

ORGANIC SYNTHESSES

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

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ORGANIC SYNTHESIS

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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

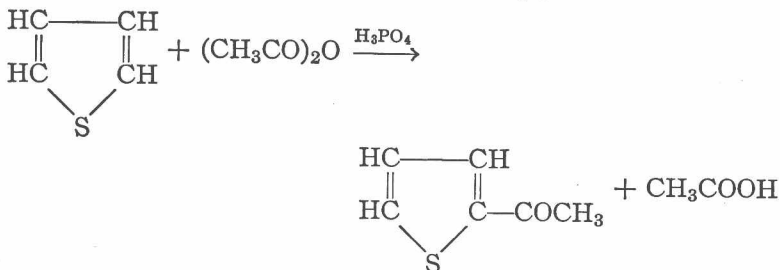
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TABLE OF CONTENTS

	PAGE
2-ACETOTHIENONE	1
2-ACETYLFUORENE	3
9-ACETYLPHENANTHRENE	6
2-ALLYLCYCLOHEXANONE	8
<i>o</i> -AMINOBENZALDEHYDE	11
<i>p</i> -AMINOPHENYL DISULFIDE	14
BENZOYL DISULFIDE	16
9-BROMOPHENANTHRENE	19
4-BROMO- <i>o</i> -XYLENE	22
3-CARBETHOXYCOUMARIN	24
<i>p</i> -CHLOROACETYLACETANILIDE	26
<i>m</i> -CHLOROPHENYLMETHYLCARBINOL	28
<i>m</i> -CHLOROSTYRENE	31
9-CYANOPHENANTHRENE	34
<i>trans</i> -1,2-CYCLOHEXANEDIOL	35
4,7-DICHLOROQUINOLINE	38
2,5-DIHYDROXYACETOPHENONE	42
DIISOVALERYLMETHANE	44
3,4-DIMETHYLANILINE	46
2,4-DIMETHYLQUINOLINE	49
1,4-DINITRONAPHTHALENE	52
DIPHENYLACETONITRILE	55
ETHYL AZODICARBOXYLATE	58
ETHYL ETHOXYMETHYLENEMALONATE	60
FLUORENONE-2-CARBOXYLIC ACID	63
HEXAMETHYLENE CHLOROHYDRIN	65
HYDROQUINONE DIACETATE	68
2-HYDROXYCINCHONINIC ACID	70
<i>dl</i> -ISOPROPYLDENEGLYCEROL	73
METHYL 4-KETO-7-METHYLOCTANOATE	75
4-NITRO-1-NAPHTHYLAMINE	80
<i>p</i> -NITROPHENYL SULFIDE	82
PHENANTHRENE-9-ALDEHYDE	83
1-PHENYL-3-AMINO-5-PYRAZOLONE	87
α -PHENYLTHIOUREA	89
2,4,7-TRINITROFLUORENONE	91
VINYL CHLOROACETATE	94
SUBJECT INDEX FOR VOLUMES 20-28	99

2-ACETOTHIENONE

(Ketone, methyl 2-thienyl)



Submitted by ALVIN I. KOSAK and HOWARD D. HARTOUGH.

Checked by GEORGE T. GMITTER, F. LEE BENTON, and CHARLES C. PRICE.

1. Procedure

In a 1-l. three-necked flask fitted with a mechanical stirrer, a thermometer, and a reflux condenser are placed 168 g. (2 moles) (Note 1) of thiophene (Note 2) and 107 g. (1 mole) of 95% acetic anhydride (Note 3). The solution is heated to 70–75°, the source of heat is removed, and 10 g. (6 ml.) of 85% phosphoric acid is added with stirring. After 2–3 minutes an exothermic reaction occurs, and it is necessary to immerse the flask in a cold water bath to control the reaction. The boiling subsides in a few minutes; heat is again applied, and the mixture is refluxed for a total of 2 hours. The cooled mixture is washed successively with one 250-ml. portion of water and two 100-ml. portions of 5% sodium carbonate and is dried over anhydrous sodium sulfate. The orange-red liquid is distilled through a short fractionating column. After the removal of 76–80 g. of unchanged thiophene (b.p. 83–84°) by distillation at atmospheric pressure the residue is distilled under reduced pressure. The yield of 2-acetothienone, b.p. 89–90°/10 mm. (m.p. 9.2–10.5°; n_D^{20} 1.5662), is 93–100 g. (74–79%).

