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Asymmetric trimethylsilylcyanation of aldehydes utilizing chiral bismuth compounds. A frontier in bismuth mediated synthetic reactions †

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Abstract: Bismuth(III) chloride ($BiCl_3$) was found to work efficiently as a versatile catalyst for cyanation of aldehydes with trimethylsilyl cyanide to afford the corresponding cyanohydrins in high yields. Triphenylbismuthan (Ph_3Bi) is also effective. The reaction has been applied to the asymmetric cyanation of a variety of aldehydes in high yields with moderate to good enantioselectivities by use of a chiral bismuth catalyst prepared *in situ* from $BiCl_3$ and (2*R*,3*R*)-(+)-diethyl tartrate. © 1997 Elsevier Science Ltd. All rights reserved.

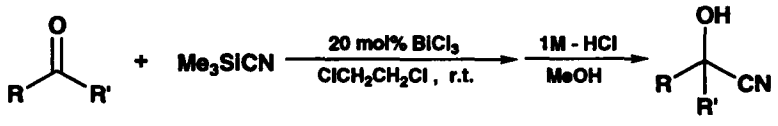
Most metallic elements have been used for synthetic purposes with varied usefulness and selectivity. Among group 15 elements, bismuth metal is cheaper and less toxic than arsenic or antimony and has enhanced metallic character. However, the usefulness of this element in organic synthesis had been little recognized until the last decade, when extensive work by Barton, Suzuki and ourselves revealed the uniqueness and promising potential of bismuth as a reagent for organic transformations.[1] In the course of our investigations, we found and reported some useful reactions by using metallic bismuth and $BiCl_3$.[2] To our knowledge, however, asymmetric reactions utilizing chiral bismuth compounds are hitherto unknown. In order to explore the new field of asymmetric synthesis by use of chiral bismuth compounds, we decided to examine the asymmetric cyanation of aldehydes as our preliminary study since the products, optically active cyanohydrins, are good precursors for the synthesis of optically active α-hydroxy carboxylic acids, β-hydroxy amines, etc. Also, many methods, using a variety of catalytic systems, have been developed for such enantioselective hydrocyanations[3] and can serve for comparison.

Recently, we showed that $BiCl_3$ is a good activator for cyanation reactions of aldehydes and ketones with trimethylsilyl cyanide.[4] In the course of our continuing investigations, we also found that triphenylbismuthan (Ph_3Bi) activates the reaction for aldehydes. We now wish to record full details of the $BiCl_3$ and Ph_3Bi mediated trimethylsilylcyanations and to report the first asymmetric trimethylsilylcyanations of aldehydes utilizing chiral bismuth compounds.

Most commercially available bismuth(III) salts are low in price, non-toxic and easy to handle, and several recent reports show their usefulness as catalysts.[5,6] We have already reported that $BiCl_3$ is a new efficient catalyst for Aldol and Michael reactions[2d,f] and for $BiCl_3$–Al mediated allylation of aldehydes with allylic halides.[2c] Similarly, when aldehydes and ketones were treated with trimethylsilyl cyanide in the presence of 20 mol% of bismuth trichloride in 1,2-dichloroethane at room temperature, the reactions proceeded smoothly to give the cyanated products in excellent yields (Scheme 1).

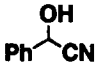
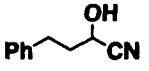
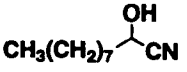
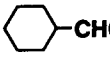
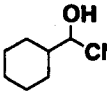
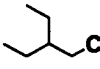
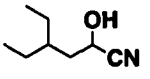
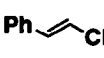
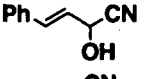
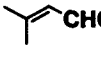
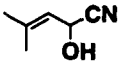
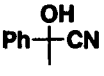
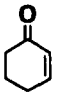
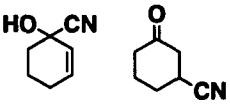
† Dedicated to Professor Herbert C. Brown on the occasion of his 85th birthday.

* Corresponding author.



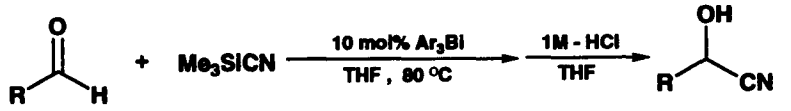
Scheme 1.

