Keywords: density functional calculations · Moessbauer spectroscopy · photoelectron spectroscopy · solid-state structures

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[1] M. Zabel, S. Wandinger, K.-J. Range, *Z. Naturforsch. B* **1979**, *34*, 238.
[2] K.-J. Range, personal communication.
[3] D. Briggs, M. P. Seak, *Practical Surface Analysis*, Salle-Sauerländer, Frankfurt am Main, **1990**.
[4] N. Greenwood, T. C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall, London, **1971**.
[5] P. Gütlich, R. Link, A. Trautwein, *Mößbauer Spectroscopy and Transition Metal Chemistry*, Spinger, Berlin, **1978**, p. 113.
[6] U. von Barth, L. Hedin, *J. Phys. C4* **1971**, 2064.
[7] a) O. K. Andersen, O. Jepsen, *Phys. Rev. Lett.* **1984**, *53*, 2571; b) O. K. Andersen, Z. Pawlowska, O. Jepsen, *Phys. Rev. B* **1986**, *34*, 5253.
[8] O. K. Andersen, O. Jepsen, D. Glötzel in *Highlights of Condensed-Matter Theory* (Eds.: F. Bassani, F. Fumi, M. P. Tosi), North-Holland, New York, **1985**.
[9] O. K. Andersen, *Phys. Rev. B* **1975**, *12*, 3060.
[10] H. L. Skriver, *The LMTO Method*, Springer, Berlin, **1984**.
[11] O. Jepsen, O. K. Andersen, *Solid State Commun.* **1971**, *9*, 1763.
[12] O. Jepsen, O. K. Andersen, *Z. Phys. B* **1995**, *97*, 35.
[13] F. Boucher, O. Jepsen, O. K. Andersen, unpublished results; R. Dronskowski, P. Blöchl, *J. Phys. Chem.*, **1993**, *97*, 8619.
[14] a) A. Savin, O. Jepsen, H. J. Flad, O. K. Andersen, H. W. Preuss, H. G. von Schnering, *Angew. Chem.* **1992**, *104*, 187; b) *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 187.
[15] C. Felser, K. Thieme, R. Seshadri, *J. Mater. Chem.*, in press.
[16] C. Felser, K. Ahn, R. K. Kremer, R. Seshadri, A. Simon, *J. Solid. State Chem.*, submitted.

Samarium-Mediated *β*-Elimination in Dihalo Alcohols: Diastereoselective Synthesis of (*Z*)-Vinyl Halides[**]

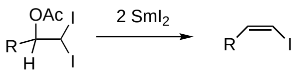
José M. Concellón,* Pablo L. Bernad, and
Juan A. Pérez-Andrés

Diastereoselective formation of carbon–carbon double bonds has received considerable attention in organic chemistry.[1] Among many other methods, the 1,2-elimination reaction is a powerful route to alkenes.[2] Usually, the alkene obtained in these processes is isolated as a *Z*/*E* mixture, and only the use of starting materials with defined stereochemistry affords single diastereoisomers.[3] Vinyl halides[4] are synthetically even more interesting, since they readily undergo carbon–carbon bond formation.[5] Some years ago we reported a useful process for the synthesis of vinyl chlorides and bromides by lithium-promoted *β*-elimination in 1,1-dihalo-2-silyloxyalkanes, but this reaction took place with poor diastereoselectivity.[6] Zinc was also used, but again no diastereoselectivity was achieved.[7]

In recent years we have used samarium diiodide as an alternative to traditional organometallic compounds[8] and have described iodo-[9a] and diiodomethylations[9b] of carbonyl compounds with this reagent. We considered the possibility of using samarium diiodide to promote a *β*-elimination reaction in 1,1-dihaloalkan-2-ols. The use of SmI_2 in reductive elimination reactions has not been studied as widely as other transformations. Only *β*-hydroxy- or *β*-acetoxysulfones have received some attention, providing the thermodynamically favored (*E*)-olefin.[10] The treatment of epoxides with samarium diiodide and various additives gave mixtures of *Z* and *E* diastereoisomers.[11]

