ABi_4Se_7 in a single-crystal to single-crystal fashion. We anticipate that the zipperlike action in these materials will also be feasible using electrochemical means.

Experimental Section

$Rb_2Bi_4Se_7$: A mixture of Rb_2Se (0.060 g, 0.240 mmol) and Bi_2Se_3 (0.314 g, 0.480 mmol) was transferred to a carbon-coated silica tube which was flame-sealed under vacuum. The tube was heated at 810 °C for 6 d, then cooled to 510 °C at 7 °Ch^{-1} and to 50 °C over 10 h. The product consisted of silver-gray long laths. Semiquantitative energy-dispersive analysis (EDS) using a scanning electron microscope (SEM) on several needles gave an average composition of $Rb_2Bi_4Se_{6.8}$. $Cs_2Bi_4Se_7$: The procedure was similar to the one above but using a mixture of Cs_2Se (0.060 g, 0.174 mmol) and Bi_2Se_3 (0.228 g, 0.348 mmol). A single-phase product was obtained. The optical band gaps of these two compounds were measured spectroscopically and are 0.53 and 0.56 eV, respectively.

ABi_4Se_7 (A = Rb, Cs): $Rb_2Bi_4Se_7$ (0.1 g, 0.064 mmol) was ground into powder and added to a 2.5 mM solution of I_2 in degassed, wet CH_3CN (100 mL) at 23 °C. The mixture was continuously stirred under an N_2 atmosphere. The oxidation to ABi_4Se_7 was complete in less than 1 h. The optical band gaps of both compounds are ~0.4 eV.

A Bruker SMART Platform CCD diffractometer using graphite monochromatic $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) was used for data collection in all cases. Several different sets of frames, covering a random area of the reciprocal space, were collected using 0.3° steps in ω. The SMART[8a] software was used for data acquisition and the SAINT[8a] program for data extraction. The absorption correction was carried out with SADABS[8a] and the structure solution (direct methods) and refinement (full-matrix least squares on F^2) were done with the SHELXTL[8a] and/or the SHELX97[8b] package of crystallographic programs.

Received: December 27, 1999 [Z 14475]

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[6] a) $Rb_2Bi_4Se_7$: Crystal dimensions $0.65 \times 0.025 \times 0.025$ mm^3, space group $P2_1/m$, $a = 13.062(2)$, $b = 4.2072(5)$, $c = 15.301(2)$ Å, $\beta = 93.137(2)°$, $V = 839.61(17)$ Å^3, $Z = 2$, $\rho_{calcd} = 6.169$ g cm^{-3}, $2\theta_{max} = 50.18°$, $T = 173(2)$ K, 3887 reflections collected, 1689 independent, 1201 observed $[I > 2\sigma(I)]$, $\mu = 62.69$ mm^{-1}, $T_{max/min} = 0.064/0.029$, 85 parameters, final R indices $[I > 2\sigma(I)]$: $R1 = 0.066$, $wR2 = 0.16$, max/min residual electron density $6.60/-3.15$ e Å^{-3}. b) $Cs_2Bi_4Se_7$: Crystal dimensions $0.5 \times 0.025 \times 0.015$ mm^3, space group $P2_1/m$, $a = 13.227(1)$, $b = 4.1857(4)$, $c = 15.556(2)$ Å, $\beta = 94.592(2)°$, $V = 858.49(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 6.400$ g cm^{-3}, $2\theta_{max} = 56.92°$, $T = 173.1(1)$ K, 5978 reflections collected, 2224 independent, 1975 observed $[I > 2\sigma(I)]$, $\mu = 59.86$ mm^{-1}, $T_{max/min} = 1.00/0.43$, 86 parameters, final R indices $[I > 2\sigma(I)]$: $R1 = 0.036$, $wR2 = 0.094$, max/min residual electron density $3.79/-3.03$ e Å^{-3}.

