

# ORGANIC SYNTHESSES

AN ANNUAL PUBLICATION OF SATISFACTORY  
METHODS FOR THE PREPARATION  
OF ORGANIC CHEMICALS

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# ORGANIC SYNTHESSES

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## NOMENCLATURE

Preparations are listed under the names which are used commonly for the compounds. For the convenience of those who wish to make a complete survey of the literature on any preparation, the *Chemical Abstracts* **indexing name** for each compound is given as a subtitle when that name differs from the title of the preparation.

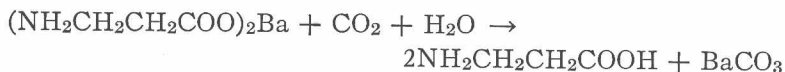
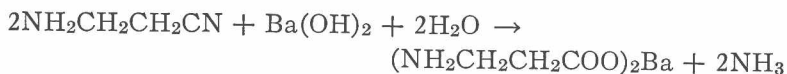
## NOTICE TO SUBMITTERS OF PREPARATIONS

*Organic Syntheses* invites the submission of preparations of compounds which are of general interest or which illustrate useful synthetic methods. Preparations are welcomed particularly from those who have had occasion to work out the optimum conditions of preparation. The directions should be written in the style employed in the latest volume of *Organic Syntheses*. A copy of the current style sheet will be sent to those who request it. Full details for all steps in the procedures should be included, and the range of yields should be reported rather than the maximum yield obtainable. Wherever possible the melting point, the boiling range at various pressures, and the refractive index of each product should be given. The method of preparation or source of compounds used should be recorded as well as criteria of purity. Two copies of the directions should be sent to the Secretary. Additions, corrections, and improvements to previously published preparations are likewise welcomed.

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## **$\beta$ -ALANINE**



Submitted by JARED H. FORD.

Checked by HOMER ADKINS and JAMES M. CAFFREY.

### **1. Procedure**

In a 2-l. three-necked flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel is placed 185 g. (0.55 mole) of technical barium hydroxide octahydrate. The flask is heated on a steam bath in a hood. When the barium hydroxide has dissolved in its water of crystallization, the stirrer is started and 70.1 g. (1.00 mole) of  $\beta$ -aminopropionitrile (p. 3) is added dropwise over a period of 40 minutes. The temperature is maintained at 90–95° during the addition and for 40 minutes thereafter. Forty grams of asbestos filter aid (Note 1) and 1 l. of hot water are added, and the mixture is saturated with carbon dioxide (Note 2) while the temperature is held at 85–90°. The mixture is filtered with suction, the precipitate is returned to the flask with 500 ml. of hot water, and the mixture is heated and stirred for 20 minutes. After the barium carbonate has been filtered the washing procedure is again repeated with a second 500 ml. of hot water. The combined filtrates and washings are concentrated under reduced pressure on the steam bath (Note 3) until solid material separates. To the residue are added 200 ml. of hot water and 0.5 g. of decolorizing carbon (Note 4). The resulting solution is warmed on the steam bath for a few minutes and then filtered into a weighed 500-ml. Erlenmeyer flask. The flask

is heated on a steam bath, and a jet of clean compressed air is directed at the surface of the solution. When the total weight of the solution is 130 g., it is cooled to 15–20° and diluted slowly with 400 ml. of methanol. After the solution has stood for several hours in the refrigerator, the product is filtered with suction and washed with two 100-ml. portions of methanol. The yield of  $\beta$ -alanine melting at 197–198° (dec.) is 75–80 g. (85–90%).

## 2. Notes

1. Standard Super-Cel (Johns-Manville, Inc.) was used.
2. Either carbon dioxide gas or Dry Ice may be used, and the saturation may be completed in 15–20 minutes by either method. The pH of the saturated solution is about 8–9 when tested with a universal indicator paper, such as Alkacid or Hydrion.
3. The submitter used a special apparatus suitable for the rapid evaporation of water under reduced pressure. The checkers used standard flasks.
4. The solution is nearly colorless at this point, but the carbon aids in the removal of finely divided insoluble material.

