using $LiAlH_4$ (see Table 1).

Table 1. Yields of diacetates and iodoacetates.

	% Yield		
Reactant	*trans*-Diacetate from 'dry' reaction	*cis*-Diacetate from 'wet' reaction[a]	Iodoacetate
Cyclohexene	80	93	84
1-Methylcyclohexene	—	95[b]	84
3-Methylcyclohexene	67	89	91
4-Methylcyclohexene	62	86	91
4-t-Butylcyclohexene	66	70	86
α-Methylstyrene			91
(*E*)-1-Phenylpropene			70

[a] After conversion of hydroxy acetate to diacetate using Ac_2O/pyridine. [b] Yield of hydroxyacetate.

Reactions of 3- and 4-methylcyclohexenes and of 4-t-butylcyclohexene were also carried out under similar conditions. Yields of *cis*-diacetates from 'wet' reactions were in the range 70—90% and yields of *trans*-diacetates from 'dry' reactions were in the range 60—70%. In contrast to the reactions of cyclohexene itself, the reactions of these substituted cyclohexenes gave *ca.* 5% of the *cis*-products in the 'dry' reactions and a similar amount of *trans*-products in the 'wet' reactions. The *cis*- and *trans*-products were mixtures of stereoisomers except for the product of the 'wet' reaction of 3-methylcyclohexene which surprisingly gave only 3α-methyl-2β-1α-diacetoxycyclohexane after acetylation, in contrast to the silver or thallium promoted reaction of 3-t-butylcyclohexene which gave a mixture of stereoisomers.[4]



Scheme 1

In the 'wet' reactions it was important to keep the water concentration around 0.6% w/w. Addition of further amounts of water led to loss of stereospecificity in the reaction with cyclohexene. Thus the *cis*:*trans* ratios for a reaction in 10% aqueous acetic acid was 64:36 (73% yield) and 59:41 (80% yield) for a reaction in 50% aqueous acetic acid. The effect of water is thus similar to that on reactions with silver(I) and mercury(II)[5] but different from thallium(I) where the reaction remains *cis*-stereospecific even in 50% aqueous acetic acid.[2] It is possible that as the iodides of silver(I), mercury(II), and bismuth(III) are stronger Lewis acids than the iodide of thallium(I),[6] they can catalyse the equilibration of one of the intermediates leading to the *cis*- and *trans*-hydroxyacetates. The product *cis*-1-hydroxy-2-acetoxycyclohexane was shown not to equilibrate under the reaction conditions in the presence of the metal iodides.

Bismuth(III) acetate can thus be used to give *cis*- or *trans*-diacetates (or diols) in good yields with very high stereoselectivity. The reaction has advantages over the analogous reactions using silver(I),[1,7] mercury(II),[8] thallium(I),[2] and copper(II)[9,10] in that the bismuth residues are non-toxic and bismuth oxycarbonate is inexpensive. As all three acetoxy groups can be transferred, less metal is used than in reactions involving silver(I), thallium(I), or mercury(II) compounds. The bismuth based reactions also have advantages over the more recently developed systems based on $I_2/KIO_3/KOAc$,[11] and $Te^{IV}O_2/LiBr/AcOH$[12] which give only the *cis*-addition products in single-stage reactions.

The intermediate iodoacetoxy-compounds can be isolated from reactions using the bismuth(III) acetate. Thus iodoacetates were prepared from cyclohexene, 1-methylcyclohexene, α-methylstyrene, and (*E*)-1-phenylpropene when bismuth(III) acetate (from bismuth oxycarbonate), iodine, and alkene were allowed to react in dry acetic acid at ambient temperature in a molar ratio of 1:3:3. The substituted cyclohexenes gave mixtures of stereo- and regio-isomeric *trans*-cyclohexane-1,2-iodoacetates in good yields (see Table 1). Interestingly, reaction of 3-methylcyclohexene gave predominantly 3α-methyl-2β-iodo-1α-acetoxycyclohexane with only *ca.* 10% of minor isomers. The yields from these reactions are thus comparable with or better than those obtained from the established methods[4,8] and the recently reported methods based on $I_2/CuO{\cdot}HBF_4/AcOH$[13] and $I_2/Al_2O_3/KOAc$[14] systems.

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