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Trimethylsilylcyanation of aromatic aldehydes catalyzed by Pybox–$AlCl_3$ complex[1]

Irina Iovel,* Yuris Popelis, Mendel Fleisher and Edmunds Lukevics

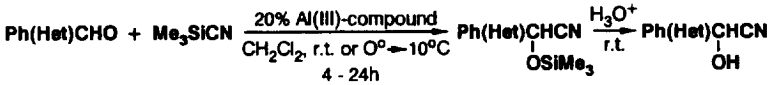
Latvian Institute of Organic Synthesis, Riga, LV-1006, Latvia

Abstract: A series of aromatic and heterocyclic cyanohydrins and their O-silyl ethers have been synthesized by trimethylsilylcyanation of aldehydes using a catalyst generated *in situ* from (*S,S*)-2,6-bis(4′-isopropyloxazolin-2′-yl)pyridine (Pybox) with $AlCl_3$. Mandelonitrile was prepared in isolated yield 92% with more than 90% ee. The structure of $AlCl_3$–Pybox complex was studied by means of ^1H NMR and quantum-chemical calculations. © 1997 Elsevier Science Ltd

Introduction

The (hetero)aromatic cyanohydrins and cyanohydrin derivatives are versatile and important synthetic intermediates of several natural products and biologically active compounds.[2] The achiral and asymmetric catalytic addition of Me_3SiCN (TMSCN) to aldehydes producing O-silylated cyanohydrins is an area of intensive study (for recent reports see[3]). Trimethylsilylcyanation, as one of the C–C bond-forming reactions of carbonyl compounds, is mediated by Lewis acids.[4] ZnI_2 has been known as a catalyst of this reaction for a long time.[5] The enantioselective syntheses of cyanohydrins were investigated mainly in the presence of chiral Ti(IV) complexes composed from titanium alkoxides with optically active ligands (for instance, tartaric acid derivatives and tartrates,[6] peptides,[7] Schiff's bases (including salens),[3b,8] sulfoximine;[9] these and other examples have been reviewed.[10] The Al(III)-compounds, which were reported for asymmetric cyanosilylation giving cyanohydrins with moderate enantioselectivity, have been prepared from organoaluminium (Me_3Al, Et_2AlCl) and chiral diols,[4c] amino acid derivatives[11] or peptides.[7c]

On the other hand, the tridentate optically active compound Pybox was offered as an efficient ligand in the complex with $RhCl_3$ developed[12] for the rhodium-catalyzed hydrosilylation. This ligand was also used for enantioselective cyclopropanation.[13] We have recently carried out the asymmetric hydrosilylation and hydrogen transfer reduction of (hetero)aromatic ketones in the presence of $RhCl_3$–Pybox and $[Rh(COD)Cl]_2$–Pybox complexes.[14] In this paper, a new system prepared from $AlCl_3$ and Pybox has been used for the first time as a catalyst of TMSCN addition to aldehydes.



1 2 3

Het = 2-furyl (Fur), 5-methyl-2-furyl (MFur), 2-thienyl (Th), 5-methyl-2-thienyl (MTh)

Results and discussion

Trimethylsilylcyanation of (hetero)aromatic aldehydes catalyzed by Al(III)-compounds

Benzaldehyde, furfural, 2-methylfurfural, 2-thiophenecarboxaldehyde and its 5-methyl derivative were used as reactants in this investigation. The addition of TMSCN to aldehydes was carried out at room temperature or 0→10°C in methylene chloride. We have observed that under these conditions

* Corresponding author. Email: iovel@osi.lanet.lv

Table 1. Trimethylsilylcyanation[a] of heterocyclic aldehydes catalyzed by $AlCl_3$ (followed by hydrolysis)

Het	Conversion of aldehyde, % (GC)		Yield of siloxy nitrile, % (GC)		Isolated yield of cyanohydrin, %
	2.5 h	22 h	2.5 h	22 h	
Fur	70	74	53	57	52
MFur	58	66	51	52	50
Th	54	63	48	50	46

[a]The addition reactions were carried out in CH_2Cl_2 at room temperature; the molar ratio of reagents was HetCHO:Me_3SiCN:$AlCl_3$ = 1:1.1:0.2.