## 3. Methods of Preparation

$\beta$ -Alanine has been prepared by the catalytic reduction of cyanoacetic esters<sup>1</sup> or salts;<sup>2</sup> by heating acrylonitrile,<sup>3</sup>  $\beta$ -aminopropionitrile,<sup>4</sup> *bis*-( $\beta$ -cyanoethyl)-amine,<sup>5</sup>  $\beta$ -hydroxypropionitrile,<sup>6</sup>  $\beta$ -alkoxypropionitriles,<sup>7</sup> *bis*-( $\beta$ -cyanoethyl) ether,<sup>8</sup> or *bis*-( $\beta$ -cyanoethyl) sulfide<sup>8</sup> with aqueous ammonia at 150–225°; by the hydrolysis of  $\beta$ -aminopropionitrile with concentrated hydrochloric acid and subsequent removal of the acid with anion exchange resins.<sup>9</sup> The method as described above has been published.<sup>10</sup> Additional references to methods of preparation are given in connection with a procedure for the making of  $\beta$ -alanine from succinimide through the action of potassium hypobromite.<sup>11</sup>

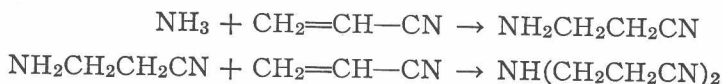
<sup>1</sup> Schaaf and Pickel, U. S. pat. 2,365,295 [C. A., **39**, 4626 (1945)].

<sup>2</sup> Ruggli and Businger, U. S. pat. 2,367,436 [C. A., **39**, 3012 (1945)].

- <sup>3</sup> Carlson and Hotchkiss, U. S. pat. 2,335,997 [C. A., **38**, 2972 (1944)].  
<sup>4</sup> Carlson, U. S. pat. 2,336,067 [C. A., **38**, 2971 (1944)].  
<sup>5</sup> Kirk, U. S. pat. 2,334,163 [C. A., **38**, 2667 (1944)].  
<sup>6</sup> Kirk and Paden, U. S. pat. 2,364,538 [C. A., **39**, 3556 (1945)].  
<sup>7</sup> Paden and Kirk, U. S. pat. 2,335,605 [C. A., **38**, 2970 (1944)].  
<sup>8</sup> Dean, U. S. pat. 2,335,653 [C. A., **38**, 2970 (1944)].  
<sup>9</sup> Buc, Ford, and Wise, *J. Am. Chem. Soc.*, **67**, 92 (1945).  
<sup>10</sup> Ford, *J. Am. Chem. Soc.*, **67**, 876 (1945).  
<sup>11</sup> *Org. Syntheses* Coll. Vol. **2**, 20 (1943).

## $\beta$ -AMINOPROPIONITRILE and bis-( $\beta$ -CYANOETHYL)-AMINE

(Propionitrile,  $\beta$ -amino-, and propionitrile,  $\beta, \beta'$ -iminodi-)



Submitted by SAUL R. BUC.

Checked by HOMER ADKINS and JAMES M. CAFFEY.

### 1. Procedure

*Acrylonitrile is a poisonous compound. All steps in the procedure up to the distillation of the products should be carried out in a hood.*

The reactions are carried out in 1-l. heavy-walled bottles provided with rubber stoppers which must be wired securely in place (Note 1). In each of four bottles are placed 400 ml. of concentrated ammonium hydroxide (28–30% ammonia) and 100 ml. (80 g., 1.5 moles) of cold acrylonitrile (Note 2). The rubber stoppers are immediately wired in place (Note 3). Each bottle is then shaken intermittently until after about 5 minutes the reaction mixture becomes homogeneous. Thereupon, the bottle, wrapped in a towel, is immediately set away under a hood (Note 4).

The reaction mixtures are allowed to stand a few hours or overnight and then are transferred to a 3-l. flask. The water and ammonia are distilled under reduced pressure as rapidly as



possible until the boiling point is about  $50^{\circ}/20$  mm. (Note 5). The higher-boiling products (395 g.) are then transferred to a 1-l. Claisen flask and fractionated under reduced pressure.

The crude primary amine (138–149 g.) is distilled over the range  $75\text{--}110^{\circ}/21$  mm. (Note 6), and the crude secondary amine (213–226 g.) in the range  $130\text{--}150^{\circ}/1$  mm. The primary amine, b.p.  $79\text{--}81^{\circ}/16$  mm. or  $87\text{--}89^{\circ}/20$  mm. ( $n_D^{20}$  1.3496), after refractionation, is obtained in a yield of 130–140 g. (31–33%) (Note 7). The secondary amine, b.p.  $134\text{--}135^{\circ}/1$  mm. ( $n_D^{20}$  1.4640), is obtained in a yield of about 210 g. (57%).

