planarity, and number of π electrons, see K. Müllen, *Chem. Rev.* **1984**, *84*, 603 – 646.
[10] The reductions of **1** and **2** were carried out as previously described; K. Müllen, T. Meul, P. Schade, H. Schmickler, E. Vogel, *J. Am. Chem. Soc.* **1987**, *109*, 4992 – 5003.
[11] A triad of $(4n+2)\pi$ dications, $[4n]$annulenes, and $(4n+2)\pi$ dianions analogous to **1**/**3**/**5** and **2**/**4**/**6** has been reported by K. Müllen, T. Meul, E. Vogel, U. Kürschner, H. Schmickler, O. Wennerström, *Tetrahedron Lett.* **1985**, 3091 – 3094.
[12] Depending on whether the π-electron system is planar and fourfold or just fourfold, the Soret and Q transitions belong to symmetry E_u or E.
[13] P. R. Callis, T. W. Scott, A. C. Albrecht, *J. Chem. Phys.* **1983**, *78*, 16 – 22.

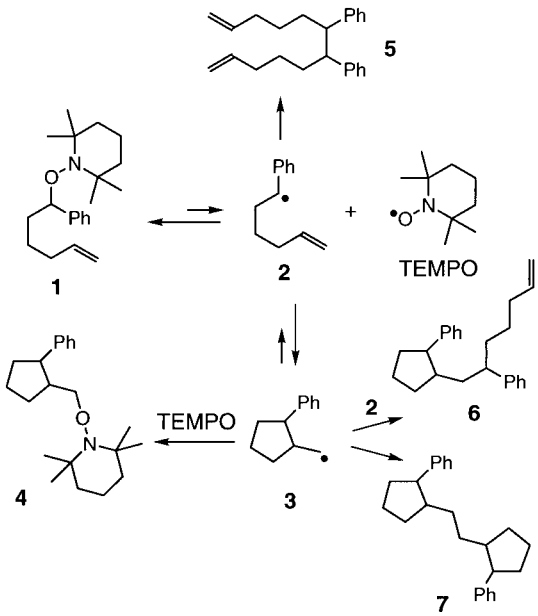
Tin-Free Radical Cyclization Reactions Using the Persistent Radical Effect**

Armido Studer*

Organotin compounds have found widespread application in conducting various types of radical reactions.[1] Despite this important utility, there are drawbacks associated with tin-based radical chemistry, namely, toxicity of organostannanes that necessitate special handling of disposal, and in many instances problems with product purification. Therefore, various research groups have been looking for alternatives.[2] Herein we report new tin-free radical cyclization reactions based on the persistent radical effect (PRE).

The PRE[3, 4] is a general principle that explains the highly specific formation of the cross-coupling product (R^1–R^2) between two radicals R^1 and R^2 when one species is persistent (long-lived) and the other transient; the two radicals must be formed at equal rates. The initial buildup in concentration of the persistent species, caused by self-termination of the transient radical, steers the reaction to follow a single pathway for the cross-reaction. The PRE has already been used in various chemical systems[3, 5] and is important in stable free radical polymerization (SFRP).[6]

In Scheme 1, an application of the PRE for a 5-*exo* cyclization with the 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) radical as persistent species is suggested. It is known that α-phenyl-substituted alkoxyamines such as **1** have weak C–O bonds which are homolytically cleaved upon heating.[6, 7] C–O bond homolysis in **1** will therefore lead to the persistent TEMPO radical and the transient radical **2**.[6–10] Radical **2** can either be trapped by TEMPO to reform **1**, or it can undergo a 5-*exo* cyclization (the 6-*endo* cyclization is omitted in Scheme 1) to form a new radical **3**, which after trapping with TEMPO affords **4**. The trapping of **3** with TEMPO is irreversible, because the C–O bond in an alkoxyamine derived from TEMPO and a primary alkyl radical is too strong to be homolytically cleaved.[7] Due to the low concentration of TEMPO during the isomerization,[6b] **3** is long-lived and the cyclization from **2** to **3** is probably reversible.[11] According to the PRE, the coupling products **5** – **7** from the transient radicals **2** and **3** should be formed in very low yields, and the isomerization of **1** should occur almost quantitatively.[4] Furthermore, degenerate radical reactions (reversible initial C–O bond homolysis in our system) have been shown to suppress potential side reactions by reforming starting material when the desired cyclization does not proceed effectively.[5b]



Scheme 1. Radical 5-*exo*-cyclization with use of the persistent 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) radical.