Table 1. Cyanation of aldehydes and ketones according to Scheme 1

Entry	Aldehyde or Ketone	Product	Time / min.	Yield / %
1	PhCHO		20	quant.
2	$Ph(CH_2)_2CHO$		20	quant.
3	$CH_3(CH_2)_7CHO$		20	quant.
4			20	quant.
5			20	quant.
6			60	quant.
7			60	80
8	$PhCOCH_3$		120	quant.
9			120	67 / 31

Some typical results are described in Table 1. Both aromatic and aliphatic aldehydes reacted smoothly to afford the corresponding cyanohydrins in quantitative yields. When acetophenone was used, the desired product was also obtained in quantitative yield, although a prolonged reaction time was needed. When α,β-unsaturated aldehydes were used, 1,2-addition products were obtained exclusively, but a mixture of 1,2- and 1,4-adducts was obtained using cyclohexenone.

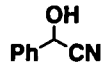
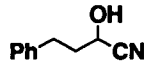
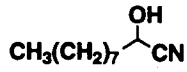
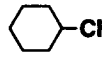
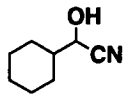
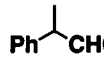
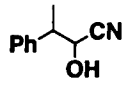
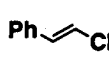
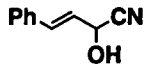
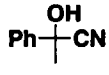
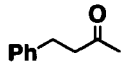
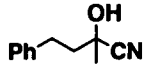
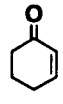
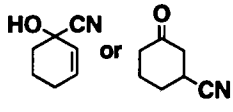
Although many catalyst have been employed for trimethylsilylcyanation reactions,[7] $BiCl_3$ is cheap and commercially available and offers a new efficient process under extremely mild conditions [room temperature and weakly acidic ($BiCl_3$ is a weak Lewis acid)]. We also found that Ph_3Bi and $(p\text{-}MeOC_6H_4)_3Bi$ were efficient Lewis base catalysts for the reaction of aldehydes (Scheme 2).[8]



Scheme 2.

Some of the results are described in Table 2. Both aromatic and aliphatic aldehydes reacted smoothly

Table 2. Cyanation of aldehydes and ketones according to Scheme 2

Entry	Aldehyde or Ketone	Product	Time / h	Yield / % [a]
1	PhCHO		8	64 (86)
2	$Ph(CH_2)_2CHO$		4	80 (quant.)
3	$CH_3(CH_2)_7CHO$		4	quant. (quant.)
4			4	64 (91)
5			4	79 (quant.)
6			6	93 (quant.)
7	$PhCOCH_3$		8	0 (0)
8			8	0 (0)
9			9	0 (0)

a) The first figure is for use of Ph_3Bi and the figure in parentheses for when $(p\text{-}MeOC_6H_4)_3Bi$ was used as a catalyst.

to afford the corresponding cyanohydrins in good yields. Cinnamaldehyde gave the 1,2-addition product but the desired products were not obtained at all when ketones were used.

In view of the success in utilizing $BiCl_3$ for trimethylsilylcyanation of aldehydes, we turned our attention to the development of asymmetric counterparts. First, the reaction of benzaldehyde with trimethylsilyl cyanide was examined in the presence of 20 mol% of bismuth trichloride and an excess of a variety of chiral co-catalysts that have found considerable use for asymmetric induction. The results are shown in Table 3.

No asymmetric induction was observed with any of the chiral co-catalysts, as shown in Table 3. In addition, the reactions were much slower than in the absence of the co-catalysts. In particular, almost no reaction was observed in the conditions shown in entries 1, 4 and 5. The reason for the low reactivity of this system is probably that the chiral co-catalysts complex with the bismuth trichloride and decrease its Lewis acidity.

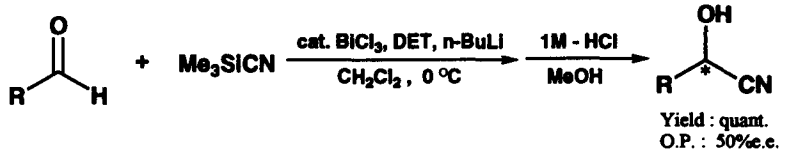
In order to improve the system, therefore, we examined the generation of the chiral bismuth catalyst *in situ* from equimolar quantities of bismuth trichloride and a chiral diol. (2*R*,3*R*)-(+)-Diethyl tartrate (L form of DET) was chosen as the chiral auxiliary for the initial investigation since it is not expensive and has C_2 symmetry. The reaction of benzaldehyde with trimethylsilyl cyanide was examined with 20 mol% of catalyst prepared *in situ* from $BiCl_3$ and the lithium salt of (2*R*,3*R*)-(+)-diethyl tartrate in Et_2O at 0°C for 1 h (Scheme 3).