## 2. Notes

1. The 1-l. centrifuge bottles (Corning No. 1280) carrying No. 6 rubber stoppers, as used for catalytic hydrogenation, are suitable for carrying out reactions under pressures up to at least 3 atmospheres. The submitter used a heavy, selected 2-l. round-bottomed flask instead of the four bottles specified in the procedure above.

2. The acrylonitrile should be free of polymer. If there is uncertainty as to its quality, the acrylonitrile should be redistilled.

3. The temperature of the mixture does not rise during the period of solution of the acrylonitrile in the ammonium hydroxide. However, almost immediately thereafter the temperature of the solution begins to rise slowly, reaching a value of about  $65^{\circ}$  after an interval of perhaps 10 minutes. There is no significant rise in pressure within the bottle until the temperature of the reaction mixture begins to rise. The maximum pressure reached is apparently less than 2 atm.

4. The checkers placed the wrapped bottles within a 10-gal. crock located under a hood. There is no danger that the bottles will be broken by the pressure developed. However, if a stopper is not firmly held, it may be pushed out, in which event a portion of the reaction mixture will foam out of the bottle.

5. The submitter used a special apparatus suitable for the rapid evaporation of water under reduced pressure. The checkers

used standard flasks. Better yields result from the rapid removal of water.

6. It is not necessary to purify the crude primary amine by redistillation if it is to be used immediately for the preparation of  $\beta$ -alanine. However, the moist nitrile is not stable in storage, pressure being developed in a container stored at room temperature.

7. Yields of 60–80% of the primary amine<sup>1</sup> have been obtained by introducing the acrylonitrile below the surface of the aqueous ammonia preheated to 110° in a steel reactor suitable for pressure reactions.

### 3. Methods of Preparation

$\beta$ -Aminopropionitrile and *bis*-( $\beta$ -cyanoethyl)-amine have been made by the addition of anhydrous<sup>2,3</sup> or aqueous<sup>4</sup> ammonia to acrylonitrile.

<sup>1</sup> Ford, Buc, and Greiner, *J. Am. Chem. Soc.*, **69**, 844 (1947).

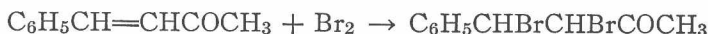
<sup>2</sup> Hoffmann and Jacobi, U. S. pat. 1,992,615 [*C. A.*, **29**, 2548 (1935)].

<sup>3</sup> Whitmore, Mosher, Adams, Taylor, Chapin, Weisel, and Yanko, *J. Am. Chem. Soc.*, **66**, 725 (1944).

<sup>4</sup> Buc, Ford, and Wise, *J. Am. Chem. Soc.*, **67**, 92 (1945).

## BENZALACETONE DIBROMIDE

### (2-Butanone, 3,4-dibromo-4-phenyl-)



Submitted by NORMAN H. CROMWELL and RICHARD BENSON.

Checked by R. L. SHRINER and WILLIAM O. FOYE.

### 1. Procedure

In a 1-l. three-necked round-bottomed flask fitted with an efficient mechanical stirrer, a thermometer, and a 125-ml. dropping funnel are placed 100 g. (0.68 mole) of pure, redistilled benzal-

acetone<sup>1</sup> and 300 ml. of carbon tetrachloride. The reaction flask is immersed in an ice-water bath to maintain the reaction mixture between 10° and 20°. With stirring, a cooled solution of 109.5 g. (34.2 ml., 0.68 mole) of bromine in 60 ml. of carbon tetrachloride is run through the dropping funnel as rapidly as the color is destroyed (Note 1). During this addition the reaction flask should be shielded from direct sunlight (Note 2).

After all the bromine has been added, stirring is continued for 4 to 5 minutes longer and the dibromide is collected by filtration on an 11-cm. Büchner funnel, using suction. The product is washed with 100 ml. of warm 75% ethanol (Note 3). The crude product is purified by dissolving in the minimum amount of boiling methanol (800–1000 ml.) and cooling the solution in an ice bath for 4 hours. The product is collected by filtration and dried in a vacuum desiccator in the absence of light for 24 hours. The yield amounts to 110–120 g. (52–57%) of white needles which melt at 124–125° (Note 4).