To test the concept of the PRE in cyclization reactions, alkoxyamine **1** was prepared from 1-bromo-1-phenyl-5-hexene and the Ca alkoxide (2 equiv) of 1-hydroxy-2,2,6,6-tetramethylpiperidine in refluxing THF (14 h, 80 %).[12, 13] The isomerization reaction depicted in Scheme 1 was studied under different conditions (Table 1). In *tert*-butylbenzene and *N*,*N*′-dimethyl-*N*,*N*′-propylene urea (DMPU), no isomerization was observed (entries 1 and 2). In DMF after 16 h, **4** was isolated in 56 % yield (*trans*:*cis* = 2.5:1)[14] along with the 6-*endo* product **8** (10 %, *trans*:*cis* = 1:1; entry 3). In *t*BuOH (0.1 M) clean but slower isomerization occurred (entry 4) and lowering the concentration (0.1 M → 0.01 M) has no significant effect (entry 5). Interestingly, the reaction was accelerated by addition of camphorsulfonic acid (CSA, entry 6),[15] with the best results obtained in *t*BuOH (0.02 M) with 10 % CSA (entry 7). The isomerization products were isolated in 83 % yield along with **9** (2 %).[16]

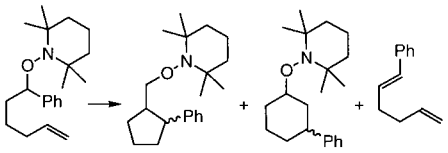
[*] Dr. A. Studer
Laboratorium für Organische Chemie
Eidgenössische Technische Hochschule
ETH-Zentrum, Universitätstrasse 16, 8092 Zürich (Switzerland)
Fax: (+41) 1-632-1144
E-mail: studer@org.chem.ethz.ch

[**] I am grateful to Prof. Dieter Seebach for generous financial support and to Prof. Hanns Fischer for helpful discussions. Dr. Sylvain Marque is acknowledged for conducting the ESR experiments, and Dr. Volker Gramlich for carrying out the X-ray analysis. I also thank Christian Wetter and Elisabeth Baier for conducting some experiments.

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

  0570-0833/00/3906-1108 $ 17.50+.50/0

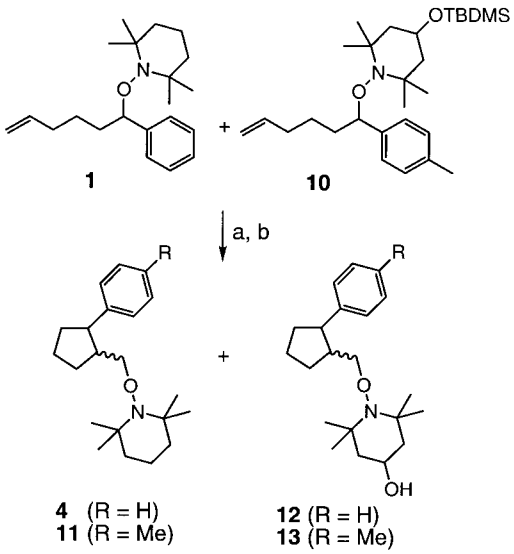
Table 1. Isomerization of **1** under different conditions (130–132 °C, sealed tube).



1 **4** **8** **9**

Entry	Solvent	Conc. [M]	*t* [h]	**4** [%]	**8** [%]	**9** [%]
1	*t*BuPh	0.1	22	< 2[a]	< 2[a]	20
2	DMPU	0.1	14	< 2[a]	< 2[a]	< 2[a]
3	DMF	0.1	16	56	10	< 2[a]
4	*t*BuOH	0.1	16	n.d.[b]	n.d.[b]	< 2[a]
5	*t*BuOH	0.01	36	n.d.[c]	n.d.[c]	< 2[a]
6	*t*BuOH	0.01	24[d]	53	10	< 2[a]
7	*t*BuOH	0.02	24[d]	70	13	2

[a] In the 300-MHz ^{1}H NMR spectrum of the crude product, no signals of the corresponding compound were observed. [b] After 16 h, 62% of the starting material remained. Products **4** and **8** were not isolated. [c] After 36 h, about 10% of starting material remained. Products **4** and **8** were not isolated. [d] 10% CSA was added.



