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for the Preparation
of Organic Compounds

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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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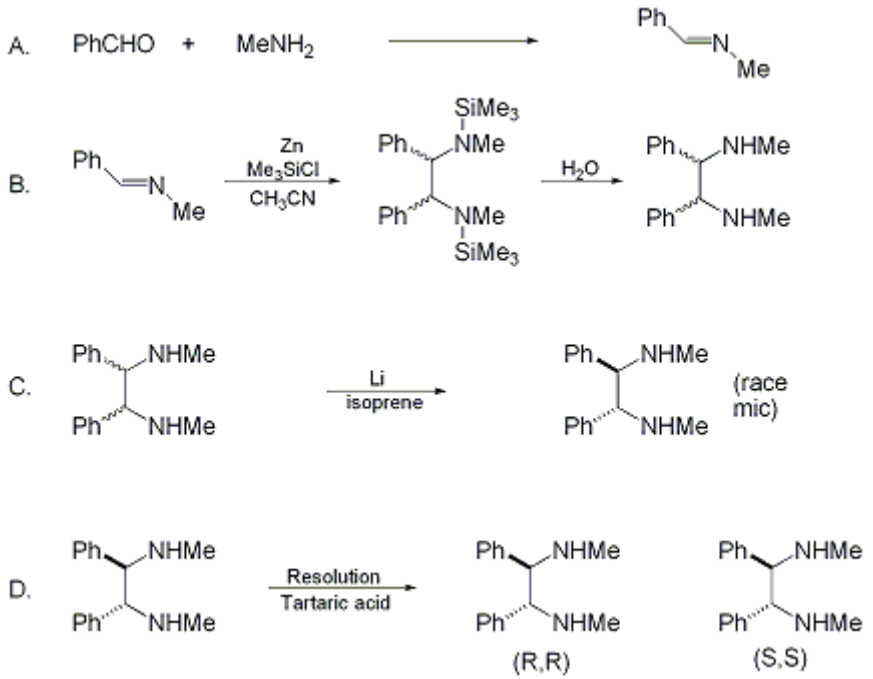
(R,R)- AND (S,S)-N,N'-DIMETHYL-1,2-DIPHENYLETHYLENE-1,2-DIAMINE

[1,2-Ethanediamine, N,N'-dimethyl-1,2-diphenyl-, [R-(R,R)]- and [S-(R,R)-]]



Submitted by Alex Alexakis, Isabelle Aujard, Tonis Kanger, and Pierre Mangeney[1] .
Checked by Nabi Magomedov and David J. Hart.

1. Procedure

A. N-Methylbenzimine . Under a well-ventilated hood, a 250-mL Erlenmeyer flask is equipped with a magnetic stirrer and charged with an aqueous solution (40% w/w, 100 mL) of methylamine . Freshly distilled benzaldehyde (26.5 g, 0.25 mol) is added to the stirred solution of methylamine at room temperature. A mildly exothermic reaction occurs resulting in a milky white emulsion. The Erlenmeyer flask is stoppered and the mixture is stirred overnight (15 hr). The milky emulsion is transferred to a separatory funnel, diethyl ether (200 mL) is added, and the organic phase is separated and dried over potassium carbonate (K_2CO_3). The solids are removed by filtration, washed with ether (50 mL), and the combined filtrate and washings are concentrated on a rotary evaporator. The residue is distilled through a 10-cm Vigreux column using a water aspirator to give 28.3 g (95%) of imine as a water white liquid (bp 99-100°C/25 mm) (Note 1).