## 2. Notes

1. Until a considerable amount of the dibromide has precipitated the bromine solution may be run into the reaction mixture as fast as the color is discharged, within the temperature limits of 10–20°. As the mixture becomes thick with the precipitated bromide it is necessary to reduce the speed of the addition of the bromine solution considerably.
2. Strong sunlight seems to favor the substitution of the available  $\alpha$ -hydrogen as evidenced by the strong evolution of hydrogen bromide.
3. If the crude product is dried it is found to melt at 114–117° and to weigh 138–144 g. This is probably a mixture of the two racemic forms.
4. Evaporation and subsequent cooling of the filtrate give a second crop of white crystals, about 15 g., melting at 112–115°. This may be the lower-melting racemate.

### 3. Methods of Preparation

Benzalacetone dibromide has been prepared by the addition of bromine to a solution of benzalacetone in chloroform,<sup>2</sup> in carbon disulfide,<sup>3</sup> and in carbon tetrachloride.<sup>4</sup>

<sup>1</sup> *Org. Syntheses Coll. Vol. 1*, 77 (1941).

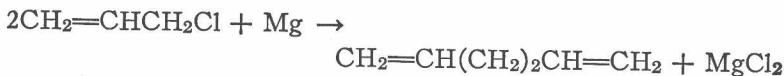
<sup>2</sup> Claisen and Claparede, *Ber.*, **14**, 2463 (1881).

<sup>3</sup> Watson, *J. Chem. Soc.*, **85**, 464 (1904).

<sup>4</sup> Cromwell, *J. Am. Chem. Soc.*, **62**, 3471 (1940).

## BIALLYL

### (1,5-Hexadiene)



Submitted by AMOS TURK and HENRY CHANAN.

Checked by ARTHUR C. COPE and FRANK S. FAWCETT.

### 1. Procedure

In a 5-l. three-necked flask fitted with a mercury-sealed stirrer (Note 1), dropping funnel, and an efficient reflux condenser protected by a calcium chloride drying tube is placed 82 g. (3.5 gram atoms) of magnesium turnings. A solution of 459 g. (6 moles) of dry, freshly distilled allyl chloride in 2.4 l. of anhydrous ether is added to the flask through the dropping funnel in the following manner: A 100- to 200-ml. portion of the solution and a small crystal of iodine are added, and the mixture is warmed, if necessary, until the reaction starts. The remainder of the solution is added with stirring and cooling in an ice bath as rapidly as possible without loss of material through the condenser (Note 2). By sponging the upper part of the flask with ice water from the cooling bath, the addition can be completed in 1-1.5 hours. When the addition is complete, the thick slurry is allowed to stand at room temperature for 5 hours with stirring for as much

of that period as is practicable (Note 1). The flask is again cooled in an ice bath, and a cold 5% solution of hydrochloric acid is added through the dropping funnel until the evolution of heat has practically ceased (Note 2) and the magnesium chloride is in solution. The mechanical stirrer is started again when the mixture becomes sufficiently fluid (Note 1).

The contents of the flask are transferred to a separatory funnel; the ether layer is separated and distilled without washing or drying through a small packed column (Note 3) until the distillation temperature begins to rise (38–40°). The residue is transferred to a separatory funnel, washed with two 500-ml. portions of water, dried over 10 g. of calcium chloride, and fractionated through the small packed column. After distillation of ether and some allyl chloride (b.p. 45°) biallyl is collected as a colorless liquid in a yield of 135–160 g. (55–65%), b.p. 59–60°/760 mm.;  $n_D^{20}$  1.4040;  $n_D^{25}$  1.4012.

## 2. Notes

1. Efficient stirring is essential during the early part of the reaction. The submitters used a double-loop-type Hershberg wire (Nichrome, Chromel, or tantalum) stirrer<sup>1</sup> and a motor<sup>2</sup> powerful enough to stir the mixture during the entire preparation. The checkers used the simpler Hershberg wire (No. 16 B and S gauge Chromel or stainless steel) stirrer<sup>3</sup> and an ordinary good laboratory motor. Although the slurry became so thick that it could not be stirred with this equipment, the yield of pure biallyl obtained equaled that reported by the submitters.