Surprisingly, a remarkable rate enhancement resulted. Next, we examined several reaction conditions

Table 3. The effect of chiral co-catalysts

Entry	Chiral co-catalyst	Time / h	Yield / %	%e.e. [a]
1	SAMP	24	0	0
2	L-(-)-Sparteine	19	quant.	0
3	L-(-)-Sparteine [b]	26	quant.	0
4	(2R,3R)-(+)-Diethy tartrate	24	trace	0
5	(R)-(+)-BINOL	24	trace	0

a) Enantiomeric excesses were determined by specific rotation or chiral HPLC analysis.
b) The reaction was examined without $BiCl_3$.



Scheme 3.

Table 4. The effect of temperature on the reaction

Entry	Temp. / °C [a]	Time / h	Yield / %	%e.e. [b]
1	r.t.	19.0	quant.	25
2	0	0.5	quant.	50
3	- 23	0.5	quant.	58
4	- 45	0.5	quant.	35
5	- 78	6.0	65	38

a) Reaction temperature.
b) Enantiomeric excesses were determined by specific rotation.

in an attempt to improve the asymmetric induction. First, we examined the effect of temperature on the reaction (Table 4).

The enantioselectivity was much influenced by the reaction temperature. The best performance was at −23°C, while at lower temperatures the reaction was slow and at higher temperatures the enantioselection was poorly controlled. The conditions during preparation of the chiral bismuth catalyst were also important and the best asymmetric induction was observed when it was prepared *in situ* at 0°C for 3 h with a slight excess of $BiCl_3$. It would be of interest to know the structure of the chiral bismuth catalyst but this has not been determined due to the difficulty in purification and low solubility in any solvent.

Solvent effects for the reaction were also investigated and the results are summarized in Table 5.

The results showed that CH_2Cl_2 was the best solvent for asymmetric induction. $ClCH_2CH_2Cl$ was only slightly poorer, but polar solvents and several other solvents were not useful for asymmetric induction although the reaction took place in reasonable yield.

Next, we examined the use of other chiral bismuth catalysts (Table 6).

As shown in Table 6, diethyl tartrate gave the best asymmetric induction while the less hindered dimethyl tartrate and more hindered diisopropyl tartrate were not as effective. Therefore, we applied

Table 5. The effect of solvents

Entry	Solvent	Time / h [a]	Yield / %	%e.e. [b]
1	CH_2Cl_2	0.5	quant.	65
2	$ClCH_2CH_2Cl$	0.5	92	53
3	$CHCl_3$	8	75	8
4	CCl_4	1.5	81	22
5	n-Hexane	8	66	0
6	toluene	8	75	8
7	THF	0.5	quant.	25
8	CH_3CN	0.75	quant.	3

a) The time to completion.
b) Enantiomeric excesses were determined by specific rotation.

Table 6. The effect of different chiral esters

Entry	Chiral reagent	Time / h [a]	Yield / %	%e.e. [b]
1	Dimethyl-L-tartrate	0.75	50	0
2	Diethyl-L-tartrate	0.5	quant.	73 (*S*)
3	Diethyl-D-tartrate	5	quant.	64 (*R*)
4	Diisopropyl-L-tartarate	1	quant.	7 (*S*)
5	(1S,2S,3R,5S)-Pinanediol	1.5	75	0

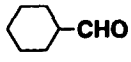
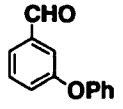
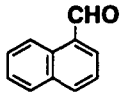
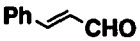
a) The time to completion.
b) Enantiomeric excesses were determined by specific rotation.
c) Major isomer indicated in parentheses.

the DET/$BiCl_3$ system to several aldehydes in order to show the scope and limitations of the reaction (Table 7).