2. Notes

1. Acetic anhydride rather than thiophene may be used in excess, but the unchanged reagent cannot be recovered by the procedure given. With a 3:1 mole ratio of thiophene to anhydride the yield is of the order of 85%.

2. Commercial 99+ % thiophene was employed.

3. The use of an equivalent amount of freshly distilled 100% acetic anhydride does not improve the yield.

3. Methods of Preparation

In addition to the methods of preparation given in connection with the procedure ¹ for the acetylation of thiophene with acetyl chloride in the presence of stannic chloride, 2-acetothienone has been prepared from thiophene and either acetyl chloride or acetic anhydride in the presence of iodine,² hydriodic acid,² silica-metal oxides,³ zinc chloride,⁴ or inorganic oxyacids.⁵ It has also been prepared from thiophene and acetic acid in the presence of hydrogen fluoride ⁵ or phosphorus pentoxide.⁶ The acylation in the presence of phosphorus pentoxide is particularly useful with higher aliphatic acids.⁶

¹ *Org. Syntheses* Coll. Vol. 2, 8 (1943).

² Hartough and Kosak, *J. Am. Chem. Soc.*, **68**, 2639 (1946).

³ Hartough, Kosak, and Sardella, *J. Am. Chem. Soc.*, **69**, 1014 (1947).

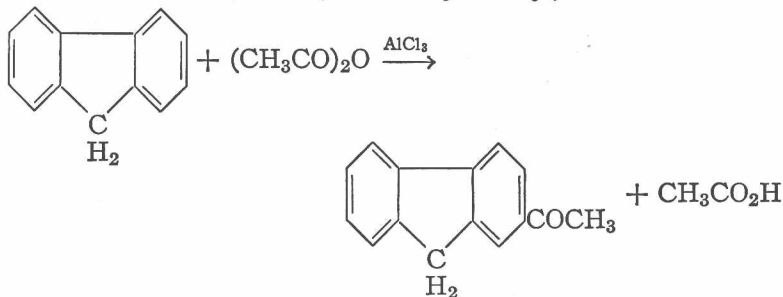
⁴ Hartough and Kosak, *J. Am. Chem. Soc.*, **69**, 1012 (1947).

⁵ Hartough and Kosak, *J. Am. Chem. Soc.*, **69**, 3093 (1947).

⁶ Hartough and Kosak, *J. Am. Chem. Soc.*, **69**, 3098 (1947).

2-ACETYLFLUORENE

(Ketone, 2-fluorenyl methyl)



Submitted by F. E. RAY and GEORGE RIEVESCHL, JR.
 Checked by R. L. SHRINER and ARNE LANGSJOEN.

1. Procedure

Caution! Carbon disulfide, used as a solvent in this preparation, is highly inflammable; its vapor may ignite on contact with a hot laboratory steam line.

A 1-l. three-necked round-bottomed flask is fitted with a dropping funnel, a reflux condenser attached to a hydrogen chloride absorption trap,¹ and a very sturdy mechanical stirrer (Note 1), which may be of the mercury-sealed or rubber-sleeve type. In the flask are placed 350 ml. of dry carbon disulfide and 80 g. (0.48 mole) of fluorene (Note 2). The stirrer is started, and, after the fluorene has dissolved, 128 g. (0.96 mole) of anhydrous aluminum chloride is added in one portion. In the dropping funnel is placed 49.4 g. (0.48 mole) of redistilled acetic anhydride, and about 1 ml. of it is added dropwise to the vigorously stirred dark red reaction mixture. If the reaction does not start immediately it is initiated by warming the reaction flask in a water bath (Note 3). After the reaction has started, the balance of the acetic anhydride is added at such a rate that the carbon disulfide refluxes gently; about 45–55 minutes is required. When approximately one-half of the acetic anhydride has been added an addition complex sepa-

rates as a heavy mass which makes stirring very difficult. However, stirring must be maintained to prevent excessive local reaction at the point of introduction of the acetic anhydride. The mixture is stirred and refluxed on the water bath for an hour after the addition of the acetic anhydride is complete.

