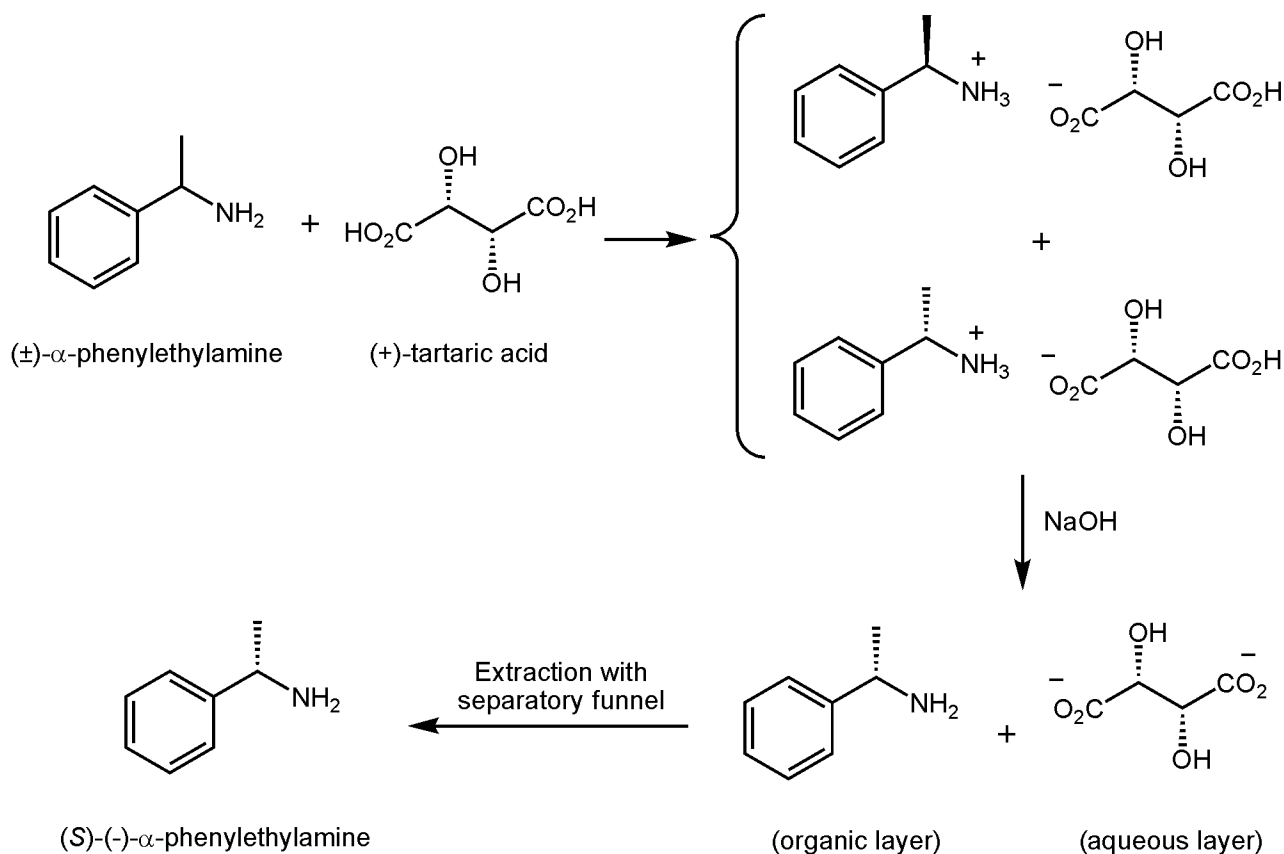## Resolution of Racemic α-Phenylethylamine (aka, α-Methylbenzylamine)

Reading   Experiment 30/30A in Pavia (5th). Review the techniques in the Required Reading section. See also Section 5.9 in Klein. This experiment is based on the original reference, which was published in *Organic Syntheses*, orgsyn.org . The citation is *Organic Syntheses*, Vol. 49, p. 93 (1969); Coll. Vol. 5, p. 932 (1973)(use the search feature and look for phenylethylamine).   Download the HTML version since there is an issue with the .pdf file. Finally, read through the manual for the type of polarimeter you will use (the SR-6). The manual can be found in the Laboratory folder on-line.

General

The resolution of chiral amines can be performed by treatment with a chiral enantiopure carboxylic acid such as tartaric acid (more generally referred to as a chiral auxiliary). The resulting mixture of diastereomers can be separated, since diastereomers have different physical properties, such as melting points, NMR spectra, density, and, in this case, solubility. Conversion of the derivative back to the free amine constitutes a resolution of enantiomers. The procedure described in this experiment is a typical example this type of separation which is termed a *classical resolution*. The efficiency of any resolution is measured by determining the enantiomeric excess (%ee) of the final product – you will use optical rotation to do this.

(±)-α-phenylethylamine   (+)-tartaric acid

NaOH

(*S*)-(-)-α-phenylethylamine

Extraction with separatory funnel

(organic layer)   (aqueous layer)

Prelab

Title, **Name**, **Date**, **Reagent Table** with as much physical data for the expected product as you can find (mp, bp, [α], density, etc.). Be sure that the data for the expected final product is for the (S)-(-) isomer is in your table. Note what the theoretical yield of the resolved amine should be. Also, note the melting point of the expected intermediate salt (which can be found in the Org. Syn. reference).

Also include a **Separation Scheme** which shows the isolation of the resolved amine, starting from the point of the solid crystalline salt – the ammonium carboxylate. Show each step involved in isolating the pure resolved amine. (see the guide on-line **Separation Schemes Tips and Notes**) The separation scheme should be in your notebook as part of your separation scheme.

Procedure

Follow the procedure described for Experiment 30A. During the first laboratory period, mix the tartaric acid and amine as described. Then stopper the flask with a *natural* cork stopper and leave in your bench drawer until the following laboratory period (the instructor will provide seed crystals at this time). During the next laboratory period you will spend some time making sure that you have obtained the correct prismatic crystals (as described in the text). Be sure to weigh the crystals and save a sample for melting point determination. You will be using **Method 1** described in the text for removing the methylene chloride. When you have obtained your final product, combine it with the other students' material for the optical rotation measurement (see below).

Combine your sample with the "class" sample in the hood (see instructor for details) for measurement of the optical rotation. Obtain the observed rotation ( ) of the class sample and then calculate the specific rotation, [α].

$$[\alpha]_D^T = \frac{\alpha}{c \times l}$$

where T is temperature in C, *c* is the concentration in g/mL and *l* is the path length of the cell in units of dm.

In this case, T is the room temperature at the time of measurement, *c* is the density of the amine, and *l* is either 1.00 or 2.00 dm depending on which sample cell is used.

To Complete the Experiment – Partial Report

From the mass of the crystalline tartrate salt that you obtained, calculate the corresponding amount of free amine. Compare this value to the actual mass you obtained after the isolation of your sample of amine. From the observed rotation of the combined class sample calculate the specific rotation of your product and determine the optical purity (%*ee*) of your product.

$$\frac{|d-l|}{d+l} \times 100 = \frac{[\alpha]_{exp}}{[\alpha]_{lit}} \times 100 = \text{optical purity} = \%ee$$

(where *d* and *l* are the percentages of the (+) and the (-) isomers in the sample)

Answer Questions 1-4 from p. 276 of Pavia (5th).
To complete the Partial report, see the **Laboratory Report Format and Check-List** at the Laboratory website.