4 (R = H)
11 (R = Me)
12 (R = H)
13 (R = Me)

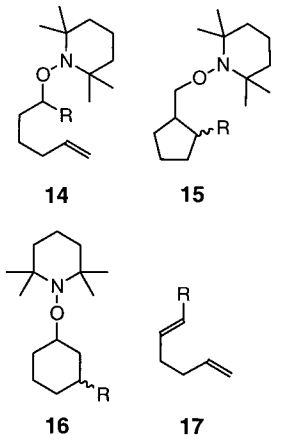
Scheme 2. Cross-over experiment with an equimolar mixture of the alkoxyamines **1** and **10**. a) *t*BuOH (0.02 M), 130 °C, 10% CSA, 24 h; b) TBAF, THF. TBAF = tetrabutylammonium fluoride; TBDMS = *tert*-butyldimethylsilyl.

It is known that the reaction of nitroxides with various C-centered radicals is dependent on solvent, with decreasing rates in polar protic solvents.[17] Furthermore, the homolytic cleavage is faster in polar solvents.[18] These synergistic effects[6b] lead to the observed rate enhancement in the isomerization upon using polar solvents.

An ionic mechanism (C–O heterolysis) can be excluded since clean cationic isomerizations in *t*BuOH are unlikely. To further corroborate the radical nature of the process, we also conducted ESR experiments. A deoxygenated sample of **1** in *t*BuOH/*t*BuPh (1/1) containing an excess of the C-radical scavenger 2,2,10,10-tetraperdeuteromethyl-isoindolin-^{15}N-oxyl (10 equiv) was heated to the reaction temperature, and the evolution of the ESR signal of the TEMPO radical was followed by continuous wave (CW) ESR spectroscopy.[19] Almost 100% of the TEMPO was generated, thus establishing initial C–O bond homolysis under these conditions.

To exclude a mechanism where isomerization occurs in a solvent cage, we also conducted a cross-over experiment. The alkoxyamines **1** and **10** (1/1 mixture) were isomerized under the optimized conditions. After desilylation, roughly equal amounts of the scrambled alkoxyamines **4** (19%), **11** (19%), **12** (16%), and **13** (16%) were isolated (Scheme 2).[20]

To further examine the scope and the limitations of the reaction, we tested whether isomerization also occurs with alkoxyamines **14a–j** (variation of substitutent R, Table 2).[21–23] For bromide **14a**, a clean reaction occurred, and **15a** was isolated in 71% (*trans*:*cis* = 2.7:1)[24] with **16a** (8%, entry 1). Isomerization of **14b** led to **17b** (10%), and the products **15b** and **16b** were isolated in 54% yield (**15b**:**16b** = 5.8:1, entry 2). Clean reactions were observed for heteroarenes **14c** and **14d** (entries 3 and 4). With **14e**, no 6-*endo* product was formed, and **15e** was isolated in 67% yield (d.r. = 1:1, entry 5) along with 10% of **17e**. The reaction with nitrile **14f** afforded 61% of the 5-*exo* product and 7% of **16f** (entry 6). No isomerization occurred with **14g** (R = H), **14h** (R = Me), and **14i** (R = SPh). It is likely that the C–O bond in **14g–i** is too strong to be effectively cleaved.[7] As expected, sulfone **14j** was not stable at higher temperatures (elimination of $PhSO_2H$).



14 **15** **16** **17**

R	Compound
4-BrC_6H_4	**a**
4-$CH_3OC_6H_4$	**b**
2-thienyl	**c**
2-pyridyl	**d**
tBuO_2C	**e**
NC	**f**
H	**g**
Me	**h**
PhS	**i**
$PhSO_2$	**j**