Here we describe our studies on diastereoselective 1,2-elimination in O-acetylated 1,1-dihaloalkan-2-ols with samarium diiodide. Our first trials were carried out with 1,1-diiodononan-2-ol (prepared by reaction of octanal with SmI_2/CHI_3[9b] or diiodomethyllithium[12]) as a model substrate. When this alcohol was added to a solution of SmI_2 in THF, vinyl iodide **2a** was obtained in high yield but with very poor diastereoselectivity.[13] A similar result was obtained with O-silylated 1,1-diiodononan-2-ol. However, when O-acetylated 1,1-diiodononan-2-ol was used, (*Z*)-1-iodonon-1-ene[14] was obtained with high diastereoselectivity (Table 1).[15] Transformation was complete after a few minutes at room temperature. The usual diastereoselectivity/temperature trend was not observed; instead, increasing the temperature enhanced the diastereoselectivity (Table 1, entries 1–3).[16] Solvent effects were also studied: addition of *N*,*N*′-dimethyl-*N*,*N*′-propylene urea (DMPU) as co-solvent to the solution of SmI_2 in THF leads to lower diastereoselectivity (entry 4); when the

Table 1. Diastereoselective SmI_2-mediated *β*-elimination reaction of *O*-acetyl diiodo alcohols.



1a-f **2a-h**

Entry	1	R	*T* [°C]	*Z*/*E*[a]	Yield [%][b]
1	**1a**	C_7H_{15}	50	94/6	88
2	**1a**	C_7H_{15}	20	92/8	86
3	**1a**	C_7H_{15}	−20	89/11	88
4	**1a**	C_7H_{15}	20[c]	62/38	72
5	**1a**	C_7H_{15}	55[d]	84/16	40
6	**1b**	Cyclohexyl	50	94/6	64
7	**1c**	MeCH(Ph)	50	94/6	83
8	**1d**[e]	$Me_2C{=}CHCH_2CH_2CH(Me)CH_2$	50	94/6	70
9	**1e**[e]	(*S*)-MeCH(OBn)	50	87/13	75
10	**1f**[f]	$C_6H_{13}CH(Cl)$	50	93/7	77
11	**1g**	Ph	50	72/28	92
12	**1h**	MeCH=CH	50	83/17	–[g]
13	**1h**	MeCH=CH	20	71/29	–[g]

[a] Determined on crude reaction products by ^1H NMR spectroscopy and/or GC-MS. [b] Yield of isolated products. [c] With addition of DMPU. [d] With acetonitrile as solvent. [e] A 1/1 mixture of diastereoisomers. [f] A 3/1 mixture of diastereoisomers. [g] This compound decomposed on purification.

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[*] Dr. J. M. Concellón, Dr. P. L. Bernad, J. A. Pérez-Andrés
Departamento de Química Orgánica e Inorgánica
Facultad de Química, Universidad de Oviedo
E-33071 Oviedo (Spain)
Fax: (+34) 98-510-34-46
E-mail: jmcg@sauron.quimica.uniovi.es

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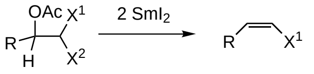
reaction was carried out acetonitrile diastereoselectivity also decreased (entry 5).[17]

This reaction is general for other acetylated diiodo alcohols, and (*Z*)-vinyl iodides were isolated with high diastereoselectivity (Table 1). The reaction also showed tolerance to other functional groups (entries 8–10). It is noteworthy that even when mixtures of diastereoisomers were used (entries 8–10), the corresponding vinyl iodides were obtained with high *de*. Elimination took place with lower diastereoselectivity only when the resulting double bond was conjugated (entries 11–13).

O-Acetyl 1,1-dibromo- and 1,1-dichloroalkan-2-ols were also suitable substrates for the β-elimination, and vinyl bromides or chlorides were obtained (Table 2, entries 1 and 2). In the latter case, heating to reflux and longer reaction times were necessary.