The dark green mass is collected on a large Büchner funnel and transferred as quickly as possible (Note 4) to a 1-l. beaker in which it is stirred mechanically for 10 minutes with 300 ml. of carbon disulfide (Note 5). The solid is again collected and washed on the filter with two 50-ml. portions of carbon disulfide (Note 6) and with one 100-ml. portion of petroleum ether (b.p. 28–35°). The resulting granular aluminum chloride complex is decomposed by portionwise addition to a well-stirred mixture of 800 ml. of water and 30 ml. of concentrated hydrochloric acid in a 2-l. beaker under a hood. Each portion is allowed to hydrolyze before the next is added. The hydrolysis mixture should not be cooled. The crude 2-acetylfluorene is collected on a filter and washed three times with 100-ml. portions of water. After drying in an oven at 100° for 3 hours the light orange ketone weighs 83–95 g. (83–95%) and melts over the range 113–117° (Note 7). This crude product is transferred to a 2-l. round-bottomed flask containing 800 ml. of 95% ethanol and 5 g. of decolorizing carbon. The mixture is refluxed for 1 hour and filtered hot. On cooling the filtrate deposits 71–83 g. of light tan solid melting at 120–123°. A second recrystallization from 800 ml. of ethanol yields 55–63 g. (55–53%) of a light cream-colored powder which melts at 124–126° and which is pure enough for most purposes (Note 8).

2. Notes

1. The stirrer, which may be of either the half-round or the propeller type, must be of heavy construction and must be driven by one of the more powerful laboratory stirring motors. Agitation must be maintained throughout the reaction period.

2. If technical fluorene (m.p. 103–107°) from Eastman Kodak Company or the Barrett Company is used, much difficulty is experienced in the purification of the product. Technical fluorene can be rendered suitable for the preparation by recrystallization

from hot 95% ethanol (1 l. for 150 g.). The once-recrystallized material melts at 114–115° (lit. 116°).

3. It is necessary to make sure that the reaction has started before the addition of more acetic anhydride in order to prevent a violent reaction.

4. Exposure to the air causes the addition product to become sticky and difficult to handle.

5. Unless this operation can be conducted at a point remote from flames, hot plates, and other sources of heat, a flask should be substituted for the open beaker.

6. The carbon disulfide extracts unchanged fluorene and other impurities. Any lumps in the crude material should be crushed during the first washing. The rinsing with petroleum ether removes the last of the carbon disulfide.

7. This crude 2-acetylfluorene is completely soluble in carbon disulfide and thus is free of the insoluble 2,7-diacetylfluorene. It may be used directly for the oxidation to fluorenone-2-carboxylic acid (p. 63).

8. The pure product ² melting at 128–129° (cor.) can be obtained in 42–45% yield by two more recrystallizations from 400-ml. portions of acetone. Pure 2-acetylfluorene has also been reported ³ as melting at 132°, but this value has not been checked.

3. Methods of Preparation

2-Acetylfluorene has been prepared by the reaction of fluorene with acetic anhydride ^{2,4} or with acetyl chloride ^{3,5} in the presence of aluminum chloride in carbon disulfide or in nitrobenzene. When nitrobenzene is employed as the solvent it must be removed by a time-consuming steam distillation, and the use of acetyl chloride as a reagent leads to the formation of considerable amounts of 2,7-diacetylfluorene.

¹ *Org. Syntheses* Coll. Vol. 2, 4¹ (1943).

² Bachmann and Sheehan, *J. Am. Chem. Soc.*, **62**, 2688 (1940).

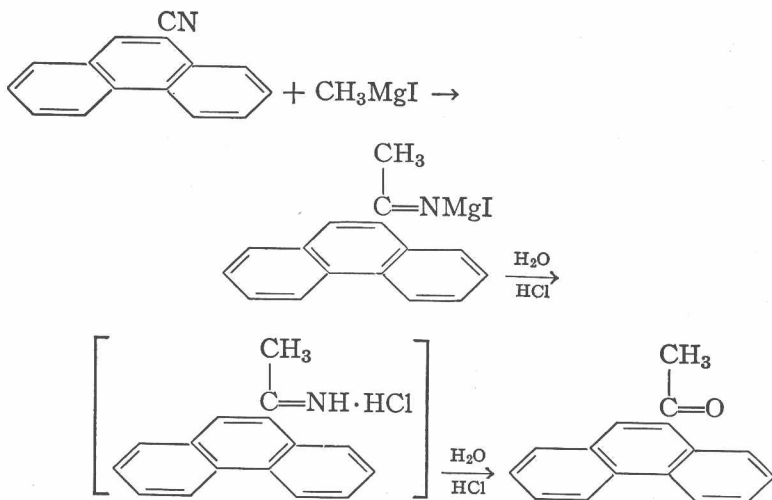
³ Dziejowski and Schnayder, *Bull. intern. acad. polon. sci.*, **1930A**, 529 [*C.A.*, **25**, 5416 (1931)].