[7] $RbBi_4Se_7$: Data on this compound were collected on two different crystals. One of them was the same crystal (now transformed) initially used to determine the structure of $Rb_2Bi_4Se_7$. The other was selected from a converted batch of sample: Crystal dimensions $0.35 \times 0.025 \times 0.025$ mm^3, space group $C2/m$, $a = 22.286(5)$, $b = 4.1760(8)$, $c = 19.794(4)$ Å, $\beta = 116.89(3)°$, $V = 1642.9(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 5.960$ g cm^{-3}, $2\theta_{max} = 50.44°$, $T = 293(2)$ K, 4127 reflections collected, 1651 independent, 1186 observed $[I > 2\sigma(I)]$, $\mu = 61.13$ mm^{-1}, $T_{max/min} = 1.00/0.51$, 80 parameters, final R indices $[I > 2\sigma(I)]$: $R1 = 0.082$, $wR2 = 0.209$, max/min residual electron density $5.64/-3.75$ e Å^{-3}. $CsBi_4Se_7$: Crystal dimensions $0.42 \times 0.02 \times 0.02$ mm^3, space group $C2/m$, $a = 22.224(7)$, $b = 4.178(1)$, $c = 19.742(6)$ Å, $\beta = 116.384(1)°$, $V = 1642.2(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 6.154$ g cm^{-3}, $2\theta_{max} = 57.16°$, $T = 173.1(1)$ K, 7393 reflections collected, 2154 independent, 1201 observed $[I > 2\sigma(I)]$, $\mu = 60.39$ mm^{-1}, $T_{max/min} = 1.00/0.46$, 80 parameters, final R indices $[I > 2\sigma(I)]$: $R1 = 0.053$, $wR2 = 0.123$, max/min residual electron density $6.11/-3.59$ e Å^{-3}. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-411071, -411072, -411073, and -411074).

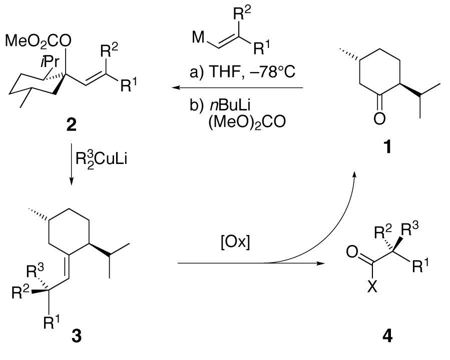
[8] a) SMART versions 4 and 5 (1996–1998), SAINT versions 4, 5, and 6 (1994–1999), SADABS, SHELXTL V-5, Bruker Analytical Xray Systems Inc. Madison, Wisconsin 53719 USA; b) G. M. Sheldrick, University of Göttingen, Germany.

A Novel Method To Generate Chiral Quaternary Carbon Centers of High Enantiomeric Purity Using a Highly Stereoselective Addition of Vinylalanes to a Chiral Aldehyde**

Claude Spino* and Christian Beaulieu

In memory of Larry Weiler

We recently reported on a novel alternative to the alkylation of chiral enolates using the S_N2' addition of cuprates to chiral carbonates **2** derived from menthone (**1**, Scheme 1).[1] Oxidative cleavage of **3** furnished aldehydes, carboxylic acids, or alcohols having a tertiary α-chiral center ($R^2 = H$) with enantiomeric purities greater than 99%.



Scheme 1. Generation of tertiary chiral carbon centers from menthone (**1**).

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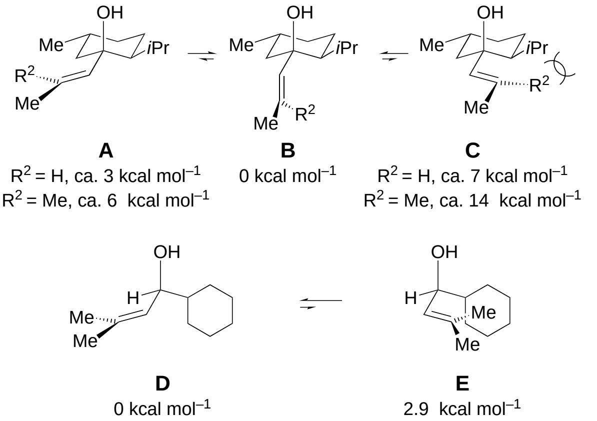
[*] Prof. C. Spino, C. Beaulieu
Université de Sherbrooke
Département de Chimie
Sherbrooke, PQ, J1K 2R1 (Canada)
Fax: (+1) 819-821-8017
E-mail: cspino@courrier.usherb.ca

[**] We acknowledge the Natural Sciences and Engineering Council of Canada and Merck–Frosst for financial support.

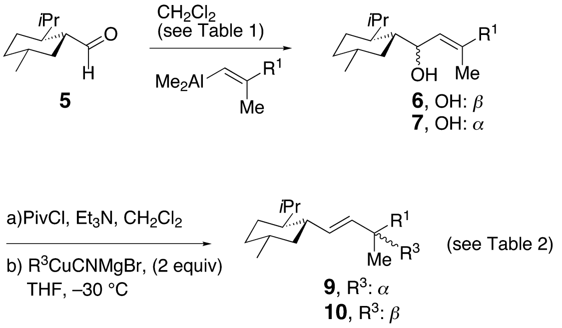
Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

Quaternary centers of high optical purity are notoriously difficult to construct. Several ingenious strategies have helped to surmount this synthetic obstacle, but many compromise on the generality for the benefit of selectivity.[2–4] The prospect of making quaternary carbon centers using the approach described above (Scheme 1, $R^2 = Me$) was appealing because the cuprate addition step should be selective regardless of the substitution on the allylic moiety.[5] However, trisubstituted carbonates such as **2** ($R^2 = Me$) did not react with cuprate reagents because of the high energy required to attain one of the two reactive conformations **A** or **C** (Scheme 2, top).



