

ORGANIC SYNTHESSES

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

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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

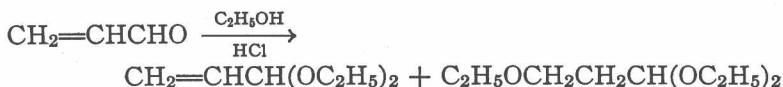
Organic Syntheses invites the submission of preparations of compounds which are of general interest or which illustrate useful synthetic methods. Preparations are welcomed particularly from those who have had occasion to work out the optimum conditions of preparation. The directions should be written in the style employed in the latest volume of *Organic Syntheses*. Full details for all steps should be included, and the range of yields should be reported rather than the maximum yield obtainable. 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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ACROLEIN ACETAL AND β -ETHOXYPROPIONALDEHYDE ACETAL

(Acrolein, diethyl acetal, and propionaldehyde, β -ethoxy-, diethyl acetal)



Submitted by F. P. PINGERT.

Checked by NATHAN L. DRAKE and W. MAYO SMITH.

1. Procedure

A mixture of 158 g. (5.6 moles) of acrolein (Note 1) and 450 ml. of absolute alcohol (Note 1) is placed in a 1-l. Florence flask. The neck of the flask is closed by a plug of cotton,¹ and the flask is then immersed up to its neck in an ice bath containing about 1.5 kg. of ice. When the temperature of the mixture is about 0°, 50 ml. of absolute alcohol containing 2 g. of hydrogen chloride is added with swirling. The temperature is apt to rise very rapidly. The flask is clamped firmly in place and left 48–60 hours; the ice is allowed to melt and is not renewed.

The contents of the flask are transferred to a 1.5-l. round-bottomed flask, 0.5–1 g. of copper carbonate is added, and the liquid is fractionally distilled *in vacuo* with the aid of a Fenske column (Fig. 1) (Notes 2 and 3). The following fractions are collected.

Below 45°/24 mm.	Acrolein and alcohol (Note 4)
45°/24 mm.	Acrolein acetal (Note 5)
80–84°/21 mm.	β -Ethoxypropionaldehyde acetal (Note 6)

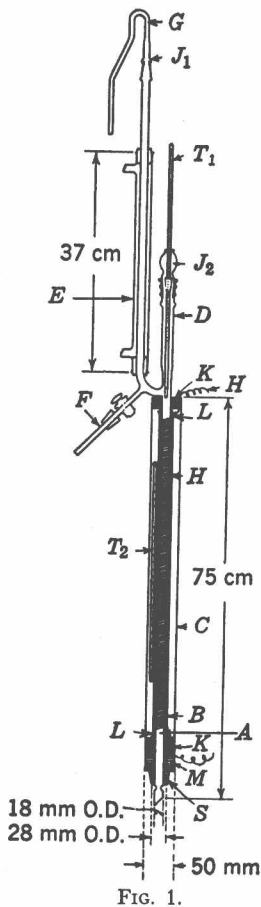
The yield of acrolein acetal is 89–108 g. (24–30%), and of β -ethoxypropionaldehyde acetal, 104–132 g. (21–26%) (Note 7).

¹ *Org. Syntheses*, 20, 9 (1940).

2. Notes

1. The commercial products are used. The stabilizer in acrolein is not removed.

2. This design of a Fenske² fractionating column (Fig. 1) consists essentially of a packed glass tube (A) which is provided with two heat-insulating jackets (B and C) and a total reflux variable take-off head (D, E, and F).



It is constructed of Pyrex glass and filled with single helix copper spirals.³ Although the dimensions are probably not critical, trial and error have proved this particular design to be efficient, rugged, and well adaptable to numerous laboratory separations. Mixtures of compounds boiling from about 0° to 400° at 1 to 760 mm. have been fractionated successfully by means of this column.

The heating element (H) consists of about 165 turns of No. 24 B & S gauge nichrome wire wound onto the jacket (B) directly or, preferably, over strands of asbestos string glued longitudinally to this jacket (B)—an arrangement that prevents side-slipping and short-circuiting of the individual wire loops. The central jacket (B) should not be omitted, and the heating element should not be wound directly onto the column (A) itself. This would be poor economy, as it would largely defeat the purpose of maintaining

a heat gradient throughout the column and would introduce the hazard of cracking by local overheating, particularly in work under reduced pressure. The cork spacers (L and K) between the

² Whitmore and Lux, *J. Am. Chem. Soc.*, **54**, 3448 (1932).

³ *Org. Syntheses*, **20**, 96 (1940).

jackets must be carefully fitted with the aid of sandpaper and a rasp, since the whole weight of the column is supported by the outer jacket. If this adjustment is not made with precision and care, a single bump of a superheated distilland may shatter the column. If replacement of the cork spacers becomes necessary, the apparatus need not be torn down, but the new spacers may be sawed diametrically and the halves cemented after appropriate fitting. The outer jacket (C) may be replaced by pipe insulation, but glass is preferable in experimental work.

The heating element is connected to a 110-volt line through a rheostat (such as a 140-ohm, 3-ampere resistor), and the temperature is adjusted with the aid of two thermometers (T_1 and T_2), a reasonable differential, depending upon the materials to be distilled, being allowed.

The water condenser (E) should be sufficiently large to permit a high rate of reflux; with high-boiling substances it may be advantageous to cool with air or with steam. An attachment (G) provides for vacuum distillation with the aid of a glass Y and pressure tubing. An all-glass head² is more elegant but not so flexible. Ground-glass joints at J_1 and J_2 are convenient but not essential.