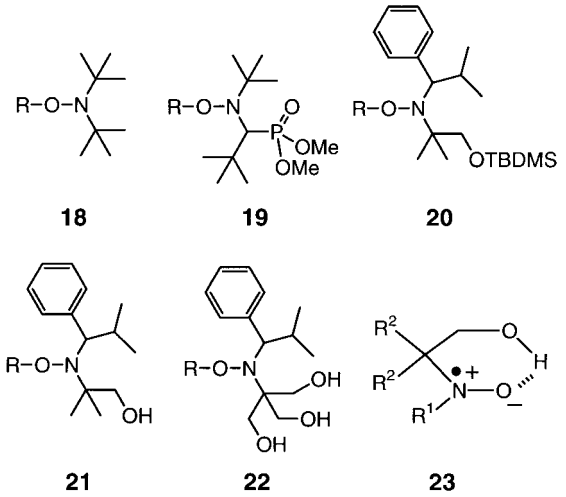
Table 2. Isomerization of **14a–f** under optimized conditions (*t*BuOH, 0.02 M, 24 h, 130–132 °C, 10% CSA, sealed tube). Yields refer to chromatographically (SiO_2) purified compounds.

Entry	Starting material	**15** [%]	d.r. (**15**) (*trans*:*cis*)	**16** [%][a]	**17** [%]
1	**14a**	71	2.7:1	8	< 2[b]
2	**14b**	46	2.8:1	8	10
3	**14c**	67	2.1:1	11	5
4	**14d**	57	1.6:1	12	5
5	**14e**	67	1:1	< 2[b]	10
6	**14f**	61	1.1:1[c]	7	< 2[b]

[a] The 6-*endo* product was formed as a 1:1 mixture of the diastereoisomers. [b] In the 300-MHz ^{1}H NMR spectrum of the crude product, no signals of the corresponding compound were observed. [c] The relative configuration of the two isomers was not assigned.

  0570-0833/00/3906-1109 $ 17.50+.50/0

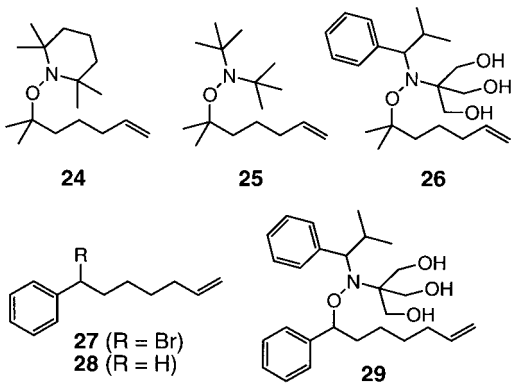
We then tested alkoxyamines **18**–**22** (R = 1-phenyl-5-hexenyl, variation of the nitroxide) in the isomerization.[25–28] The reactions were conducted in *t*BuOH (0.02 M) with or



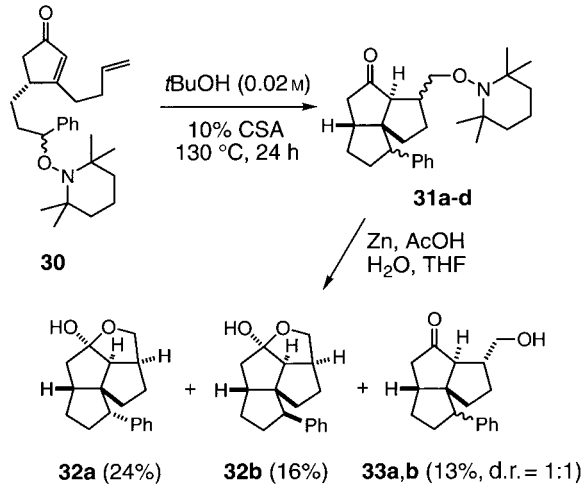
without added CSA (10%) at 130 °C, and the time necessary for complete consumption of the starting material was measured. The success of the isomerization is dependent on the bond dissociation energy (BDE) of the C–O bond (see above), which should correlate with the reaction time. The fastest isomerization (3 h) was observed for **18**. This acceleration, as compared to the cyclization of **1** (24 h with CSA), is not surprising, since it is known that alkoxyamines derived from di-*tert*-butyl nitroxide have very weak C–O bonds.[18] Only 4.5 h were necessary to completely isomerize phosphonate **19**. Addition of CSA led to decomposition of the starting alkoxyamine (for **18** and **19**).