2. Care must be taken to avoid loss of material (and reduction in yield) through evaporation of allyl chloride or biallyl, both of which are very volatile.

3. A simple total-condensation, partial take-off column with a 2.2 by 25 cm. section packed with  $\frac{3}{32}$ -in. single-turn glass helices was used with a reflux ratio of 7 or 8 to 1.

### 3. Methods of Preparation

This procedure is a modification of one described by Cortese.<sup>4</sup> Allyl chloride is employed rather than allyl bromide because of its low cost. Biallyl has been prepared by the action of sodium<sup>5</sup> or aluminum<sup>6</sup> on allyl iodide; from allyl mercuric iodide by dry distillation<sup>7</sup> or by the action of potassium cyanide solution;<sup>8</sup> and by the action of magnesium on allyl bromide,<sup>4,9</sup> on allyl chloride,<sup>4,10</sup> on allyl iodide,<sup>11</sup> or on 1,2,3-tribromopropane.<sup>12</sup>

<sup>1</sup> *Org. Syntheses Coll. Vol. 2*, 117 (1943).

<sup>2</sup> Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **12**, 293 (1940).

<sup>3</sup> Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

<sup>4</sup> Cortese, *J. Am. Chem. Soc.*, **51**, 2266 (1929).

<sup>5</sup> Berthelot and Luca, *Ann. chim. phys.*, (3), **48**, 294 (1856).

<sup>6</sup> Domanitzkii, *J. Russ. Phys.-Chem. Soc.*, **46**, 1078 (1914) [*C. A.*, **9**, 1899 (1915)].

<sup>7</sup> Linnemann, *Ann.*, **140**, 180 (1866).

<sup>8</sup> Oppenheim, *Ber.*, **4**, 670 (1871).

<sup>9</sup> Lespieau, *Ann. chim. phys.*, (8), **27**, 149 (1912); Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

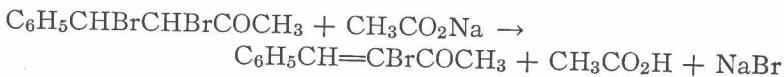
<sup>10</sup> Henne, Chanan, and Turk, *J. Am. Chem. Soc.*, **63**, 3474 (1941).

<sup>11</sup> Meisenheimer and Casper, *Ber.*, **54**, 1655 (1921).

<sup>12</sup> Krestinskii, *J. Russ. Phys.-Chem. Soc.*, **58**, 1078 (1926) [*C. A.*, **22**, 1324 (1928)].

### $\alpha$ -BROMOBENZALACETONE

#### (3-Buten-2-one, 3-bromo-4-phenyl-)



Submitted by NORMAN H. CROMWELL, DONALD J. CRAM,  
and CHAS. E. HARRIS.

Checked by R. L. SHRINER and WILLIAM O. FOYE.

### 1. Procedure

*Precautions must be taken to avoid contact with  $\alpha$ -bromobenzalacetone since it is a skin irritant (Note 1).*

In a 500-ml. round-bottomed flask fitted with a reflux condenser are placed 100 g. (0.33 mole) of benzalacetone dibromide

(p. 5), 30 g. (0.37 mole) of anhydrous sodium acetate, and 250 ml. of 95% ethanol, and the mixture is refluxed vigorously for 4 hours in the absence of direct sunlight. The precipitate of sodium bromide is removed by filtration, and the alcohol is removed from the filtrate by distillation under reduced pressure (Note 2). The residual salt-oil mixture is extracted with two 50-ml. portions of ether, and the ether solution is transferred to a 250-ml. separatory funnel (Caution! Note 1).

The ether solution is washed thoroughly six times with 25-ml. portions of saturated sodium chloride solution and twice with 25-ml. portions of 5% sodium bicarbonate solution (Note 3). The ether layer is allowed to dry over anhydrous sodium sulfate at room temperature for 24 hours. The ether is removed by distillation, and the residual oil is distilled from a Claisen flask under reduced pressure, using an oil bath. A yield of 47–54 g. (64–73%) of a pale yellow oil, boiling at 114–117°/1 mm. (Note 4), is obtained. On cooling, the oil crystallizes; m.p. 30–31°. The product is stored in a dark bottle in the ice chest (Notes 5 and 6).