⁴ Ray and Rieveschl, *J. Am. Chem. Soc.*, **65**, 836 (1943).

⁵ Ardashev, Lomovatskaya, and Kacher, *J. Applied Chem. U.S.S.R.*, **11**, 1344 (1938) [*C.A.*, **33**, 5844 (1939)].

9-ACETYLPHENANTHRENE

(Ketone, methyl 9-phenanthryl)

Submitted by JOSEPH E. CALLEN, CLINTON A. DORN-FELD, and GEORGE H. COLEMAN.¹

Checked by ROBERT E. CARNAHAN and HOMER ADKINS.

1. Procedure

A dry 12-l. three-necked flask is equipped with an efficient motor-driven stirrer (Note 1), a nitrogen inlet tube, a large Allihn condenser, and a 1-l. separatory funnel. Both the condenser and the funnel are provided with calcium chloride drying tubes. To the flask is added 146 g. (6 gram atoms) of magnesium turnings (Note 2), and nitrogen gas, first bubbled through concentrated sulfuric acid, is passed in to displace the air. During the reaction the nitrogen atmosphere is maintained. The magnesium is covered with 200 ml. of anhydrous ether, and a few milliliters of a solution of 852 g. (6 moles) of methyl iodide in 1 l. of anhydrous ether is added from the separatory funnel. The reaction starts spontaneously, and then the remainder of the methyl iodide solu-

tion is added slowly. When the reaction is complete (Note 3), 4 l. of dry benzene is added, a condenser is arranged for downward distillation, and about 1.2 l. of solvent is distilled (Note 4). The condenser is changed to a reflux position, 609 g. (3 moles) of 9-cyanophenanthrene (p. 34) is added quickly through a powder funnel, and the mixture is heated and stirred under reflux for 3 hours. It is then cooled in an ice bath to 0°, 3 l. of cold 6 *N* hydrochloric acid is slowly added (*Caution!*) from a separatory funnel with stirring, and the mixture is refluxed for 6 to 8 hours (Note 5).

After cooling, the layers are separated, the organic layer is washed with dilute sodium bicarbonate solution and placed in a flask equipped for distillation, and the solvent is distilled. The oily residue is transferred while still warm to a 1-l. Claisen flask, and the product is distilled under reduced pressure; b.p. 190–200°/2.5 mm. (168–170°/1 mm.). The yield is 400–430 g. (61–65%). The distilled ketone is recrystallized once from ethanol (1.5–2 l.) to yield 345–390 g. (52–59%) of 9-acetylphenanthrene of m.p. 73–74°.

2. Notes

1. If a 12-l. three-necked flask is not available, a three-way adapter tube may be used in making the necessary connections. Although a mercury seal may be used, a glycerol-rubber tube seal² is adequate.

2. The checkers operated on one-tenth the scale specified.

3. In several runs the Grignard reagent was filtered at this point, but the improvement in yield was not appreciable.

4. The addition of benzene and distillation of part of the solvent raises the reaction temperature.

5. The oily layer of ketimine hydrochloride usually dissolves during 6 hours' refluxing.

3. Methods of Preparation

The method described above is a modification of that of Bachmann and Boatner.³ 9-Acetylphenanthrene has also been

obtained by a Claisen condensation of methyl phenanthrene-9-carboxylate with ethyl acetate followed by scission of the resulting phenanthroylacetic ester,⁴ by the reaction of 9-phenanthrylmagnesium bromide with acetyl chloride,⁵ and by dehydrogenation of 9-acetyl-1,2,3,4-tetrahydrophenanthrene by heating with sulfur.⁶

¹ Work done under contract with the Office of Scientific Research and Development.

² *Org. Syntheses*, **21**, 40 (1941).

³ Bachmann and Boatner, *J. Am. Chem. Soc.*, **58**, 2098 (1936).

