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

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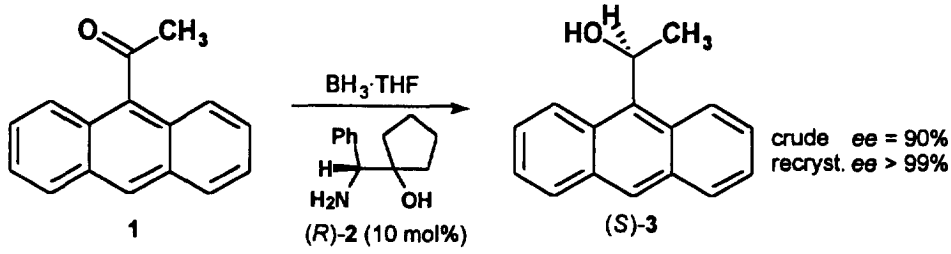
Abstract: Enantioselective reduction of prochiral 9-anthryl ketones to the corresponding chiral alcohols proceeds with high enantiomeric excess. The chiral alcohol 1-(9-anthryl)-2-bromo-ethanol can be converted to the corresponding chiral oxirane. © 1996, Elsevier Science Ltd. All rights reserved.

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].

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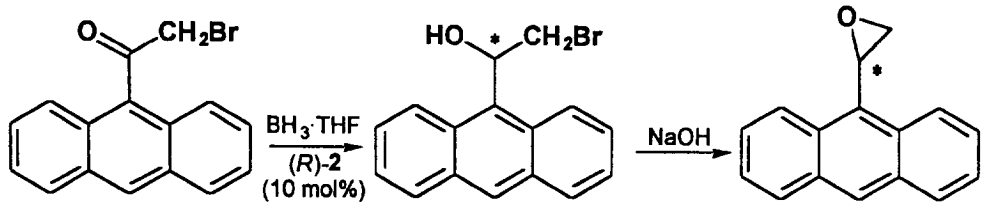

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The chiral alcohol **5** was obtained without recrystallization with an enantiomeric excess *ee* >99% (determined with ^{1}H-NMR after derivatisation with (*S*)-O-acetyl mandelic acid). The chiral oxirane **6**[9] was synthesized from crude by treatment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

Acknowledgements

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

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9. 9-Anthryloxirane **6**: mp. 98–100°C, $[\alpha]_D^{20}=-98.1$ (c=0.9, $CHCl_3$).

(Received in UK 18 October 1996)