As the results in Table 7 show, the catalyst system promotes the asymmetric reaction of simple aliphatic and aromatic aldehydes. α,β-Unsaturated aldehydes also react, although the rate and selectivity are low for this type of aldehyde. Benzaldehyde showed the best asymmetric induction (Entry 1), which is not surprising since the conditions were developed for this case. The enantiomeric excesses decreased for aliphatic aldehydes (Entries 2 and 3) and no reaction was observed when 1-naphthaldehyde was used as substrate (Entry 6), possibly due to steric hindrance. It is clear that the chiral bismuth catalyst introduced here does not provide sufficient control for a general asymmetric synthetic method, even though 72% e.e. was achieved in the case of benzaldehyde. However, the work has established the principle that the combination of a cheap and readily available bismuth catalyst with a chiral modifier can produce a system capable of providing asymmetric induction. There is therefore a good incentive to study such systems further.

In conclusion, optically active cyanohydrins have been obtained from both aliphatic and aromatic aldehydes by use of a chiral bismuth catalyst although the level of asymmetric induction is not sufficient

Table 7. Asymmetric cyanohydrin formation from several aldehydes

Entry	Aldehyde	Time / h [a]	Yield / %	%e.e. [b]
1	PhCHO (1a)	0.5	quant.	72
2	$Ph(CH_2)_2CHO$ (1b)	0.5	quant.	53
3	$CH_3(CH_2)_7CHO$ (1c)	0.5	quant.	28
4	 (1d)	3.5	87	58
5	 (1e)	3.0	quant.	58
6	 (1f)		no reaction	
7	 (1g)	20	quant.	20

a) The time to completion
b) Enantiomeric excesses were determined by chiral HPLC analysis.

for general use. This is the first demonstration of an asymmetric reaction with a chiral bismuth catalyst and opens up new possibilities in bismuth chemistry. Bismuth compounds are showing increasing potential for organic synthesis and we are currently investigating another synthetic organic reaction that makes use of such compounds.

Experimental section

General

^1H NMR spectra were recorded on a JEOL PMX 60SI spectrometer. IR spectra were recorded on a HORIBA FT-210 Fourier transform infrared spectrometer. Enantiomeric excesses were measured with a JASCO DIP-360 digital polarimeter and/or by chiral HPLC analysis using DAICEL CHIRALCEL OD-H.

All reactions were carried out under a nitrogen or argon atmosphere with anhydrous solvents. Aldehydes were pre-distilled before use. All other reagents are commercially available and were used without further purification. Reactions were monitored by thin layer chromatography on 0.25 mm Merck silica gel sheets (60F-254) (4×2 cm) developed with UV light, I_2 or an aqueous phosphoric and sulfuric acid solution of sodium phosphomolybdate followed by heat.

*Preparation of a chiral bismuth catalyst (*in situ*)*

To a solution of n-BuLi (1.68 M solution in hexane, 2.6 equiv.) in a dry, two-necked round-bottomed flask equipped with a three-branched stopcock, rubber septa and a magnetic stirring bar was added *via* syringe (2*R*,3*R*)-(+)-diethyl tartrate (1.3 equiv.) in diethyl ether (5 ml), with stirring, at 0°C. After stirring for 30 min., the reaction temperature was elevated to r.t. and the solvent was removed under reduced pressure. CH_2Cl_2 (3 ml) was added and the mixture was transferred to a second dry, two-necked, round-bottom flask equipped like the first, containing a solution of $BiCl_3$ (1.0 equiv.) in CH_2Cl_2 (1 ml). Further CH_2Cl_2 (1 ml) was added and the mixture was stirred for 3 h at 0°C. The product, a chiral bismuth compound, was used directly without any purification.

Asymmetric cyanation of benzaldehyde (typical procedure)

To a solution of the chiral bismuth compound (0.25 equiv.) in CH_2Cl_2 (2 ml) at −23°C in a dry, two-necked round-bottom flask equipped with a three-branched stopcock, rubber septa and a magnetic stirring bar, a solution of benzaldehyde **1a** (1.0 equiv.) in CH_2Cl_2 (1.5 ml+0.5 ml for washing) was

added *via* a syringe. Trimethylsilyl cyanide (2.0 equiv.) in CH_2Cl_2 (1.5 ml+0.5 ml for washing) was added. The mixture was stirred for 30 min. and then quenched by addition of sat. aq. NH_4Cl (5 ml). The organic phase was separated, dried ($MgSO_4$) and evaporated and the product was purified by silica gel column chromatography (eluent: hexane:ethyl acetate=15:1). A solution of 1 M HCl in MeOH (1:2, 5 ml) was added and the mixture was stirred for 1 h at room temperature to hydrolyse the trimethylsilyl ether. The product was purified by silica gel column chromatography (eluent: hexane:ethyl acetate=4:1). The desired product, 2-hydroxy-2-phenylacetonitrile **2a**, was obtained in excellent chemical yield and 72% optical yield.