Table 2. SmI_2-promoted β-elimination in *O*-acetyl dihalo alcohols.[a]



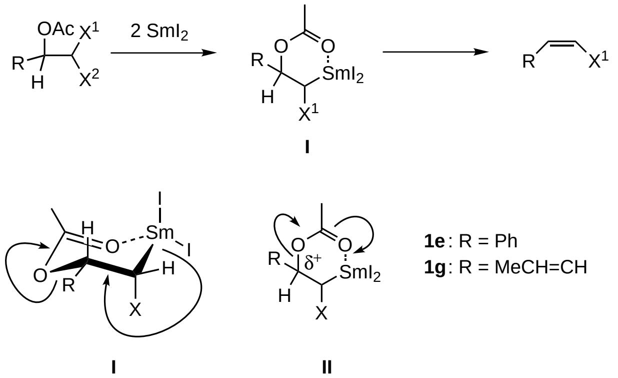
3a-f **4a-f**

En-try	3	R	X^1	X^2	Z/E[b]	Yield [%][c]
1	**3a**	C_7H_{15}	Br	Br	91/9	61
2	**3b**[d]	C_7H_{15}	Cl	Cl	91/9	54
3	**3c**[e]	C_7H_{15}	Cl	I	91/9	90
4	**3d**[e]	Cyclohexyl	Cl	Br	91/9	83
5	**3e**[e]	MeCH(Ph)	Cl	I	90/10	95
6	**3f**[f]	$Me_2C{=}CHCH_2CH_2CH(Me)CH_2$	Cl	Br	91/9	93

[a] Reactions were performed at 50°C for 35 min with 2.2 equiv of SmI_2. [b] Determined on crude reaction products by ^{1}H NMR spectroscopy and/or GC-MS. [c] Yield of isolated products. [d] Performed at 65°C for 12 h with 4 equiv of SmI_2. [e] A 1/1 mixture of diastereoisomers. [f] Mixture of four diastereoisomers.

More interesting is the β-elimination of dihaloalkanols bearing two different halogen atoms. These were obtained as 1/1 mixtures of diastereoisomers, treatment of which with SmI_2 afforded (*Z*)-vinyl halides with high diastereoselectivity and total chemoselectivity: only products resulting from metalation of the more reactive halogen (I > Br > Cl) were found.

The observed stereochemistry of products **2** and **4** may be explained by assuming a chelation-control model (Scheme 1). Thus, metallation of the most reactive halogen generates intermediate **I**. Chelation of the Sm^{III} center with the carbonyl oxygen atom of the acetoxy group produces a six-membered ring.[18] Tentatively, we propose a chair transition state model **I** with an equatorial R group (to avoid 1,3-diaxial interactions) and axial halogen atom (no 1,3-diaxial interactions are present and dipoles due to C–X and Sm–I are opposed). Elimination from **I** affords (*Z*)-vinyl halides.



Scheme 1. Proposed mechanism.

Reactions of SmI_2 with optically active halides that result in racemization have been reported.[19] The isolation of **4** with high *de* from the mixture of diastereoisomers of **3** could be explained by assuming that the diastereoisomer with a more appropriate conformation for coordination of the samarium(III) center with the carbonyl oxygen atom could react directly, while the other diastereoisomer epimerizes before elimination. The lower *de* observed when a conjugated C=C bond is generated may be explained by assuming a non-concerted process: stabilization of the positive charge by resonance would induce prior cleavage of the C–O bond (Scheme 3, **II**).

In summary, a novel and synthetically valuable SmI_2-promoted 1,2-elimination reaction has been developed and provides (*Z*)-vinyl halides with high diastereoselectivity.

Experimental Section

A solution of the *O*-acetyl dihaloalkohol (0.2 mmol) in THF (2 mL) was added dropwise to a solution of SmI_2 in THF (0.44 mmol, 0.1M) under a nitrogen atmosphere at the appropriate temperature. After 35 min, HCl 1M (5 mL) was added. Usual workup and purification by short-column chromatography (silica gel, hexane as eluent) provided the pure (*Z*)-vinyl halide.

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[1] a) *The Chemistry of Alkenes*, *Vol. 2* (Ed.: S. Patai), Interscience, New York, **1968**; b) Y. Shen, *Acc. Chem. Res.* **1998**, *31*, 584.

[2] a) A. Krebs, J. Swienty-Busch, *Comprehensive Organic Synthesis*, *Vol. 6* (Eds.: B. M. Trost, I. Flemming, E. Winterfeldt), Pergamon, Oxford, **1991**, pp. 949–974; b) P. Kocienski, *Comprehensive Organic Synthesis*, *Vol. 6* (Eds.: B. M. Trost, I. Flemming, E. Winterfeldt), Pergamon, Oxford, **1991**, pp. 975–1010.