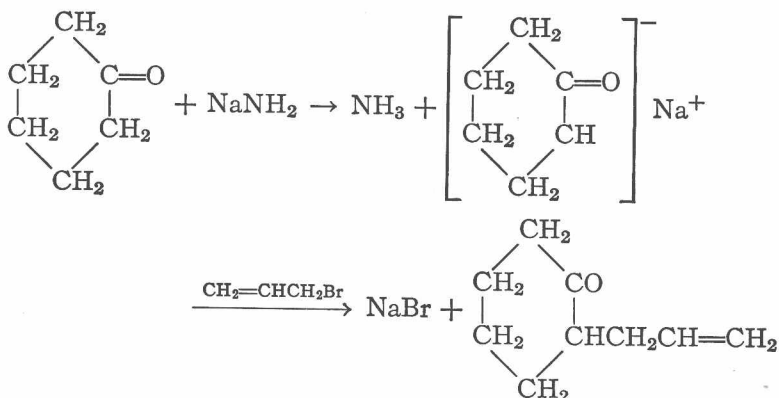
⁴ Mosettig and van de Kamp, *J. Am. Chem. Soc.*, **55**, 3445 (1933).

⁵ Miller and Bachman, *J. Am. Chem. Soc.*, **57**, 768 (1935).

⁶ Bachmann and Struve, *J. Org. Chem.*, **4**, 476 (1939).

2-ALLYLCYCLOHEXANONE

(Cyclohexanone, 2-allyl-)



Submitted by CALVIN A. VANDERWERF and LEO V. LEMMERMAN.
 Checked by ARTHUR C. COPE and THEODORE T. FOSTER.

1. Procedure

Approximately 1.5 l. of anhydrous liquid ammonia is introduced into a dry 5-l. three-necked flask fitted with a sealed mechanical stirrer and an efficient reflux condenser which is con-

nected through a soda-lime tube to a gas-absorption trap.¹ Freshly cut sodium (47.2 g., 2.05 gram atoms) is converted to sodium amide by addition to the liquid ammonia in the presence of a small amount of ferric nitrate, according to a procedure previously described in detail.² A 1-l. dropping funnel and a gas inlet tube connected to a source of dry nitrogen are attached to the third neck of the flask, and, after the blue color of the solution has disappeared and a gray suspension of sodium amide remains (Note 1), 1.2 l. of dry ether is added as rapidly as the rate of vaporization of ammonia will permit. The ammonia is removed by warming the flask on a steam bath until refluxing of the ether occurs. Cyclohexanone (Note 2) (220 g., 2.24 moles) is added through the dropping funnel (Note 3), and the mixture is stirred and heated under reflux on a steam bath for 3 hours. Nitrogen is then introduced through the gas inlet tube to maintain an inert atmosphere (Note 4), and the mixture is cooled in an ice bath. A solution of 246 g. (2.03 moles) of allyl bromide (Note 5) in 1 l. of anhydrous ether is added rapidly through the dropping funnel with stirring. If the reaction does not start soon after the completion of this addition the mixture is warmed cautiously on the steam bath. When the exothermic reaction has started it is controlled by cooling in the ice bath while refluxing continues for 20–30 minutes. The mixture is finally heated under reflux on the steam bath for 3 hours.

The mixture is cooled in an ice bath, any sodium or sodium amide which may remain in the necks of the flask is scraped into the reaction mixture with a spatula, and enough water is added to dissolve the sodium bromide. The ether layer is separated and combined with five 100-ml. ether extracts of the aqueous phase, washed with 150 ml. of saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The ether is removed by distillation, and the residue is fractionated carefully under reduced pressure through a 4-ft. heated column packed with glass helices and fitted with a total-condensation variable take-off head. The yield of 2-allylcyclohexanone boiling at 90–92°/17 mm. is 153–174 g. (54–62%). In addition, 28–38 g. of unchanged cyclohexanone boiling at 51–52°/17 mm., 15–35 g. of diallylcyclohexa-

none boiling at 123–124/17 mm., and small intermediate fractions are obtained.

2. Notes

1. The conversion of the sodium to sodium amide requires 30–90 minutes. More liquid ammonia may be added if too much is lost by vaporization before the conversion is complete.

2. Redistilled cyclohexanone, b.p. 154–156°, was used.

3. The submitters obtained equally good results by adding 80 g. (2.05 moles) of freshly prepared finely powdered sodium amide³ in portions to a solution of the cyclohexanone in 1.2 l. of dry ether, heating under reflux for 3 hours, and continuing the preparation in the manner described.

4. The submitters state that the yield is increased appreciably if a nitrogen atmosphere is maintained after this point. Loss of ether may be avoided by stopping the flow of nitrogen when refluxing begins.