B. meso- and dl-N,N'-Dimethyl-1,2-diphenylethylenediamine . A flame-dried, three-necked, round-bottomed flask (500 mL) is equipped with a mechanical or magnetic stirrer, a thermometer, water condenser connected to a nitrogen inlet, and a septum, and then charged with zinc (Zn) powder (13.1 g, 0.2 mol) and anhydrous acetonitrile (50 mL) under an atmosphere of nitrogen (Note 2). The zinc powder is activated by the addition of 1,2-dibromoethane (1.5 mL, 3.5 g, 0.02 mol) via syringe followed by warming the mixture at reflux for 1 min and then allowing the mixture to cool to room temperature. A small amount of chlorotrimethylsilane (Me_3SiCl) is added via syringe, whereupon evolution of ethylene gas is observed (Note 3). The mixture is stirred for 45 min, and then N-methylbenzimine (23.8 g, 0.2 mol) is added in one portion via syringe, followed by anhydrous acetonitrile (100 mL). The septum is replaced with an addition funnel (100 mL), and chlorotrimethylsilane (Note 4) (32.5 g, 38 mL, 0.3 mol) is slowly added (30 min) at a rate that maintains the internal temperature below 30°C. The

reaction mixture is stirred for 2 hr and then cooled to 0°C with an ice bath. The vigorously stirred mixture is hydrolyzed by *cautiously* adding, via the addition funnel, a solution prepared by mixing concentrated aqueous ammonium hydroxide (60 mL) with saturated aqueous ammonium chloride (140 mL). The excess zinc is removed by filtration at 1 atm, washed with ether (200 mL), and the residual zinc is covered with water (Note 5). The organic layer is separated, and the aqueous phase is extracted with diethyl ether (1 × 200 mL) and dichloromethane (2 × 200 mL) (Note 6). The combined organic phases are dried over anhydrous K_2CO_3. The salts are removed by filtration, washed with diethyl ether (50 mL), and the solvent is removed on a rotary evaporator to afford 24.3 g of a semi-solid residue that is used directly in the next reaction (Note 7) and (Note 8).

C. Isomerization of the diamine: dl-N,N'-Dimethyl-1,2-diphenylethylene-diamine . A solution of the crude diamine (24.3 g) in anhydrous tetrahydrofuran (THF) (200 mL) is placed in a three-necked, round-bottomed flask equipped with a mechanical or magnetic stirrer, a thermometer, an addition funnel, and a water condenser fitted with a nitrogen inlet. The addition funnel is removed, and small pieces of freshly cut lithium wire (1.8 g, 0.26 mol) are added in one portion (Note 9). Isoprene (10.2 g, 15 mL, 0.15 mol) is slowly added from the addition funnel while the solution is stirred vigorously. An exothermic reaction occurs, and the internal temperature is maintained below 40°C with the aid of a water bath. The lithium pieces become brilliant and the solution turns dark red. The course of the reaction is carefully monitored by TLC (Note 10) until the meso-diamine is isomerized into the dl-isomer. This takes approximately 1-2 hr. The reaction mixture is then cooled to 0°C, and the excess lithium metal is removed by gravity filtration through a funnel containing a plug of glass wool. The excess lithium is stored under oil. The filtrate is cooled in an ice bath and hydrolyzed by slow addition of aqueous 2.5 N hydrochloric acid (HCl, 200 mL). The layers are separated, and the aqueous phase is extracted with ether (Et_2O, 2 × 100 mL). The organic layer is discarded, and the aqueous layer is made basic with aqueous 35% (w/w) sodium hydroxide (50 mL). The aqueous solution is extracted with Et_2O (2 × 200 mL). The ether extracts are dried over K_2CO_3, the solids are removed by filtration, and the solvent is removed using a rotatory evaporator to give 23.4 g (95%) of crude dl-diamine as a brown oil (Note 11). Pure dl-diamine is isolated as follows. A 1-L, round-bottomed flask, equipped with a magnetic stirrer and a water condenser, is charged with the above crude diamine, racemic dl-tartaric acid (14.4 g, 0.096 mol) (Note 12) and absolute ethanol (700 mL). The heterogeneous mixture is brought to reflux at which point the precipitate is mainly dissolved. After 10 min at reflux, the mixture is left at room temperature for 2-4 hr. The resulting precipitate is collected by suction filtration and rinsed with ethanol (50 mL). The collected salt is added to a mixture of aqueous 35% (w/w) sodium hydroxide (60 mL), demineralized water (200 mL) and Et_2O (200 mL). The mixture is stirred for 30 min, the phases are separated and the aqueous layer is extracted with Et_2O (2 × 200 mL). The combined organic phases are dried over K_2CO_3, the salts are removed by filtration and the solvent is removed on a rotatory evaporator to give 12.2 g (51%) of pure dl-diamine as a colorless oil (Note 13).