Table 2. Trimethylsilylcyanation[a] of benzaldehyde in the presence of $AlCl_3$ and chiral ligands (L*)

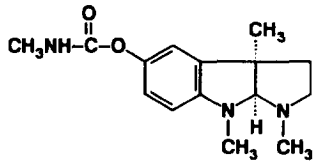
L*	Reaction time, h	Yield of mandelonitrile, % (GC)	ee, %[b]	Configuration[c]
eserine	10		no reaction	
(-) DIOP	10	92	6	*(S)*
Pybox	4	90	44	*(S)*

[a]The addition reactions were carried out in CH_2Cl_2 at room temperature; the molar ratio of reagents was PhCHO:Me_3SiCN:$AlCl_3$:L* = 1:1.1:0.2:0.2.
[b]Determined by capillary GC for *(1S)*-camphanic acid derivatives of mandelonitrile.
[c]Determined by polarimetry for mandelonitrile based on data.[6c]

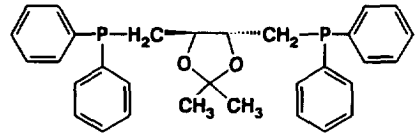
in the presence of Al(III)-compounds the TMSCN added to aldehydes **1** affording the cyanohydrin O-silyl ethers **2**, and subsequent acid-catalyzed hydrolysis gave the cyanohydrins **3**.

At the beginning we studied the catalytic activity of individual $AlCl_3$ in the addition of TMSCN to a number of aldehydes (Table 1).

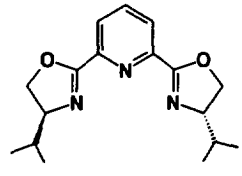
The heterocyclic aldehydes **1** (Het=Fur, MFur, Th) reacted with TMSCN in the presence of $AlCl_3$ (20 mol%) at room temperature to give the corresponding siloxy nitriles **2** in 50 to 57% GC yield after 22 h. Finally, the compounds **2** were hydrolyzed using aq. 1 N HCl at ambient temperature into the cyanohydrins **3** in isolated yields of 46–52%. The reactions were monitored by GC analysis. The products **2** and **3** were identified by ^1H NMR spectra.



eserine



(–) DIOP



Pybox

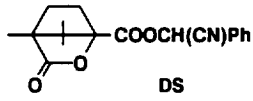
To study the enantioselective trimethylsilylcyanation of benzaldehyde in the presence of the catalytic system generated *in situ* from $AlCl_3$ and several chiral ligands, this reaction was carried out at ambient temperature using eserine {$[\alpha]_D^{25}$ −116 (c=1, C_6H_6)}, (−) DIOP: (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane {$[\alpha]_D^{19}$ −26 (c=2.3, $CHCl_3$)}, and Pybox {$[\alpha]_D^{26}$ −116 (c=1, CH_2Cl_2)} synthesized preliminary by the method.[12a] The results are given in Table 2.

The system $AlCl_3$–eserine did not catalyse this reaction. In the presence of the catalysts Pybox–$AlCl_3$ and (−) DIOP–$AlCl_3$, mandelonitrile was prepared in yield 90–92% (GC) after 4 and 10 hours, respectively. Then the diastereomeric derivatives (**DS**) were synthesized by the reaction of mandelonitrile with (1*S*)-camphanic acid chloride, which was prepared first from camphanic acid according to the known procedure.[15] The enantiomeric excess was detected by capillary GC analysis of the compounds **DS**. The enantioselectivity values of the synthesis of mandelonitrile were 6 and 44% ee by reactions in the presence of (−) DIOP and Pybox, respectively. The absolute configuration of mandelonitrile determined by polarimetry based on the sign of specific rotation using the data[6c] was (*S*) in both cases.

Table 3. Addition of Me_3SiCN to hetero(aromatic) aldehydes catalysed by the generated *in situ* complex $AlCl_3$–Pybox[a]

Ar	Conversion of aldehyde, % (GC)	Yield of siloxy nitrile, % (GC)
Ph	100	96
Fur	96	93
MFur	91	88
Th	87	85
MTh	80(84)[b]	78(81)[b]

[a]The reactions were carried out in CH_2Cl_2 at temperature 0 → 10 °C for 22 h; the molar ratio of reagents was ArCHO:Me_3SiCN:$AlCl_3$:Pybox = 1:1.1:0.2:0.2.
[b]Reaction time was 24 h.



DS

The results of trimethylsilylcyanation of several aldehydes in the presence of 20% of the complex $AlCl_3$–Pybox (1:1 mol) at the temperature 0→10°C are presented in Table 3. The conversion of aldehydes was 84–100% for 22–24 h. The synthesized (hetero)aromatic cyanohydrin O-silyl ethers **2** were obtained in yields 81 to 96% (GC).

Analysis of the results (see Tables 1 and 3) shows that the catalytic activity of the complex $AlCl_3$–Pybox in the addition of TMSCN to HetCHO (Het=Fur, MFur, Th) is much higher than that of the individual $AlCl_3$. In both cases the aldehydes **1** are arranged with respect to the reactivity in the same order: Ph>Fur>MFur>Th>MTh.

