Pergamon

Tetrahedron: Asymmetry, Vol. 8, No. 1, pp. 27–28, 1997

Printed in Great Britain
PII: S0957-4166(96)00476-4 0957-4166/97 $17.00 + 0.00

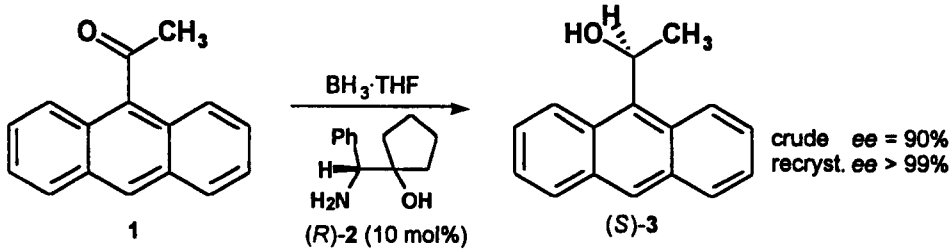
Preparation of 1-(9-anthryl)-ethanol and 9-anthryloxirane via catalytic enantioselective reduction of prochiral 9-anthryl ketones

I. Reiners and J. Martens *

Fachbereich Chemie der Universität Oldenburg, Ammerländer Heerstraße 114-118, D-26129 Oldenburg i.O., Germany

Abstract: Enantioselective reduction of prochiral 9-anthryl ketones to the corresponding chiral alcohols proceeds with high enantiomeric excess. The chiral alcohol 1-(9-anthryl)-2-bromo-ethanol can be converted to the corresponding chiral oxirane. © 1996, Elsevier Science Ltd. All rights reserved.

1-(9-Anthryl)-2,2,2-trifluorethanol (TFAE) is generally used in NMR spectroscopy for the determination of the enantiomeric excess of optically active substances[1]. Chiral 9-anthryl derivatives exhibit a broad utility in NMR, analytical work and asymmetric reactions[2]. The enantioselective synthesis of 1-(9-anthryl)-ethanol (*S*)-**3** was described previously by *Seebach*[3]. Thus, the reaction of anthracene-9-aldehyde with stoichiometric amounts of chiral methoxytitanium complexes led to (*S*)-**3** with an enantiomeric excess of only 6%. We report now the first efficient synthesis of 1-(9-anthryl)-ethanol (*S*)-**3** by enantioselective catalysis. The prochiral ketone **1**[4] was enantioselectively reduced with borane THF complex in the presence of the chiral amino alcohol (*R*)-**2**[5].

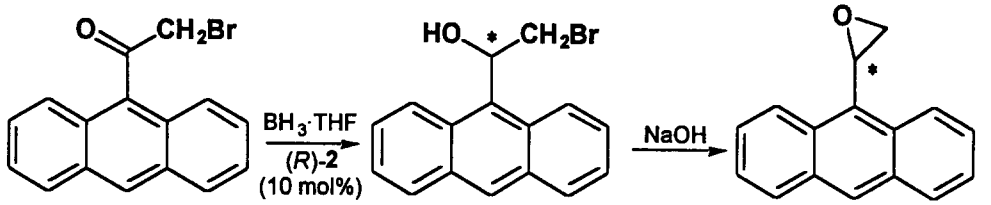


1 (*R*)-**2** (10 mol%) (*S*)-**3**

The catalytic reduction of **1** was performed with 10 mol% of amino alcohol (*R*)-**2** by addition of the prochiral ketone **1** over 60 min. to a mixture of the amino alcohol (*R*)-**2** and BH_3•THF (1 molar, 1 equiv.) at 30°C. The resulting alcohol (*S*)-**3** could be isolated by hydrolysis (2N HCl) followed by extraction with *tert*-butylmethyl ether. The combined organic layers were successively washed with 2N NaOH and NaCl solution, dried ($MgSO_4$) and concentrated under reduced pressure. The enantiomeric excess of the crude product (*S*)-**3** was determined by ^{1}H-NMR after derivatisation with (*S*)-O-acetyl mandelic acid[6]. The indicated enantiomeric excess of the crude product (*S*)-**3** was *ee*=90%. The crystallization of the crude product from CH_2Cl_2 and light petroleum 40/60 afforded the enantiomerically pure carbinol (*S*)-**3**, *ee* >99% (determined by ^{1}H-NMR, see above), mp. 118–119°C, $[\alpha]_D^{20}=-18.8$ (*c*=1.1, $CHCl_3$). The sign of the specific rotation indicated the (*S*)-configuration.