Based on results from Ingold and Beckwith on the stabilization of nitroxides by *intermolecular* hydrogen bonding,[17] we decided to prepare new nitroxides capable of *intramolecular* hydrogen bonding (**23**).[29] In addition to decreasing the trapping rate of the nitroxide with C-centered radicals, the hydrogen bonding should also influence the rate of C–O bond homolysis (late transition state). Indeed, **21** was observed to isomerize faster (7 h; 12 h without CSA) than its silylated congener **20** (16 h with CSA). With **22**, reaction was already completed after 4 h (9 h without CSA).

The advantage of our new alkoxyamines over derivatives derived from commercially available nitroxides is documented by the failure of **24** (no reaction) and **25** (decomposition) to isomerize and by the successful isomerization of triol **26** (52%).[30] We also conducted a slow 6-*exo* cyclization of a phenyl-stabilized radical. Reaction of **27** under Bu_3SnH conditions (1.2 equiv of hydride, syringe pump, 7 h, benzene, 0.1 M) afforded only 11% of the cyclized product besides the dehalogenation product **28**. Alkoxyamine **29**, however, yielded the corresponding 6-*exo* product in 48% yield. An additional advantage, besides higher yield and lower toxicity in the reaction of **29** as compared to the tin hydride mediated cyclization of **27**, is the fact that the cyclization product is functionalized (protected alcohol) in the former case.



To further illustrate the potential of the method, we conducted a radical cascade reaction (Scheme 3). Enone **30**[31] was isomerized to give the angular triquinane **31** in 78% yield as the expected mixture of stereoisomers.[32] N–O bond cleavage with Zn in AcOH/THF/H_2O (3/1/1) afforded the hemiacetals **32a**, **b** (40%) and the alcohols **33a**, **b** (13%). The relative configuration of the major isomer **32a** was assigned by X-ray crystallographic analysis.[33]



Scheme 3. Radical cascade reaction.

In conclusion, the new tin-free radical cyclization reactions afford products which can be considered as protected alcohol derivatives.

Received: November 4, 1999 [Z 14225]

[1] A. G. Davies, *Organotin Chemistry*, Wiley-VCH, Weinheim, **1997**; D. P. Curran, *Synthesis* **1988**, 417; D. P. Curran, *Synthesis* **1988**, 489.
[2] P. A. Baguley, J. C. Walton, *Angew. Chem.* **1998**, *110*, 3272; *Angew. Chem. Int. Ed.* **1998**, *37*, 3072.
[3] B. E. Daikh, R. G. Finke, *J. Am. Chem. Soc.* **1992**, *114*, 2938.
[4] H. Fischer, *J. Am. Chem. Soc.* **1986**, *108*, 3925; D. Rüegge, H. Fischer, *Int. J. Chem. Kinet.* **1989**, *21*, 703; T. Kothe, S. Marque, R. Martschke, M. Popov, H. Fischer, *J. Chem. Soc. Perkin Trans. 2* **1998**, 1553.
[5] a) For early work see references cited in ref. [3]. See also D. C. Harrowven, G. Pattenden, *Tetrahedron Lett.* **1991**, *32*, 243; B. Giese, P. Erdmann, T. Göbel, R. Springer, *Tetrahedron Lett.* **1992**, *33*, 4545; B. P. Branchaud, G.-X. Yu, *Organometallics* **1993**, *12*, 4262; J. Hartung, B. Hertel, F. Trach, *Chem. Ber.* **1993**, *126*, 1178; P. A. Macfaul, I. W. C. E.

  0570-0833/00/3906-1110 $ 17.50+.50/0

Arends, K. U. Ingold, D. D. M. Wayner, *J. Chem. Soc. Perkin Trans. 2* **1997**, 135; A. Bravo, H.-R. Bjorsvik, F. Fontana, L. Liguori, F. Minisci, *J. Org. Chem.* **1997**, *62*, 3849; T. Kothe, R. Martschke, H. Fischer, *J. Chem. Soc. Perkin Trans. 2* **1998**, 503. b) Degenerate radical reactions: B. Quiclet-Sire, S. Zard, *Pure Appl. Chem.* **1997**, *69*, 645.

[6] a) D. H. Solomon, E. Rizzardo, P. Cacioli, US-A 4,581,429, **1985**; M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer, *Macromolecules* **1993**, *26*, 2987; C. J. Hawker, *J. Am. Chem. Soc.* **1994**, *116*, 11 314; C. J. Hawker, *Trends Polym. Sci.* **1996**, *4*, 183; b) H. Fischer, *Macromolecules* **1997**, *30*, 5666.