D. Resolution of the dl-diamine: *(R,R)-(+)-N,N'-Dimethyl-1,2-diphenylethylenediamine and (S,S)-(−)-N,N'-Dimethyl-1,2-diphenylethylenediamine* . A 1-L, round-bottomed flask, equipped with a magnetic stirring bar and a water condenser, is charged with pure dl-diamine (12 g, 0.05 mol) , natural L-(+)-tartaric acid (7.1 g, 0.05 mol) (Note 14) and absolute ethanol (350 mL). The heterogeneous mixture is brought to reflux and the precipitate dissolves completely (Note 15). After 30 min the solution is allowed to cool to room temperature and stand overnight (17 hr). The precipitate is collected by filtration and washed with ethanol (2 × 50 mL). The salt is added to a mixture of aqueous 35% (w/w) NaOH (30 mL), demineralized water (100 mL) and Et_2O (100 mL). The solution is stirred for 30 min, and the phases are separated. The aqueous layer is extracted with Et_2O (2 × 100 mL), and the combined extracts are dried over K_2CO_3. The solids are removed by filtration, and the solvent is removed on a rotary evaporator to give 5.5 g (90%) of crude (R,R)-diamine as a white powder, mp 49-50°C (Note 16). The mother liquor is concentrated under reduced pressure, and the residue is stirred with a mixture of aqueous 35% (w/w) NaOH (30 mL), demineralized water (100 mL) and Et_2O (100 mL). The solution is stirred for 30 min, and the phases are separated. The aqueous layer is extracted with Et_2O (2 × 100 mL), and the combined extracts are dried over K_2CO_3. The solids are removed by filtration, and the solvent is removed on a rotary evaporator to give 6.15 g (101%) of crude (S,S)-diamine as an oil that solidifies upon drying under reduced pressure, mp 45-48°C (Note 17).