[3] a) K. Maeda, H. Shinokubo, K. Oshima, *J. Org. Chem.*, **1996**, *61*, 6770–6771; b) P. E. Sonnet, *J. Org. Chem.* **1980**, *45*, 154–157.

[4] For examples of the preparation of vinyl halides, see: a) H. C. Brown, C. Subrahmanyam, T. Hamaoka, N. Ravindran, D. H. Bowman, S. Misumi, M. K. Unni, V. Somayaji, N. G. Bhat, *J. Org. Chem.* **1989**, *54*, 6068–6075; b) H. C. Brown, T. Hamaoka, N. Ravindran, C. Subrahmanyam, V. Somayaji, N. G. Bhat, *J. Org. Chem.* **1989**, *54*, 6075; c) G. Stork, K. Zhao, *Tetrahedron Lett.* **1989**, *30*, 2173–2174.

[5] a) R. F. Heck, *Comprehensive Organic Synthesis*, *Vol. 4* (Eds.: B. M. Trost, I. Flemming, M. F. Semmelhock), Pergamon, Oxford, **1991**, pp. 851–856; b) T. Funabiki, H. Hosomi, S. Yoshida, K. Tarama, *J. Am. Chem. Soc*, **1982**, *104*, 1560–1568; c) G. C. M. Lee, B. Tobias, J. M. Holmes, D. A. Harcourt, M. E. Garst, *J. Am. Chem. Soc.* **1990**, *112*, 9330–9336; d) D. R. Willians, B. A. Barner, K. Nishitani, *J. Am. Chem. Soc.* **1982**, *104*, 4708–4710; e) K. C. Nicolau, Y. He, F. Roschangar, N. P. King, D. Vourloumis, T. Li, *Angew. Chem.* **1998**, *110*, 89–92; *Angew. Chem. Int. Ed.* **1998**, *37*, 84–87.

[6] J. Barluenga, J. L. Fernández-Simón, J. M. Concellón, M. Yus, *J. Chem. Soc. Perkin Trans. 1* **1989**, 691.

[7] H. O. House, R. S. Ro, *J. Am. Chem. Soc.* **1958**, *80*, 182–187.

[8] G. A. Molander, C. R. Harris, *Chem. Rev.* **1996**, *96*, 307.

[9] a) J. M. Concellón, P. L. Bernad, J. A. Pérez-Andrés, *J. Org. Chem.* **1997**, *62*, 8902–8906; b) J. M. Concellón, P. L. Bernad, J. A. Pérez-Andrés, *Tetrahedron Lett.* **1998**, *39*, 1409–1412.

[10] a) G. E. Keck, K. A. Savin, M. A. Weglarz, *J. Org. Chem.* **1995**, *60*, 3194–3204, and references therein; b) A. S. Kende, J. S. Mendoza, *Tetrahedron Lett.* **1990**, *31*, 7105–7108; c) G. Doisneau, J.-M. Beau, *Tetrahedron Lett.* **1998**, *39*, 3477–3480.

[11] a) M. Matsukawa, T. Tabuchi, J. Inanaga, M. Yamaguchi, *Chem Lett.* **1987**, 2101–2102. For other β-elimination reactions promoted by SmI_2, see: b) L. Crombie, L. J. Rainbow, *J. Chem. Soc. Perkin Trans. 1* **1994**, 673; c) R. Yanada, N. Negoro, *Tetrahedron Lett.* **1996**, *37*, 9313–9316.

[12] H. Taguchi, H. Yamamoto, H. Nozaki, *J. Am. Chem. Soc.* **1974**, *96*, 3010–3011.

[13] Products derived from reduction of one iodo group (or both) were not found.[11]

[14] The stereochemistry was assigned by analysis of the 300 MHz ^1H NMR coupling constant of the major and minor diastereoisomers.

[15] The diastereoisomeric excess was determined on the crude reaction products by ^1H NMR spectroscopy, GC-MS, and/or quantitative ^{13}C NMR spectroscopy and was similar to that of the purified products.

