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IMPROVED OPTICAL RESOLUTION OF R*,R* N,N'-DIMETHYL 1,2-DIPHENYL ETHYLENE DIAMINE

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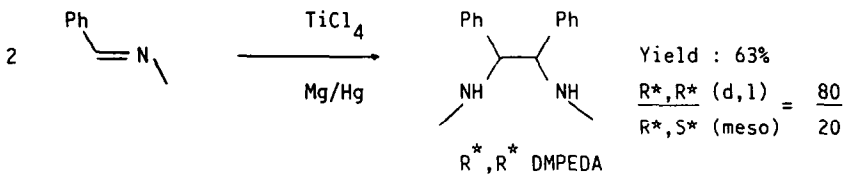
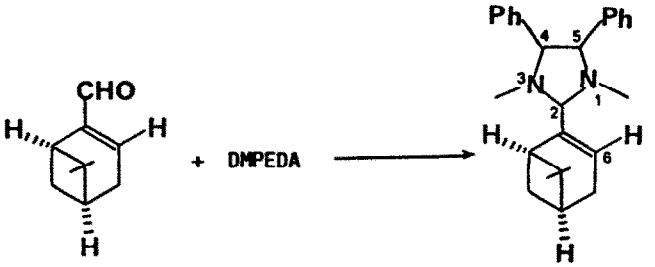
Summary - Optically active N,N'-dimethyl 1,2-diphenyl ethylenediamine (DMPEDA) is easily prepared by resolution with tartaric acid. Its e.e. is determined by NMR through imidazolidine formation with (-) myrtenal.

R*,R* N,N'-dimethyl 1,2-diphenyl ethylene diamine (DMPEDA) is an attractive chiral synthon of C_2 symmetry. However its use in the field of asymmetric synthesis [1] has been limited by lack of effective and practical methods of preparation and resolution.
The preparation of optically active DMPEDA was previously reported from resolved diphenyl ethylene diamine [2] prepared via isoamarine by a five step procedure
In this letter, we describe a very efficient optical resolution of (±) DMPEDA by fractionnal cristallisation using optically active tartaric acid.
Recently, independently from an another group[3], we disclosed a large scale and diastereoselective preparation of R*,R*(±) DMPEDA using a reductive coupling reaction with low valent titanium species



The R*,R* isomer was obtained free of R*,S* by flash column chromatography. We have now resolved it as follows.
A solution of R*,R* DMPEDA (16g, 6.66 mol) in EtOH (403 ml) was treated with (+) tartaric acid (10.08g, 6.,66 mol). The white precipitate obtained was heated to reflux and cooled to room temperature. The precipitate was separated by filtration and the salt decomposed with NaOH(5N) solution to give 6.4g (80% yield) of R,R DMPEDA $[\alpha]_D^{25}$ = +20° (C=0.15 $CHCl_3$)[4] (m.p. = 51°C, pentane).

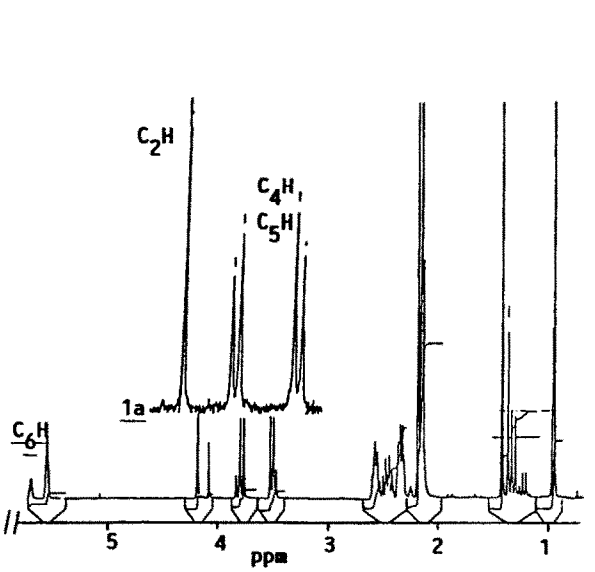
The DMPEDA recovered from the mother solution was similarly treated with (-)tartaric acid to give S,S DMPEDA $[\alpha]_D^{25}$ = -20° (C=0.15 $CHCl_3$) (m.p. =51°C, pentane) in 75% yield.
To determinate the optical purity, resolved DMPEDA was treated with an excess of optically active (-) myrtenal to give the corresponding imidazolidine 1[5].



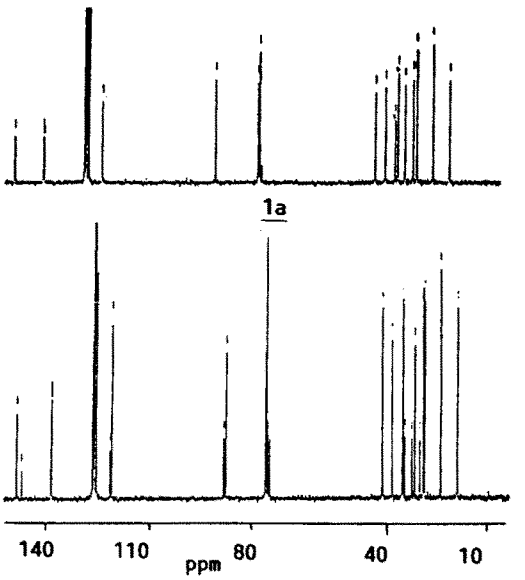
1a from DMPEDA R,R(+)

1b from DMPEDA S,S(-)

The diastereomeric purity of the obtained imidazolidine was easily determined by ^{13}C and/or ^{1}H NMR and was found to be > 95%.



70% 1b + 30% 1a ^{1}H NMR (200MHz)



70% 1b + 30% 1a ^{13}C NMR (50MHz)

Acknowledgements -

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References -

1. a/ M. Fiorini, G.M. Giongo, J. Mol. Catal., 5, 303 (1979)
   b/ U. Grusek, M. Heuschmann, Tetrahedron Lett., 28, 2681 (1987)
2. K. Sarco, N. Kubota, S. Takebayashi, M. Hasegawa, Bull. Chem. Soc. Jpn, 59, 931 (1986)
3. a/ C. Betschart, D. Seebach, Helv. Chim. Acta, 70, 2215 (1987)
   b/ P. Mangeney, T. Tejero, A. Alexakis, F. Grosjean, J. Normant, Synthesis, 255 (1988)
4. $[\alpha]_D^{25}$ Litt. : -18.02° (C=1, $CHCl_3$)[1a]
5. R.J. Ferm, J.L. Riebsomer, Chem; Rev., 54, 593 (1954)