5. Allyl bromide was dried over calcium chloride and redistilled, b.p. 70–71.5°.

3. Methods of Preparation

2-Allylcyclohexanone has been prepared by the direct alkylation of the sodium derivative of cyclohexanone with allyl iodide, sodium amide having been used in the preparation of the sodium enolate,⁴ and by ketonic hydrolysis of ethyl 1-allyl-2-ketocyclohexanecarboxylate, prepared by alkylation of ethyl 2-ketocyclohexanecarboxylate.^{5, 6}

¹ *Org. Syntheses* Coll. Vol. 2, 4 (1943).

² *Org. Syntheses*, 25, 25 (1945).

³ *Org. Syntheses*, 20, 86 (1940).

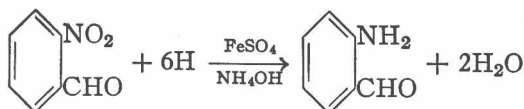
⁴ Cornubert, *Ann. chim.*, [9] 16, 145 (1921).

⁵ Cope, Hoyle, and Heyl, *J. Am. Chem. Soc.*, 63, 1848 (1941).

⁶ Grewe, *Ber.*, 76, 1075 (1943).

o-AMINOBENZALDEHYDE

(Anthranilaldehyde)

Submitted by LEE IRVIN SMITH and J. W. OPIE.¹

Checked by CLIFF S. HAMILTON, C. W. WINTER, and HARRY M. WALKER.

1. Procedure

A 1-l. three-necked flask is employed as a reaction vessel from which the product can be steam-distilled *immediately* after completion of the reaction (Note 1). It is convenient to arrange the apparatus for the reaction and that for the steam distillation on the same steam bath, with provision for the rapid connection of the flask to the distillation assembly at the desired time. For use as a reaction vessel the flask is mounted on a steam bath and fitted with a mechanical stirrer and a reflux condenser; the third neck is closed by a cork.

In the steam-distillation assembly (Note 1) one of the small necks of the flask is fitted with a steam-inlet tube, connected through a water trap to a steam line; the other small neck is closed by a cork. The central neck is fitted to a Kjeldahl trap leading to a 50-cm. Allihn condenser set downward and connected in series to a 50-cm. Liebig condenser. The second condenser leads to a 500-ml. three-necked flask used as the receiver. The receiving flask is immersed in an ice bath and fitted with an Allihn reflux condenser.

When all the apparatus has been set up and tested the flask is connected to the reaction assembly, and 175 ml. of water, 105 g. (0.38 mole) of ferrous sulfate heptahydrate, 0.5 ml. of concentrated hydrochloric acid, and 6 g. (0.04 mole) of *o*-nitrobenzaldehyde² are introduced in the order given. The stirrer is then started, and the flask is heated by means of the steam bath. When the temperature of the mixture reaches 90°, 25 ml. of con-

concentrated ammonium hydroxide is added in one portion, and at 2-minute intervals three 10-ml. portions of ammonium hydroxide are added. Stirring and heating are continued throughout. The total reaction time is 8–10 minutes.

Immediately after the addition of the last portion of ammonium hydroxide, the reflux condenser and stirrer are removed and the flask is connected to the steam-distillation assembly. The mixture is steam-distilled as rapidly as possible, and two 250-ml. fractions of distillate are collected during a period of 10–13 minutes (Note 2). The first fraction is saturated with sodium chloride, and the solution is stirred at 5° until precipitation appears complete. The solid is collected on a Büchner funnel and dried in the air. The product weighs 2.72–3.11 g. (57–65%) and melts at 38–39°. The second fraction of the distillate is saturated with sodium chloride and combined with the filtrate remaining from the first fraction. The combined solution is extracted with two 45-ml. portions of ether. The combined ether extract is filtered, dried over anhydrous sodium sulfate, and concentrated by distillation, finally under reduced pressure. The residue solidifies on cooling and weighs 0.6–1.0 g.; it can be purified by steam distillation from 40–50 ml. of saturated sodium chloride solution until 100 ml. of distillate is collected, saturation of the distillate with sodium chloride, cooling, and filtration. The pure product so obtained weighs 0.42–0.87 g. The total yield (Note 3) is 3.3–3.6 g. (69–75%).

2. Notes

1. Rapid removal of the product from the reaction mixture is essential to the success of this preparation. The steam-distillation assembly should be sturdily constructed, with all parts except the distilling flask in place at the time the reaction is started. To ensure the proper fitting of the distilling flask it is convenient to construct the distillation apparatus with the flask in place and, after testing of the apparatus, to remove the flask and incorporate it into the reaction assembly.

2. The first fraction is drawn into a round-bottomed flask through a tube inserted into the third neck of the receiver (by the