[16] This behavior was observed in other SmI_2-promoted reactions, apparently with very different mechanisms. To date, no explanation has been suggested. See a) G. A. Molander, C. R. Harris, *J. Org. Chem.* **1998**, *63*, 812–816; b) J. M. Aurrecoechea, B. López, *Tetrahedron Lett.* **1998**, *39*, 2857, and references therein; see also ref. [9a].

[17] The lower *de* obtained with DMPU can be explained in terms of the tendency of samarium(III) centers to integrate this kind of ligand into its coordination sphere: M. Shabangi, J. M. Sealy, J. R. Fuchs, R. A. Flowers, *Tetrahedron Lett.* **1998**, *39*, 4429–4432. Thus, the ability of the samarium(III) center to bind to the carbonyl oxygen atom would be lower, and the elimination reaction would take place in an open-chain intermediate. The effect of acetonitrile as solvent is less easily explained. It could change the coordination sphere, oxidation potential, and the solubility of Sm^{II} or Sm^{III} centers.

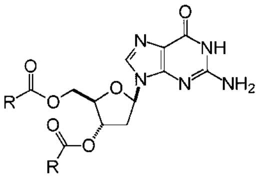
[18] A similar transition state model involving a chair transition state was proposed to explain the selectivity in other reactions of SmI_2: a) G. A. Molander, J. B. Etter, P. W. Zinke, *J. Am. Chem. Soc.* **1987**, *109*, 453–463; b) D. Urban, T. Skrydstrup, J.-M. Beau, *J. Org. Chem.* **1998**, *63*, 2507–2516.

[19] a) H. B. Kagan, P. Girard, J. L. Namy, *Tetrahedron* **1981**, *37*, 175–180; b) S. Matsubara, M. Yoshioka, K. Utimoto, *Angew. Chem.* **1997**, *109*, 631–633; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 617–618.

Enantioselective Extraction of Dinitrophenyl Amino Acids Mediated by Lipophilic Deoxyguanosine Derivatives: Chiral Discrimination by Self-Assembly**

Vincenza Andrisano, Giovanni Gottarelli,*
Stefano Masiero, Erik H. Heijne, Silvia Pieraccini, and
Gian Piero Spada

The lipophilic deoxyguanosine derivatives **1** are versatile molecules which, depending on to the experimental conditions, undergo different self-assembly patterns.[1] In the presence of K^+ ions, octamers or columnar oligomers are formed based on the G-quartet structure. In these aggregates the quartets constitute the inner part of the structure, whereas the sugars with their lipophilic pendants are on the outside and in contact with the organic solvent. Alkali metal ions act like cement to keep the quartets **Q** together: If the K^+:**1** molar ratio is 1:8 or lower, the octamer **O** is the most abundant species observed, while for higher ratios oligomeric or polymeric columnar aggregates **P** are progressively observed.[2, 3] Lipophilic guanosines and isoguanosines[4] are able to transfer alkali metal ions from water to organic solvents and act as self-assembled ionophores. Apparently the anion is also dragged into the organic phase, and, considering that the cation is inside a chiral cage, it was thought that the anion could be in contact with the chiral surface of the octamer or of the columnar oligomer. Chiral anions could possibly be discriminated by the chiral surface formed by the substituted deoxyribose moieties.



1a, R = C_9H_{19}
1b, R = p-$(C_{12}H_{25}O)C_6H_4$

The potassium salts of the *N*-2,4-dinitrophenyl (DNP) derivatives of amino acids tryptophan (K(DNP-Trp), **2**), phenylalanine (K(DNP-Phe), **3**), alanine (K(DNP-Ala), **4**), isoleucine (K(DNP-Ile), **5**), and proline (K(DNP-Pro), **6**) were chosen to test the validity of this hypothesis: They are

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[*] Prof. G. Gottarelli, Dr. S. Masiero, E. H. Heijne, S. Pieraccini,
Dr. G. P. Spada
Università di Bologna
Dipartimento di Chimica Organica "A. Mangini"
Via S. Donato 15, I-40127 Bologna (Italy)
Fax: (+39) 051244064
E-mail: gottarel@alma.unibo.it

Dr. V. Andrisano
Università di Bologna
Dipartimento di Scienze Farmaceutiche
I-40126 Bologna (Italy)

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