## 2. Notes

1.  $\alpha$ -Bromobenzalacetone or its solutions cause the formation of red spots on the skin. After several days these form large red blisters that are painful and take several days to heal. The affected parts should be treated with a mixture of peanut-oil and glycerol containing a little ammonia.

2. The reduced pressure produced by a water pump is satisfactory. The flask is warmed with a hot water bath (40–50°).

3. It is necessary that the product be entirely free from acetic acid before it is distilled in order to obtain the yields stated.

4. Boiling points at other pressures are: 136–138°/4 mm.; 150–151°/10 mm.

5. When stored in this manner the product is quite stable and darkens only slightly after 9 months.

6. The analogous  $\alpha$ -bromobenzalacetophenone may be prepared by a similar procedure. In a 1-l. three-necked round-bottomed flask fitted with a mercury-sealed stirrer and a reflux

condenser are placed 150 g. (0.41 mole) of benzalacetophenone dibromide,<sup>1</sup> 41 g. (0.50 mole) of anhydrous sodium acetate, and 250 ml. of 95% ethyl alcohol. The mixture is stirred and refluxed for 5 hours and then worked up in the same manner as described above for  $\alpha$ -bromobenzalacetone. Distillation gives a yield of 100–110 g. (85–94%) of a pale yellow oil, boiling at 170–173°/1 mm. On cooling, the oil crystallizes and melts at 42–44°. This product should also be stored in a dark bottle in the ice chest, but it is more stable and darkens less on standing than the analogous  $\alpha$ -bromobenzalacetone. This product is less irritating to the skin than  $\alpha$ -bromobenzalacetone (Note 1).

### 3. Methods of Preparation

$\alpha$ -Bromobenzalacetone has been prepared from benzalacetone dibromide by heating with alcoholic potassium hydroxide<sup>2</sup> or with sodium acetate<sup>3</sup> solutions.  $\alpha$ -Bromobenzalacetophenone is prepared by a similar procedure from benzalacetophenone dibromide.<sup>4</sup>

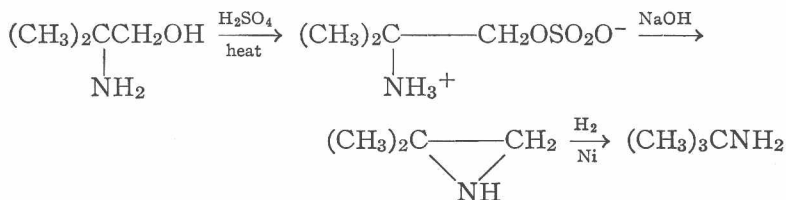
<sup>1</sup> *Org. Syntheses* Coll. Vol. 1, 205 (1941).

<sup>2</sup> Watson, *J. Chem. Soc.*, 85, 464 (1904).

<sup>3</sup> Cromwell and Cram, *J. Am. Chem. Soc.*, 65, 305 (1943).

<sup>4</sup> Wislicenus, *Ann.*, 308, 226 (1899); Cromwell, *J. Am. Chem. Soc.*, 62, 2899 (1940).



***tert.*-BUTYLAMINE**

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**1. Procedure**

A. *2,2-Dimethylethylenimine*. A cold mixture of 110 g. (60 ml., 1.06 moles) of concentrated sulfuric acid and 200 ml. of water is added in portions, with shaking, to a solution of 100 g. (107 ml., 1.12 moles) of 2-amino-2-methyl-1-propanol in 200 ml. of water contained in a 1-l. round-bottomed flask (Note 1). The flask is fitted with a thermometer extending into the liquid and a short still head carrying a downward condenser.

Water is distilled from the mixture at atmospheric pressure until the temperature of the solution reaches 115° (Notes 2 and 3) whereupon the liquid is transferred to a 500-ml. round-bottomed flask. This flask is connected to the distillation apparatus used previously except that the thermometer is replaced by a capillary tube. Distillation is then continued under the reduced pressure obtainable from a water aspirator. The bath temperature is raised to 175° over a period of about an hour and is held there until the mixture solidifies (usually 30–60 minutes longer), and for 1 hour thereafter. The flask is cooled and broken to remove the product.

The brown solid from the above operations is ground in a mortar and placed in a 500-ml. distilling flask equipped with a downward condenser and a receiver. A cold solution of 100 g.