To increase the enantioselectivity (see Table 2), the addition of TMSCN to benzaldehyde was carried out at low temperature 0→10°C in the presence of 20% $AlCl_3$–Pybox. Mandelonitrile was prepared in these reaction conditions for 16 hours followed by the hydrolysis with the isolated yield 92%. The trimethylsilylcyanation enantioselectivity detected by capillary GC analysis of the compound **DS** prepared in this case was more than 90% ee (*S*-configuration).

^1H NMR study of $AlCl_3$–Pybox complex

It was shown above, that the catalyst generated *in situ* from $AlCl_3$ and Pybox has the activity higher than $AlCl_3$ itself. This fact can be evidence for complex formation under the reaction conditions in CH_2Cl_2. To determine the structure of this compound, the system $AlCl_3$–Pybox (1:1 mol) was studied by means of ^1H NMR in CD_2Cl_2 as a solvent. The results of this investigation were compared with the data detected for the complex $RhCl_3$–Pybox studied using the same method (Table 4).

The interaction of $RhCl_3$ with Pybox leads to the considerable changes in the positions of the ligand signals. The following shifts of protons were observed in the spectrum (ppm): for $(Me_2CH)_2$ from 1.88 to 3.04; for $(NCH)_2$ from 4.18 to 4.62; for $(OCH_2)_2$ from 4.23 and 4.59 to 4.94 and 4.98, respectively; the peak of H-4 in the pyridine ring was shifted from 7.86 to 8.43. Such an increase of chemical shifts indicates the formation of coordinative bonds of Rh with N atoms of pyridine and both oxazoline rings. But the molecule symmetry of Pybox has not changed.

Another picture was found for the $AlCl_3$–Pybox compound. Comparing the ^1H NMR spectra of the ligand and the complex, we have found the changes in the positions of the signals and the appearance of new peaks. Three peaks of the Me groups appeared in the spectrum of Pybox–$AlCl_3$: 1.11 (3H), 1.15 (3H) and 1.02 (6H) instead of two 0.94 (6H) and 1.06 (6H) in the spectrum of Pybox; peaks 2.44 and 2.19 were found also instead of 1.88 $(Me_2CH)_2$; two peaks 4.71 and 4.16 arose from 4.18 $(NCH)_2$. The groups $(OCH_2)_2$ in complex gave four peaks 4.91 (1H), 5.11 (1H) and 3.78 (1H), 3.86 (1H) instead of 4.23 (2H) and 4.54 (2H) in free ligand. The exact chemical shifts of the pyridine-ring protons in complex $AlCl_3$–Pybox were determined by means of the iteration procedure using the program PANIC (Bruker). The difference between protons H-3 and H-5 (8.542 and 8.137) was defined for complex unlike of initial ligand. These spectra show that $AlCl_3$ forms the bonds with Pybox *via*

Table 4. ^{1}H NMR Data of Pybox, $RhCl_3$–Pybox (1:1 mol) and $AlCl_3$–Pybox (1:1 mol) in CD_2Cl_2, internal standard TMS, 360 MHz

Compound	Chemical shift (δ, ppm) and SSCC (J, Hz)				
	$(Me)_4$	$(Me_2CH)_2$	$(NCH)_2$	$(OCH_2)_2$	Py-ring
Pybox	**0.94** (d, J = 6.6, 6H)	**1.88** (m, 2H)	**4.18** (ddd, J = 9.5, 8.3, 6.6, 2H)	**4.23** (dd, J = 8.3, 2H)	**7.86** (t, J = 7.8, 1H)
	1.06 (d, J = 6.6, 6H)			**4.54** (dd, J = 9.5, 8.3, 2H)	**8.21** (d, J = 7.8, 2H)
$RhCl_3$·Pybox	**0.97** (d, J = 6.5, 6H)	**3.04** (m, J = 6.5, 3.0, 2H)	**4.62** (ddd, J = 10.4, 7.4, 3.0, 2H)	**4.94** (dd, J = 19.8, 7.4, 2H)	**8.43** (t, J = 7.9, 1H)
	0.99 (d, J = 6.5, 6H)			**4.98** (dd, J = 19.8, 10.4, 2H)	**8.09** (d, J = 8.3, 2H)
$AlCl_3$·Pybox	**1.11** (d, J = 6.9, 3H)	**2.44** (m, J = 6.9, 4.8, 1H)	**4.71** (m, J = 10.2, 7.2, 5.1, 1H)	**4.91** (dd, J = 9.7, 7.4, 1H)	**8.542**[a] (m, J = 2.65, 6.25, 1H, H-3)
	1.15 (d, J = 6.9, 3H)			**5.11** (dd, J = 9.7, 9.7, 1H)	
					8.137[a] (m, J = 7.76, 2.65, 1H, H-5)
	1.02 (d, J = 6.9, 6H)	**2.19** (m, J = 6.9, 1H)	**4.16** (m, 1H)	**3.78** (dd, J = 11.4, 4.1, 1H)	
				3.86 (dd, J = 11.4, 4.1, 1H)	**8.128**[a] (m, J = 7.76, 6.25, 1H, H-4)