2. Notes

1. Spectral data for the imine follow: ^{1}H NMR ($CDCl_3$) δ: 3.5 (d, 3 H, J = 1.7), 7.4 (m, 3 H), 7.7 (m, 2 H), 8.2 (q, 1 H, J = 1.7) ; ^{13}C NMR ($CDCl_3$) δ: 48.1, 127.9, 128.5, 130.5, 136.4, 162.3 .
2. Zinc powder (325 mesh) was purchased from Aldrich Chemical Company, Inc., or Prolabo . Anhydrous acetonitrile was purchased directly from Aldrich Chemical Company, Inc. , and used without purification.
3. Activation of zinc is not always needed. For zinc purchased from Prolabo, the submitters report that the coupling reaction proceeds directly. The checkers note that gas evolution begins upon addition of the 1,2-dibromoethane and increases upon addition of the chlorotrimethylsilane.
4. Commercial chlorotrimethylsilane (Janssen Chimica or Aldrich Chemical Company, Inc.) is used without any purification.
5. The excess zinc is highly reactive and when dry could be exothermically oxidized by air.
6. The meso-diamine is less soluble in Et_2O than the dl-diamine. Therefore, dichloromethane is used to extract both isomers completely.
7. This crude diamine is a 50/50 mixture of meso- and dl-isomers. The mixture also contains 2-5% of N-methylbenzylamine and small amounts of other unidentified contaminants.
8. ^{1}H NMR analysis of the mixture ($CDCl_3$) shows the following distinct signals due to the meso-isomer δ: 2.09 (s, 6 H), 3.62 (s, 2 H); the dl-isomer δ: 2.25 (s, 6 H), 3.53 (s, 2 H) ; and N-methylbenzylamine δ: 2.45 (s, 3 H), 3.75 (s, 2 H) .
9. The submitters indicate that the isomerization rate is faster when lithium containing 0.5-1.0% sodium is used.
10. An aliquot of approximately 0.5 mL is withdrawn from the reaction using a Pasteur pipette and mixed with an equal volume of aqueous saturated ammonium chloride (NH_4Cl). Approximately 0.5 mL of ethyl acetate is added followed by brief mixing and withdrawal of the upper organic layer via pipette. TLC analysis of this sample is performed over silica gel using diethyl ether-triethylamine (95:5) as the eluant with a UV lamp for visualization. The R_f values of the dl-diamine and meso-diamine are 0.8 and 0.6, respectively. Close monitoring of the reaction is important as reduction of the diamine to afford N-methylbenzylamine (R_f = 0.35) can occur. The reaction can also be monitored by ^{1}H NMR analysis of the aforementioned aliquot after drying and concentration under reduced pressure.
11. This material is a mixture of dl-diamine:meso-diamine:N-methylbenzylamine (approximately 82.6:4.4:13.0) as shown by ^{1}H NMR (see (Note 8)).
12. Any commercial source of dl-tartaric acid works well. The ratio of tartaric acid to diamine is 1:1. The checkers found that if isomerization of the meso-diamine is incomplete, this purification procedure provides a mixture of meso- and dl-diamines.
13. Spectral data for the dl-diamine follow: ^{1}H NMR ($CDCl_3$) δ: 1.95 (b s, 2 H), 2.25 (s, 6 H), 3.53 (s, 2 H), 7.05 (m, 4 H), 7.15 (m, 6 H) ; ^{13}C NMR ($CDCl_3$) δ: 34.7, 71.4, 127.0, 128.0, 128.1, 141.2 .
14. Any commercial source of (+)-tartaric acid works well.
15. The shape of the precipitate becomes lighter and finer until total dissolution. Total dissolution is achieved only with absolute ethanol. With 95% grade ethanol the fine precipitate does not dissolve completely, but the resolution proceeds equally well.
16. The crude (R,R)-diamine has $[\alpha]_D$ +19.2 ($CHCl_3$, *c* 0.01) and an enantiomeric excess of >99%. Recrystallization of a 1.0-g sample from pentane at 0°C gave 0.66-0.72 g of (R,R)-diamine with mp 50-51°C; $[\alpha]_D$ +20.0 ($CHCl_3$, *c* 0.01) and an enantiomeric excess of >99%. The enantiomeric excess was measured as follows:[2] Into a dry NMR tube under nitrogen is placed a solution of the (R,R)-diamine (32 mg, 0.13 mol) in 0.8 mL of dry deuterochloroform ($CDCl_3$). To this solution are added dry N,N-diethylaniline (80 µL) and a solution of freshly distilled phosphorus trichloride (PCl_3, 50 µL of a 3.2 M solution in dry $CDCl_3$, 0.16 mmol). The solution is shaken vigorously. ^{31}P NMR analysis indicates the formation of a "P-Cl" species at δ 176.2. Enantiomerically pure l-menthol (25 mg, 0.16 mmol) is dissolved in 0.8 mL of dry $CDCl_3$, and the resulting solution is added to the NMR tube under nitrogen. The tube is shaken, and ^{31}P NMR analysis indicates the formation of only one "P-OR" species at δ 143.5. The diastereomeric "P-OR" species derived from the (S,S)-diamine appears at δ 141.2. If the sample is contaminated with meso-diamine, the signal for the corresponding "P-OR" species appears at δ 138.9. Depending on the quality of reagents, some additional peaks may appear in the spectrum, but they do not interfere with the measurement of % ee.
17. The crude (S,S)-diamine has $[\alpha]_D$ −17.1 ($CHCl_3$, *c* 0.01) and an enantiomeric excess of approximately 96% using the method described above. Recrystallization of a 1.0-g sample from pentane at 0°C gave 0.71 g of (S,S)-diamine with mp 49.5-50.5°C, $[\alpha]_D$ −19.7 ($CHCl_3$, *c* 0.01) and an

enantiomeric excess of >99% using the method described above. A second recrystallization of this material gave 0.5 g of material with little change in physical properties: mp 50-50.5°C, $[\alpha]_D$ −20.0 ($CHCl_3$, *c* 0.01).

