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A HIGHLY STEREOSELECTIVE SYNTHESIS OF S(-)-[1,1'-BINAPHTHALENE]-2,2'-DIOL

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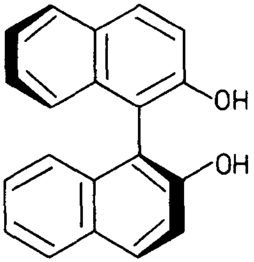
Abstract: The title compound is synthesized from 2-naphthol by a S-(+)-amphetamine-copper (II) complex in high chemical yield (85%) and high optical purity (up to 95%).

Optical pure [1,1'-binaphthalene]-2,2'-diol (1) has been used for: a) enantioselective reduction of ketones[1,2] b) stereoelective polymerization of heterocyclic monomers[3] c) induction of axial dissymmetry into the 1,1'-Binaphthyl bond via an intramolecular Ullmann coupling reaction[4] d) synthesis of chiral macrotricyclic ligands[5] and macrocycles[6].



S-(-)-(1)

The preparation of (1) has been performed by dimerization of 2-naphthol with $FeCl_3$ to the racemic binaphthol[7] followed by resolution through the cinchonine salt of its phosphate ester[8].

Dimerization of 2-naphthol can be attained also by copper-amine complexes[9].
This method was employed in the research for asymmetric oxidative coupling of phenols using optically active amines[10]. Via this method a chemical yield of 10-62% of binaphthol with an optical purity of 2.8-7.9% was obtained.
In our study on copper-amine complexes as a model for enzyme catalytic behaviour, we found a remarkable increase of optical purity when S-(+)-α-methyl-benzene-ethanamine (d-amphetamine) was used. After some experiments we improved the method obtaining (1) in 85% yield with an optical purity (enantiomeric excess) of 95%. Recovery of at least 80% of the d-amphetamine is possible without any noticeable loss of optical purity.

Experimental

6 g. S-(+)-α-methyl-benzeneethanamine-sulfate (d-amphetamine-sulfate) $[\alpha]_D^{22}$ + 23.6° (c 2, H_2O) dissolved in 150 ml H_2O was treated with 10 ml concentrated NH_4OH and extracted with ether (3 x 75 ml). The combined organic layers were washed with brine (2 x 5 ml), dried and concentrated to give 4,4 g of oil (32,5 mmol). This oil was dissolved in 20 ml MeOH and 1446 mg $Cu(NO_3)_2 \cdot 3H_2O$ (6 mmol) in 20 ml MeOH was added. The reaction flask was flushed with N_2 and the solution magnetically stirred. Within a few minutes a dark blue crystalline product precipitated. After 30 minutes a solution of 432 mg 2-naphthol (3 mmol) in 10 ml MeOH was added to the suspension while flushing with N_2. Stirring under N_2 was continued for 20 h. To the brown suspension 50 ml of 2N HCl was added. The copper-(II)-binaphthol-amine complex dissolved and after addition of 100 ml H_2O the binaphthol (1) precipitated. The precipitate was collected, washed with H_2O and dried. 367 mg, 85.5%, m.p. 197-200° C (Lit.[6] 207-208° C) $[\alpha]_D^{20}$ - 34.7° (c 0.5, THF) Lit.[4] - 35.5° (c 1.03, THF). The amphetamine was recovered from the filtrate by adding concentrated NH_4OH and extracting the solution with ether. Evaporation of the ether and treatment of the residue with 6 N H_2SO_4 in EtOH and acetone afforded 4,8 g of the amphetamine salt. 80%, $[\alpha]_D^{20}$ + 23.5° (c 2, H_2O).

References

1. M. Nishizawa, M. Yamada and R. Noyori, Tetrahedron Lett., 22, 247 (1981).
2. R. Noyori, I. Tomino, M. Nishizawa, J. Am. Chem. Soc., 101, 5843 (1979).
3. M. Sépulchre, N. Spassky, C. Mark and V. Schurig, Makromol. Chem., Rapid Commun., 2, 261 (1981).
4. S. Miyano, M. Tobita, M. Nawa, S. Sato and H. Hashimoto, J. Chem. Soc. Chem. Comm., 1233 (1980).
5. J.M. Lehn, J. Simon and A. Moradpour, Helv. Chim. Acta, 61, 2407 (1978).
6. E.P. Kyba, G.W. Gokel, F. de Jong, K. Koga, L.R. Sousa, M.G. Siegel, L. Kaplan, G.D.Y. Soga and D.J. Cram, J. Org. Chem., 42, 4173 (1977).
7. R. Pummerer, E. Prell and A. Ricche, Chem. Ber., 59, 2159 (1926).
8. J. Jacques, C. Fouquey and R. Viterbo, Tetrahedron Lett., 48, 4617 (1971).
9. W. Brackman and E. Havinga, Rec. Trav. Chim. Pays Bas, 74, 937 (1955).
10. B. Feringa and H. Wynberg, Bioorg. Chem., 7, 397 (1978).
11. E.B. Kyba, K. Koga, L.R. Sousa, M.G. Siegel and D.J. Cram, J. Am. Chem. Soc., 95, 2692 (1973).

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