[a]The result of the itteration using the program PANIC (Bruker)

the N atoms, and there are two unidentical oxazoline rings in $AlCl_3$–Pybox complex. Thus, the ^{1}H NMR study indicates that the compound $RhCl_3$–Pybox has a C_2-symmetrical structure like in the initial Pybox, but it has been changed in the case of the coordination to the aluminium center.

The quantum-chemical calculations of the complex $AlCl_3$–Pybox

To get additional information about the structure of $AlCl_3$–Pybox complex the quantum-chemical methods were employed. The computerized design of the structural parameters for $AlCl_3$ and Pybox molecules and their complex was performed using the LabVision (1992) software package.[16] The data (bond lengths and angles) of $AlCl_3$ were coincided with those taken from the handbook.[17]

The quantum-chemical calculations were carried out by means of semiempirical method MNDO using the program package of MOPAC. The MNDO (Modified Neglect of Diatomic Overlap) method[18] is now established[19–21] as a practical procedure for studying behavior, giving the results comparable[22] with those from quite good *ab initio* models (e.g. 4-31 G) while requiring only one-thousandth as much computer time.[20] The calculations were carried out using the standard parameters for carbon,[18] hydrogen,[18] nitrogen,[18] oxygen,[18] aluminium[23] and chlorine.[24] Geometries of Pybox free ligand and $AlCl_3$–Pybox complex were calculated by minimizing the energy with respect to all geometrical variables, without making any assumptions, using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm as implemented in the MOPAC package of computer programs.

The calculations of the Pybox and several models of $AlCl_3$–Pybox complex were carried out. In the free ligand the dihedral angles between planes of the pyridine ring and oxazoline rings were 94.19° and 85.24°. The net atomic charges (in units of the elementary charge) on the nitrogen atoms were −0.168 (pyridine ring) and −0.281 and −0.282 lel (oxazoline rings). Few starting models of $AlCl_3$–Pybox complex were calculated. In the first model the initial distance between atoms of aluminium (in $AlCl_3$) and nitrogen of pyridine ring (in Pybox) was chosen 2.14 Å (the sum of the Al- and N-atomic radii). Three starting distances N–Al were the same (2.7 Å) in the second model. The third initial model was analogous to the structure of the $RhCl_3$–Pybox complex[12a] (almost planar Pybox ligand and all N–Al distances were 2.1 Å). In the fourth model the initial distances between Al and N atoms of the pyridine and one oxazoline ring were 2.04 and 2.08 Å (distance from Al to N atom of the second

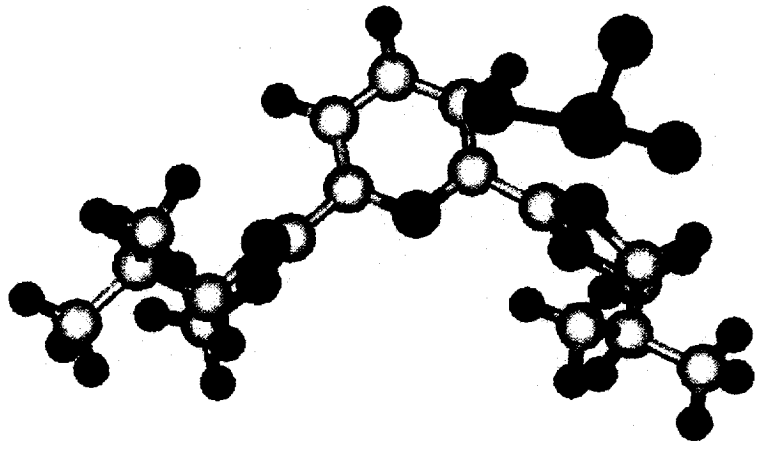


Figure 1. The optimized structure of $AlCl_3$–Pybox complex obtained by quantum-chemical calculations using MNDO method. Ball: carbon (grey), hydrogen (blue), oxygen (red), nitrogen (violet), aluminium (larger blue), chlorine (green).

oxazoline ring was 3.00 Å). In the fifth model the starting distance between Al atom and N atom of one oxazoline ring was chosen 2.06 Å (two other Al–N distances were much more: 2.86 and 3.84 Å).