Scheme 2. Calculations on the reactive conformations for models of **2** (**A**, **B**, **C**) and **11** (**D**, **E**).

We considered the chiral aldehyde **5** as a surrogate auxiliary (Scheme 3). It was prepared in two easy steps from menthone (Wittig olefination with $ClPh_3PCH_2OMe$ followed by hydrolysis with HCl/chloroform). Calculations on a model allylic system indicated a 3 kcal mol^{-1} energy difference between the two reactive conformations **D** and **E** (Scheme 2, bottom), which should provide enough bias to allow the *anti*-selective cuprate addition to take place on conformer **D** only. However, this change in chiral auxiliary (from menthone to **5**) created some uncertainties concerning issues crucial to the success of the method. Would the addition of vinyl anions to aldehyde **5** proceed stereoselectively? How could we ensure an S_N2' addition of the cuprate reagent on the corresponding carbonate or ester?



Scheme 3. Generation of quaternary chiral carbon centers from **5**. Piv = pivaloyl = 2,2-dimethylpropyl.

The answer to the first question was initially a resounding no. Not surprisingly, di- or trisubstituted vinylmagnesium and vinyllithium reagents gave, each time, approximately 2:1 mixtures of two easily separable diastereomeric alcohols. However, upon adding aldehyde **5** directly to a reaction mixture containing the carboalumination[6] intermediate of 1-hexyne obtained from a zirconium-catalyzed reaction, we obtained a surprising ratio of 13:1 of two easily separable alcohols **6** and **7** in 65% nonoptimized yield. The major alcohol was shown to have the configuration corresponding to the Felkin–Anh[7] addition product **6f** (Scheme 3, Table 1) by converting it, and its minor diastereomer **7f**, into the corresponding Mosher esters. This ratio was later reproduced with other vinylalanes prepared in a similar way. Also, the addition of vinylalane **8f** to phenylpropanal gave a 93% yield of a mixture of diastereomeric alcohols in a 17:1 ratio based on NMR integration of the crude mixture. Preliminary results therefore indicate that the preference of vinylalanes for the Felkin–Anh mode of addition on α-chiral aldehydes could be general. Instances of increased Felkin–Anh selectivity with increasing size of the metal have been noted before.[7] If the selectivity obtained here was a surprise, the chemical yields of these additions were also noteworthy. We are aware of only a few reports of vinylalanes being added directly to ketones or aldehydes, and usually in only modest yields (30–50%).[8–12] Trialkylalanes have been added selectively to β-ketosulfoxides and chiral β-ketoamides.[13,14] Alkenylalanes prepared from hydro- or carboalumination of alkynes are usually treated with other electrophiles[6] or converted into the iodide or bromide first or transmetalated directly with zinc, copper,[15] lithium (ate complex), or other metals before addition to carbonyl electrophiles.[16–18] The scope and use of this protocol to make diastereomerically enriched allylic alcohols is currently being investigated.

Table 1. Addition of vinylalanes to aldehyde **5**.

Entry	**8**	R^1	Yield [%][a]	**6**:**7**[b]
1	a	cyclohexyl	75	15:1
2	b	$PhCH_2$	76	12:1
3	c	Ph	63	20:1
4	d	$-(CH_2)_3OTBS$	68	8:1
5	e	$-CMe_2CH_2OTBS$	0	–
6	f	$-(CH_2)_3CH_3$	65	13:1
7	f[c]	$-(CH_2)_3CH_3$	93	17:1[d]

[a] Yields of isolated products. [b] Ratios of the isolated products. [c] Addition on PhMeCHCHO. [d] Ratio determined by NMR integration of crude mixtures.

On the basis of the work of Goering and co-workers we expected that derivatization of alcohols **6** into the corresponding pivalates **11** (pivalate = 2,2-dimethylpropanoate) and the use of cuprate reagents of the type RCuCNMgBr should lead to highly regioselective reactions in favor of the S_N2' product.[19] This was indeed the case, while other types of cuprate reagents (for example, R_2CuLi) or other leaving groups (for example, OAc, OCO_2Me) gave unsatisfactory mixtures of regioisomers. Also, the use of a catalytic amount of CuCN led to the recovery of starting material only.[19] Reactions using Goering's procedure with a range of alkyl cuprates proceeded to give a good yield of the cross-coupling products **9** and **10** with excellent stereoselectivities (Table 2).