The enantioselective borane reduction of the 9-anthryl ketone **4**[7] in the presence of the amino alcohol (*R*)-**2** opened the possibility to prepare the optical active 9-anthryloxirane **6**. Chiral oxiranes are used as chiral building blocks and react with various nucleophiles, e.g. amines[8].

* Corresponding author. Email: martens@hp9000.hrz.uni-oldenburg.de



4 5 6

The chiral alcohol **5** was obtained without recrystallization with an enantiomeric excess *ee* >99% (determined with ^{1}H-NMR after derivatisation with (*S*)-O-acetyl mandelic acid). The chiral oxirane **6**[9] was synthesized from crude by treatment of **5** with 2N NaOH.

Acknowledgements

Thanks are due to *Degussa AG*, *Hermann-Schlosser-Stiftung* and *Fonds der Chemischen Industrie* for support.

References

1. D. Parker, *Chem. Rev.* **1991**, *91*, 1441–1457.
2. (a) M. Kühn, J. Buddrus, *Tetrahedron: Asymmetry* **1993**, *4*, 207–210. (b) N. Bargmann-Leyder, J.-C. Truffert, A. Tambuté, M. Chaude, *J. Chromatogr.* **1994**, *666*, 27–40. (c) K. Anton, J. Eppinger, L. Frederiksen, E. Francotte, T. A. Berger, W. H. Wilson, *J. Chromatogr.* **1994**, *666*, 395–401. (d) E. Francotte, *J. Chromatogr.* **1994**, *666*, 565–601. (e) M. de Moragas, A. Port, X. Sánchez-Ruiz, C. Jaime, C. Roussel, A. Virgili, *Tetrahedron: Asymmetry* **1995**, *6*, 1307–1310. (f) I. de Riggi, A. Virgili, M. de Moragas, C. Jaime, *J. Org. Chem.* **1995**, *60*, 27–31. (g) A. Carrière, A. Virgili, *Tetrahedron: Asymmetry* **1996**, *7*, 227–230.
3. D. Seebach, A. K. Beck, R. Imwinkelried, S. Roggo, A. Wonnacott, *Helv. Chim. Acta* **1987**, *70*, 954–974. According to this literature the product with a negative optical rotation presents the (*S*)-configuration. The enantiomeric excess and the absolute configuration was determined via HPLC analysis with a *Pirkle* column: (a) W. H. Pirkle, D. W. House, J. M. Finn, *J. Chromatogr.* **1980**, *192*, 143–158. (b) W. H. Pirkle, J. M. Finn, J. L. Schreiner, B. C. Hamper, *J. Am. Chem. Soc.* **1981**, *103*, 3964–3966. (c) W. H. Pirkle, J. M. Finn, *J. Org. Chem.* **1981**, *46*, 2935–2938. (d) D. Seebach, A. K. Beck, S. Roggo, A. Wonnacott, *Chem. Ber.* **1985**, *118*, 3673–3682.
4. L. May, E. Mossettig, *J. Am. Chem Soc.* **1948**, *70*, 686–688.
5. Ch. Dauelsberg, J. Martens, *Synth. Commun.* **1993**, *23*, 2091–2099.
6. The chiral alcohol was analysed via conversion into the ester with (*S*)-O-acetyl mandelic acid. The ester may be formed under nonracemizing conditions with use of dicyclohexylcarbodiimide as a coupling agent, in the presence of catalyst dimethylaminopyridine. D. Parker, *J. Chem. Soc., Perkin Trans. 2* **1983**, 83–88.
7. E. L. May, E. Mosettig, *J. Am. Chem. Soc.* **1948**, *70*, 686–688.
8. (a) H. C. Brown, G. G. Pai, *J. Org. Chem.* **1983**, *48*, 1784–1786. (b) R. K. Atkins, J. Frazier, L. L. Moore, *Tetrahedron Lett.* **1986**, *27*, 2451–2454.
9. 9-Anthryloxirane **6**: mp. 98–100°C, $[\alpha]_D^{20}=-98.1$ (c=0.9, $CHCl_3$).

(Received in UK 18 October 1996)