The stabilization energy of the $AlCl_3$–Pybox complex was the highest for the fifth model: 19.50 kcal/mol. The results of calculations evidence for the monocoordination complex formation between Pybox and $AlCl_3$ *via* N atom of the one oxazoline ring for the models three–five. The interatomic distance Al–N_{oxaz} was 1.95 Å (stabilization energy 16.27 kcal/mol), 1.96 Å (6.25 kcal/mol) and 1.94 Å for these models, respectively. This fact shows two unidentical oxazoline rings in complex. Energies of the stabilization for models 1 and 2 were very small. The formation of the $AlCl_3$–Pybox complex *via* N atom of the oxazoline ring is conditioned by the maximum negative charge on this atom. The optimum calculated structure of the $AlCl_3$–Pybox complex is shown in Figure 1 (ball and stick model). The results of calculations (the coordination compound formation and the difference between both oxazoline rings in the $AlCl_3$–Pybox complex) are confirmed by ^1H NMR spectral data.

Experimental

Materials

Dichloromethane was dried over P_2O_5 and distilled prior to use. Trimethylsilyl cyanide (Aldrich) was used without further purification. The aldehydes were purchased from Fluka and were distilled before use. $AlCl_3$, $RhCl_3 \cdot 3H_2O$, eserine, (−) DIOP, (1*S*)-camphanic acid and the chemicals for the synthesis of Pybox were obtained from commercial sources. Kieselgel 60 (Merck) was used for column chromatography.

Methods

^1H NMR spectra were recorded on Bruker WH-90/DS (90 MHz) and AC-360 (360 MHz) spectrometers using $CDCl_3$ and CD_2Cl_2 as solvents and Me_4Si as an internal standard. The GC analyses of reaction mixtures were performed on Chrom-4 instrument equipped with a flame-ionization detector and glass column (2.4 m × 3 mm) packed with 10% SE-30 and 2.5% Reoplex 400 on Chromosorb W-AW (60–80 mesh); the carrier gas was nitrogen (60 ml/min). Optical rotation was measured with Polamat A (Carl Zeiss) polarimeter. The capillary GC analyses of mandelonitrile camphanic derivatives were performed by Hewlett–Packard 5890 instrument on column (50 m × 0.22

cm × 0.18 μm) with SE-54 phase (helium served as carrier gas), temperature was programmed from 60 to 270°C (10°C/min).

The quantum-chemical calculations of the molecule structures were carried out on a Silicon Graphics IRIS Indigo workstation by the semiempirical MNDO method[18] with full optimization of all geometric parameters (algorithm of Broyden–Fletcher–Goldfarb–Shanno) using the program package MOPAC, version 5.0 (Stewart, J.J.P. QCPE #455). The calculations were carried out entering the keyword PRECISE (the criteria for terminating all optimization are to be increased by 100 times).

General procedure for trimethylsilylcyanation of aldehydes

In a typical procedure, in 5-cm^3 Pierce reaction vial, 1.0 equivalent of aldehyde **1** in dichloromethane reacted with 1.1 equivalent of trimethylsilyl cyanide (CAUTION: Toxic!) in the presence of catalytic amounts of $AlCl_3$ (20 mol%) or generated *in situ* complex $AlCl_3$ with Pybox (1:1 mol) at ambient temperature or 0→10°C. When the reaction was completed (for 4–24 h, monitored by GC), the resulting reaction mixture was purified from catalyst on silica column (hexane/chloroform 5:1), the solvent and unreacted aldehyde were removed under reduced pressure to obtain silyl ether **2**, which was analyzed by means of ^{1}H NMR. For the synthesis of cyanohydrin **3**, the ether **2** was dissolved in acetonitrile and quenched with aq. 1 N HCl at room temperarure. After an hour (monitoring by GC) the resulting products were evaporated, extracted with benzene, and chromatographed on SiO_2. The solution was evaporated and cyanohydrin **3** was analyzed by ^{1}H NMR without further purification. All cyanohydrins **3** and their trimethylsilyl ethers **2** were found to have satisfactory ^{1}H NMR spectra. The enantiomeric excess was determined by GC analysis of mandelonitrile after its derivatization with (1*S*)-camphanic acid chloride (CAC) as described below.

Derivatization of cyanohydrins

The sample (10–20 mg) was dissolved in 1–2 ml toluene, then 0.1–0.2 ml pyridine and 20–40 mg CAC (1.5–2 mol excess) were added at room temperature. After an hour the solution was analyzed by capillary GC.

Acknowledgements

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