The following products were obtained in an identical manner.

2-Hydroxy-2-phenylacetonitrile **2a**: Yield: quant. 72% e.e. (*S*-rich) ^{1}H NMR ($CDCl_3$) δ 3.2 (br s, 1H), 5.4 (s, 1H), 7.3 (apparent s, 5H) IR (neat) 3419, 2250 cm^{-1} $[\alpha]_D$ −34.1 (c 2.01 g/100 ml, $CHCl_3$). The e.e. of the product was determined as 72% by HPLC analysis: t_R of *S*-isomer, 21 min.; t_R of *R*-isomer, 22 min. [eluent: hexane:isopropyl alcohol=9:1, 0.5 ml/min.]. Elemental analysis: Found: C, 72.05; H, 5.54; N, 10.59%. Calcd for C_8H_7NO: C, 72.22; H, 5.25; N, 10.51%.

2-Hydroxy-4-phenylbutanenitrile **2b**: Yield: quant. 53% e.e. (*S*-rich). ^{1}H NMR ($CDCl_3$) δ 2.1 (m, 2H), 2.8 (m, 2H), 3.1 (br s, 1H), 4.3 (t, 1H), 7.3 (s, 5H). The e.e. of the product was determined as 53% by HPLC analysis: t_R of *S*-isomer, 28 min.; t_R of *R*-isomer, 29 min. [eluent: hexane:isopropyl alcohol=9:1, 0.5 ml/min.].

2-Hydroxydecanenitrile **2c**: Yield: quant. 28% e.e. (*S*-rich). ^{1}H NMR ($CDCl_3$) δ 0.5–2.1 (m, 17H), 3.3 (br s, 1H), 4.5 (t, *J*=3.0 Hz, 1H). $[\alpha]_D$ −3.86 (c 3.15 g/100 ml, $CHCl_3$).

2-Cyclohexyl-2-hydroxyacetonitrile **2d**: Yield: 87%, 58% e.e. (*S*-rich). ^{1}H NMR ($CDCl_3$) δ 1.1–2.3 (m, 11H), 2.6 (br, 1H), 4.4 (br, 1H). IR (neat) 3455, 2931, 2246, 1708, 1452 cm^{-1}. $[\alpha]_D$ −5.41 (c 2.85 g/100 ml, $CHCl_3$).

2-Hydroxy-2-(3-phenoxyphenyl) acetonitrile **2e**: Yield: quant. 58% e.e. (*S*-rich). ^{1}H NMR ($CDCl_3$) δ 4.0 (br s, 1H), 5.8 (br s, 1H), 7.2–8.0 (m, 9H). The e.e. of the product was determined as 58% by HPLC analysis, t_R of *S*-isomer, 36 min.; t_R of *R*-isomer, 40 min. [eluent, hexane:isopropyl alcohol (9:1), 0.5 ml/min.].

2-Hydroxy-2-naphthylacetonitrile **2f**: No reaction was observed.

(*E*)-2-Hydroxy-4-phenyl-3-butenenitrile **2g**: Yield: quant. 20% e.e. (*S*-rich). ^{1}H NMR ($CDCl_3$) δ 3.0 (d, *J*=3.5 Hz, 1H), 5.0 (dd, *J*=3.5, 3.0 Hz, 1H), 6.1 (dd, *J*=3.0, 8.0 Hz, 1H), 6.8 (d, *J*=8.0 Hz, 1H), 7.2 (s, 5H). IR (neat) 3413, 2360, 1652 cm^{-1}. The e.e. of the product was determined as 20% by HPLC analysis before hydrolysis of the trimethylsilyl ether: t_R of *S*-isomer, 10 min.; t_R of *R*-isomer, 11 min. [eluent, hexane:isopropyl alcohol (9:1), 0.5 ml/min.].

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