Waste Disposal Information

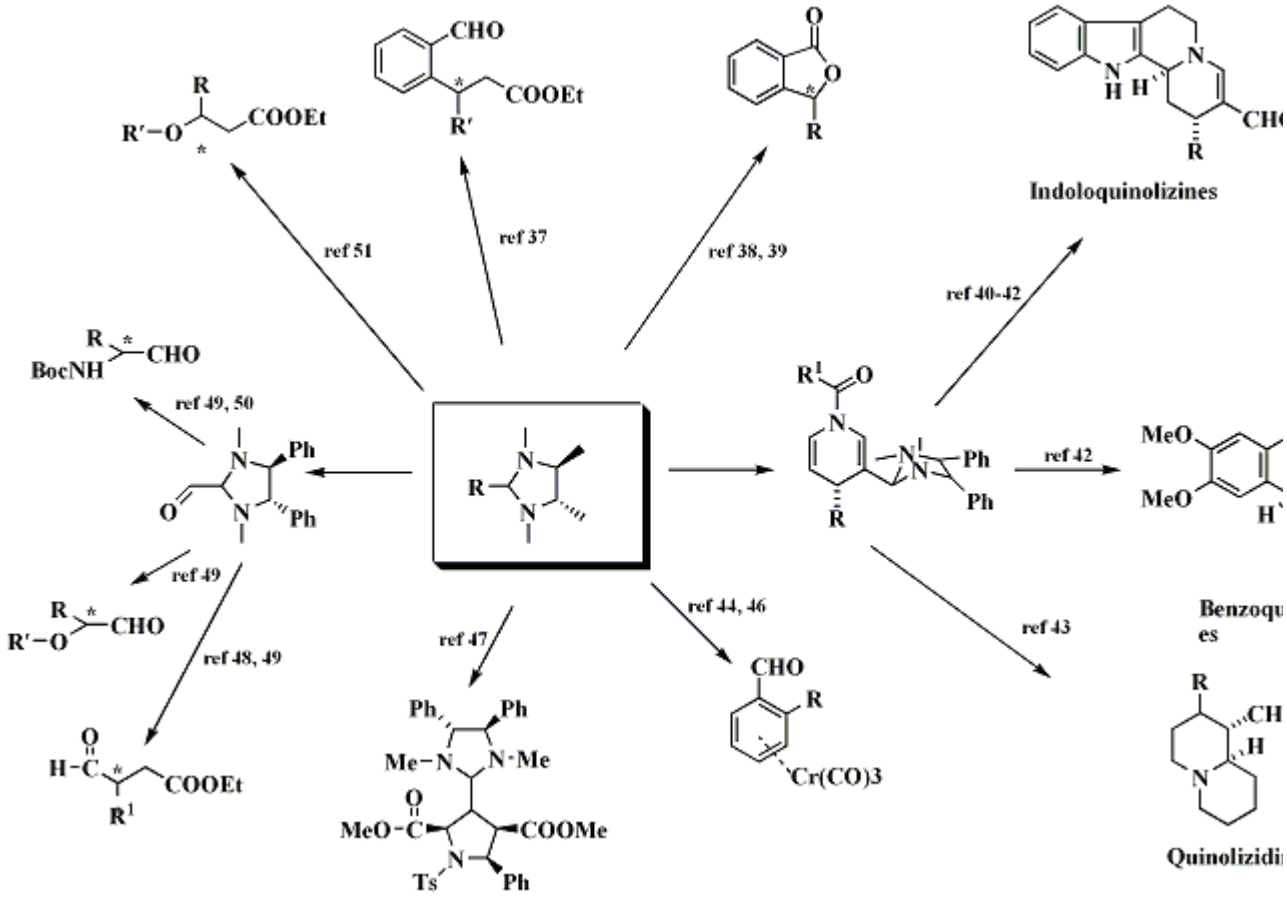
All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

There are a few reports on the synthesis of N,N'-dimethyl-1,2-diphenylethylenediamine by pinacol couplings[3,4,5,6,7,8] or by N-methylation of the primary diamine.[9,10] Pinacol type couplings of imines have been reported for the synthesis of other C_2 symmetrical N-substituted or unsubstituted 1,2-diarylethylenediamines using various reducing metals in different solvents.[11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30] However, the present synthesis of N,N'-dimethyl-1,2-diphenylethylenediamine is the most suitable for large scale preparation. There are no expensive or hazardous starting materials, and the procedure does not require tedious filtrations or chromatographic separation of diastereomers.