[7] M. V. Ciriano, H.-G. Korth, W. B. van Scheppingen, P. Mulder, *J. Am. Chem. Soc.* **1999**, *121*, 6375.

[8] Heterolytic O–N bond cleavage is possible in α-acyl-substituted alkoxyamines under acidic conditions: W. G. Skene, T. J. Connolly, J. C. Scaiano, *Tetrahedron Lett*. **1999**, *40*, 7297.

[9] Homolytic O–N bond cleavage in phenyl-substituted, TEMPO-derived alkoxyamines has not been observed.[7] The O–N bond is stronger than the C–O bond in $PhCH_2$-TEMPO (BDE(C–O): 32 kcal mol^{-1};[7] BDE(O–N) $\approx$ 53 kcal mol^{-1} [10]). In strained cyclic alkoxyamines, N–O bond homolysis is possible : F. M. Cordero, I. Barile, F. De Sarlo, A. Brandi, *Tetrahedron Lett.* **1999**, *40*, 6657, and references therein.

[10] H. G. Aurich, *Nitrones, Nitronates and Nitroxides* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1989**.

[11] H. Pines, N. C. Shi, D. B. Rosenfield, *J. Org. Chem*. **1966**, *31*, 2255; C. Walling, A. Cioffari, *J. Am. Chem. Soc*. **1972**, *94*, 6064.

[12] The Ca alkoxide was prepared by treating a suspension of TEMPO in H_2O with 1 equiv of the calcium salt of L-ascorbate dihydrate.[13]

[13] C. J. Hawker, G. G. Barclay, A. Orellana, J. Dao, W. Devonport, *Macromolecules* **1996**, *29*, 5245.

[14] The relative configuration was assigned after transformation of **4** to the corresponding known alcohol (Zn, AcOH, H_2O, THF).

[15] CSA was also used as an additive in SFRP: M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer, M. Saban, *Macromolecules* **1994**, *27*, 7228; P. G. Odell, R. P. N. Veregin, L. M. Michalak, D. Brousmiche, M. K. Georges, *Macromolecules* **1995**, *28*, 8453; R. P. N. Veregin, P. G. Odell, L. M. Michalak, M. K. Georges, *Macromolecules* **1996**, *29*, 4161; M. V. Baldovi, N. Mohtat, J. C. Scaiano, *Macromolecules* **1996**, *29*, 5497; T. J. Conolly, J. C. Scaiano, *Tetrahedron Lett*. **1997**, *38*, 1133.

[16] 1,2,3,3a,8,8a-Hexahydrocyclopent[*a*]indene[11] was formed in very low yield (< 2 %) under our conditions.

[17] A. L. J. Beckwith, V. W. Bowry, K. U. Ingold, *J. Am. Chem. Soc.* **1992**, *114*, 4983.

[18] G. Moad, E. Rizzardo, *Macromolecules* **1995**, *28*, 8722.

[19] The ESR experiments were carried out in the laboratory of Prof. Hanns Fischer at the University of Zürich. For experimental reasons the reactions were conducted in *t*BuOH/*t*BuPh (1/1). We also performed the isomerization under the conditions applied in the ESR experiment. Clean but slower isomerization was observed in *t*BuOH/*t*BuPh (1/1) without the use of CSA. Experimental details are given in: S. Marque, C. Le Mercier, P. Tordo, H. Fischer, *Macromolecules*, submitted.

[20] The 6-*endo* products also formed in the cyclization are omitted in Scheme 2 for reasons of clarity. For similar cross-over experiments in polymerizations, see: C. J. Hawker, *Acc. Chem. Res.* **1997**, *30*, 373.

[21] Arenes **14a–d** were prepared in analogy to **1** (unoptimized, 23–33 %). Ester **14e** was obtained by treatment of the corresponding Li enolate with $CuCl_2$ and TEMPO (59 %).[22] Nitrile **14f** was prepared after deprotonation (lithium diisopropylamide, LDA) of 6-cyano-1-hexene and subsequent addition of a suspension of $CuCl_2$ and TEMPO in THF at $-78\,^{\circ}C$ (67 %). Olefin **14g** was prepared from 6-iodo-1-hexene, Mg, and TEMPO (61 %).[13] Treatment of 6-iodo-1-heptene with TEMPO (6 equiv) and $(Me_3Si)_3SiH$ (4 equiv) in refluxing benzene (0.1 M) afforded **14h** (97 %). Thioether **14i** was prepared from the corresponding chloride[23] in analogy to **1**. Sulfone **14j** was available from phenyl-(5-hexenyl)sulfone after deprotonation (LDA) and subsequent oxidation ($CuCl_2$) in the presence of TEMPO (36 %).