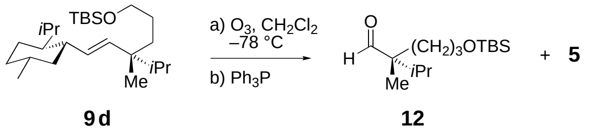
Table 2. S_N2' displacements of cuprates on the pivalates of alcohols **6**.

Entry	**11**	R^1	R^3	**9**	Yields [%]	*d.e.*[a] [%]
1	**a**	cyclohexyl	*i*Pr	**a**	95	> 98
2	**b**	$PhCH_2$	*i*Pr	**b**	92	> 98
3	**c**	Ph	*i*Pr	**c**	90	91
4	**d**	$-(CH_2)_3OTBS$	*i*Pr	**d**	95	> 98
5	**d**	$-(CH_2)_3OTBS$	Et	**e**	89	> 98[b]
6	**e**	*n*Bu	nC_7H_{15}	**f**	90	> 95[c]

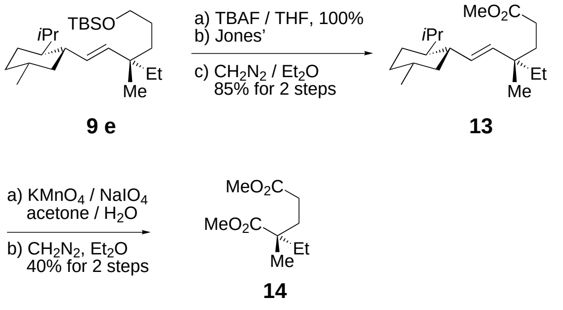
[a] Determined by comparison of the HPLC traces with authentic mixtures of **9** and **10**. [b] Inferred from the optical rotation in comparison with literature value. [c] *d.e.* value based on differences in ^{13}C NMR signals.

tert-Butyl, phenyl, and benzyl cyanocuprates were not reactive enough to take part in the reaction. The phenyl and benzyl groups could nonetheless be introduced starting from phenyl- or benzylacetylene. However, neopentyl alkynes could not be carboaluminated efficiently. Also, the stereoselectivity in the cuprate addition was slightly lower in the case of phenyl-substituted allyl pivalates **6c** and **7c**. This decrease was also observed in our first generation system with aryl-substituted allyl carbonates (Scheme 1, $R^1 = Ar$).[1b]

The disubstituted double bonds in adducts **9** were easily cleaved with ozone or with $KMnO_4/NaIO_4$ leading to good yields of aldehydes, carboxylic acids, or alcohols depending on the work-up performed. For example, **9d** was cleaved with O_3 in dichloromethane to yield 65% of the aldehyde **12** (Scheme 4). The chiral auxiliary was recovered in 80% yield after chromatography and could be re-used. The conversion of **9e** into **14** (Scheme 5) was confirmed by comparison of its optical rotation ($[\alpha]_D$) with that of its enantiomer reported in the literature ($[\alpha]_D = -9.7°$, $CHCl_3$, $c = 0.3$; literature $[\alpha]_D = +9.8°$, $c = 0.3$).[20] This observation indicated that the stereochemistry of **9e** results from an *anti*-selective cuprate addition on the configuration and conformation corresponding to **D** (Scheme 2).



Scheme 4. Oxidative cleavage of **9d**. TBS = *tert*-butyldimethylsilyl.



Scheme 5. Proof of the absolute configuration of **9e**. TBAF = tetrabutylammonium fluoride.

The present method should prove a valuable addition to the arsenal of asymmetric reactions available for the synthesis of natural or unnatural chiral compounds.

Received: January 20, 2000 [Z 14571]

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Exceptional Deshielding of ^{59}Co Caused by Deuteration of the Hydrogen Bonds in Cobaloximes**

Fioretta Asaro, Lorenza Liguori, and Giorgio Pellizer*

Transition metal shieldings are useful probes of structure and reactivity for coordination compounds, since they allow even tiny variations at the coordination site to be detected.[1] The isotope ^{59}Co exhibits the largest known shielding range. Its NMR properties have been extensively studied for

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[*] Prof. G. Pellizer, Dr. F. Asaro, Dr. L. Liguori
Dipartimento di Scienze Chimiche
Università di Trieste
via L. Giorgieri 1, 34127 Trieste (Italy)
Fax: (+39) 040-6763903
E-mail: pellizer@dsch.univ.trieste.it

[**] This work was supported by MURST under the Project Cofin (MURST 97 CFSIB).