N,N'-Dimethyl-1,2-diphenylethylenediamine and related chiral diamines are not only useful chiral auxiliaries in asymmetric synthesis, but they have also found applications as analytical reagents. They allow the resolution and the determination of enantiomeric composition of aldehydes by formation of diastereomeric aminals.[31,32,33,34] Combined with PCl_3, they allow determination of the enantiomeric composition of alcohols, biphenols, thiols and amines.[35,36] The diamine described here is used most extensively.

Formation of aminals (the nitrogen equivalent of acetals) is a very easy process and occurs without any catalyst and at room temperature. The chiral imidazolidine ring thus formed is a powerful stereodifferentiating group, acting either by steric effects or through chelation control. Aminals also serve as efficient protective groups of aldehyde functionality, allowing the easy recovery of this functionality without epimerization, even in the α-position. Several applications of this concept are summarized in Scheme 1.[37,38,39,40,41,42,43,44,45,46,47,48,49,50,51]



The present method, with additional examples, was recently published.[52,53]

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

(R,R)-N,N'-Dimethyl-1,2-diphenylethylene-1,2-diamine:
1,2-Ethanediamine, N,N'-dimethyl-1,2-diphenyl-, [R-(R,R)]- (12); (118628-68-5)

(S,S)-N,N'-Dimethyl-1,2-diphenylethylene-1,2-diamine:
1,2-Ethanediamine, N,N'-dimethyl-1,2-diphenyl-, [S-(R,R)]- (10); (70749-06-3)

N-Methylbenzimine:
Methylamine, N-benzylidene- (8);
Methanamine, N-(phenylmethylene)- (9); (622-29-7)

Methylamine (8);
Methanamine (9): (74-89-5)

Benzaldehyde (8,9); (100-52-7)

meso-N,N'-Dimethyl-1,2-diphenylethylenediamine:
1,2-Ethanediamine, N',N'-dimethyl-1,2-diphenyl-, (R,S)- (9); (60509-62-8)

meso-N,N'-Dimethyl-1,2-diphenylethylenediamine:
1,2-Ethanediamine, N,N'-dimethyl-1,2-diphenyl-, (R,S)- (9); (60508-97-6)

Zinc (8,9); (7440-66-6)

Acetonitrile: TOXIC: (8,9); (75-05-8)

1,2-Dibromoethane:
Ethane, 1,2-dibromo- (8,9); (106-93-4)

Chlorotrimethylsilane:
Silane, chlorotrimethyl- (8,9); (75-77-4)

Ethylene (8);
Ethene (9); (74-85-1)

Lithium (8,9); (7439-93-2)

Isoprene (8);
1,3-Butadiene, 2-methyl- (9); (78-79-5)

DL-Tartaric acid:
Tartaric acid, DL- (8);
Butanedioic acid, 2,3-dihydroxy-, (R,R)-(±)- (9); (133-37-9)

L-Tartaric acid:
Tartaric acid, L- (8);
Butanedioic acid, 2,3-dihydroxy-, [R-(R,R)]- (9); (87-69-4)

N-Methylbenzylamine: Aldrich: See:
Benzylmethylamine:
Benzylamine, N-methyl- (8);
Benzenemethanamine, N-methyl- (9); (103-67-3)

N,N-Diethylaniline:

Aniline, N,N-diethyl- (8);
Benzeneamine, N,N-diethyl- (9); (91-66-7)

Phosphorus trichloride (8,9); (7719-12-2)