[22] R. Braslau, L. C. Burrill II, M. Siano, N. Naik, R. K. Howden, L. K. Mahal, *Macromolecules* **1997**, *30*, 6445.

[23] D. L. Tuleen, T. B. Stephens, *J. Org. Chem*. **1969**, *34*, 31.

[24] The relative configuration of **15a–d** was assigned in analogy to that of **4**.

[25] Olefins **18–22** were prepared from 1-bromo-1-phenyl-5-hexene and the corresponding protected nitroxides (*tert*-butyldimethylsilyl (TBDMS) protecting groups for **20**[26] and orthoester protection for triol **22** (d.r. = 1:1, see the Supporting Information)) using a Cu^{I}-mediated process.[27] Phosphonate **19** (d.r. = 1:1) was prepared from the corresponding nitroxide[28] in an analogous manner. In the isomerizations of **18–22** the corresponding cyclized compounds (5-*exo* and 6-*endo*) were obtained in high yields (> 60 %).

[26] While we were carrying out our experiments, similar alkoxyamines were suggested for SFRP : D. Benoit, V. Chaplinski, R. Braslau, C. J. Hawker, *J. Am. Chem. Soc.* **1999**, *121*, 3904. The nitroxides were prepared in analogy.

[27] K. Matyjaszewski, B. M. Woodworth, X. Zhang, S. G. Gaynor, Z. Metzner, *Macromolecules* **1998**, *31*, 5955.

[28] S. Grimaldi, J.-P. Finet, A. Zeghdaoui, P. Tordo, D. Benoit, Y. Gnanou, M. Fontanille, P. Nicol, J.-F. Pierson, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1997**, *38*, 651.

[29] Intramolecular hydrogen bonding has already been suggested: E. G. Janzen, J. I-Ping Liu, *J. Magn. Reson.* **1973**, *9*, 510.

[30] Due to the complex NMR spectra, the 5-*exo*:6-*endo* ratio was not determined.

[31] The synthesis of **30** (d.r. = 1:1, racemic) is described in the Supporting Information.

[32] D. P. Curran, S.-C. Kuo, *J. Am. Chem. Soc.* **1986**, *108*, 1106; A. Matzeit, H. J. Schäfer, C. Amatore, *Synthesis* **1995**, 1432.

[33] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137891. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Pseudoprolines: Targeting a *cis* Conformation in a Mimetic of the gp120 V3 Loop of HIV-1**

Angela Wittelsberger, Michael Keller, Leo Scarpellino, Luc Patiny, Hans Acha-Orbea, and Manfred Mutter*

Pseudoprolines (ΨPro) have been introduced recently as synthetic proline analogues readily obtained by cyclocondensation of the amino acids cysteine, threonine, or serine with aldehydes or ketones.[1] Their application as structure-disrupting, solubilizing protecting groups in solid-phase peptide synthesis[2, 3] was followed by conformational investigations concerning the ΨPro preceding peptide bond.[4, 5] In fact, the propensity of the amino acid proline for forming a Xaa_{i-1}-Pro_i

[*] Prof. Dr. M. Mutter, Dipl.-Chem. A. Wittelsberger, Dr. M. Keller, Dr. L. Patiny
Institute of Organic Chemistry
University of Lausanne
BCH-Dorigny, 1015 Lausanne (Switzerland)
Fax: (+41) 21-692-39-55
E-mail: Manfred.Mutter@ico.unil.ch
L. Scarpellino, Prof. Dr. H. Acha-Orbea
Ludwig Institute for Cancer Research
Lausanne Branch and Institute of Biochemistry
University of Lausanne ISREC
Ch. des Boveresses 155, 1066 Epalinges (Switzerland)

[**] We are grateful to Dipl.-Biol. Raymond Jacquet for helpful advice. This work was supported by the Swiss National Science Foundation.

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