Details of the lower end of the column are shown in Fig. 2. S is a rubber stopper to fit the still pot, and L and K are cork stoppers. The outer jacket (C) ends at the bottom of K. M is a stack of asbestos disks which serve as a bumper between the stoppers S and K; they are indispensable for operation under reduced pressure. The disks are easily removable and provide for flexibility in the choice of stopper sizes. Still pots of 250 ml. to 12 l. can be attached to this column.

3. By taking advantage of the relatively high vapor pressure of the fore-run, the acrolein acetal may be collected practically automatically, as follows. The stopcock at F is closed, and the

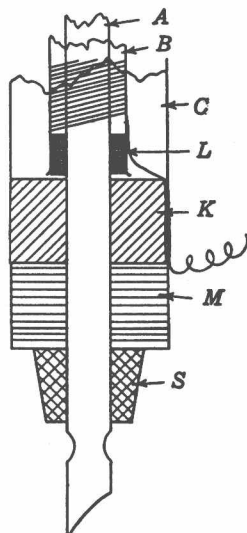


FIG. 2.

pressure is reduced to 25 mm. No heat is supplied to the still pot, and the cooling water is adjusted to minimum flow. The fore-run escapes at *G* and is collected, if desirable, in suitable traps. When evaporation ceases (4–5 hours), stopcock *F* is opened, the flow of cooling water is increased sharply, the heating jacket is adjusted to 45° (at T_2), and the still pot is heated gently with low-pressure steam. After suitable adjustment of the reflux and take-off rates at *F*, the acrolein acetal distills without further attention. It is convenient to do this overnight. The cutting of fractions is automatic, inasmuch as the higher-boiling β -ethoxypropionaldehyde acetal will not come over under these conditions and distillation simply ceases. An oil bath is needed to distil the higher fraction. Though some loss may be incurred in this short-cut procedure, it is more than offset by the economy in operator's attention and the higher purity of the product.

4. The recovered acrolein and alcohol fractions may be used in subsequent runs after suitable drying.

5. Other boiling points of acrolein acetal are 40°/18 mm. and 52°/36 mm.

6. Other boiling points for β -ethoxypropionaldehyde acetal are 78°/14 mm. and 92°/32 mm.

7. Among the advantages of this procedure over an alternative synthesis ⁴ are the following. The material is obtained in one step by a method which obviates most of the disagreeable features of the older two-step procedure. The overall yield by the older method is at best 25% and falls off badly if the hydroxide is not meticulously dry. Furthermore, the acrolein acetal prepared by the dehydrohalogenation of β -chloropropionaldehyde acetal ⁵ does not keep well, whereas samples of the product obtained by this procedure showed no discoloration and no change in boiling point on storage in an ice chest for 18 months. Only a faint odor of acrolein was noted at the end of that period.

3. Methods of Preparation

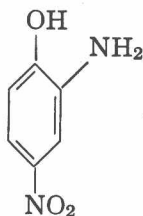
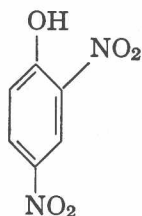
These have been recently summarized.⁴

⁴ *Org. Syntheses* Coll. Vol. 2, 17 (1943).

⁵ *Org. Syntheses* Coll. Vol. 2, 137 (1943).

2-AMINO-4-NITROPHENOL

(Phenol, 2-amino-4-nitro-)



Submitted by W. W. HARTMAN and H. L. SILLOWAY.
 Checked by H. R. SNYDER and J. WAYNE KNEISLEY.

1. Procedure

In a 5-l. three-necked flask, suspended over a steam bath, are placed 300 g. (1.63 moles) of technical 2,4-dinitrophenol and 2.5 l. of water. The flask is fitted with an efficient stirrer, a reflux condenser, and a thermometer which dips below the surface of the mixture. After the stirrer has been started, 600 g. (11.6 moles) of ammonium chloride and 100 ml. of concentrated aqueous ammonia (about 28%) are added, and the mixture is heated to 85°. The steam is turned off, and the mixture is allowed to cool. When the temperature reaches 70° (Note 1), 700 g. (5.4 moles) of 60% fused sodium sulfide is added in portions of about 100 g. at 5-minute intervals. After two or three such additions the temperature of the reaction mixture reaches 80–85°; it is kept in this range either by adding the remaining portions of sodium sulfide at 10-minute intervals or by wrapping the flask with a wet cloth and continuing the additions at 5-minute intervals. After all the sodium sulfide has been added, the reaction mixture is

heated at 85° for 15 minutes and then filtered through a heated 6-in. Büchner funnel (Note 2).

The hot filtrate is transferred to a 5-l. round-bottomed flask and cooled overnight by a stream of cold water. The mixture is filtered, and the crystals are pressed nearly dry. The solid is dissolved in 1.5 l. of boiling water, and the solution is acidified with glacial acetic acid (about 100 ml. is required, Note 3). The solution is heated with 10 g. of Norite, filtered hot, and cooled to 20°. The brown crystals are collected and dried for several hours in an oven at 65° or in a vacuum desiccator (Note 4). The yield of 2-amino-4-nitrophenol melting at 140–142° is 160–167 g. (64–67%). If a purer product is desired, the crude substance is recrystallized from 1.5 l. of hot water; 147–153 g. (58–61%) of material melting at 142–143° is obtained.

2. Notes

1. If the reaction is run at temperatures below 70° it is impossible to obtain a pure product even after several recrystallizations.

2. The Büchner funnel is preheated by inverting it over a steam bath and passing a lively current of steam through it for at least 10 minutes. During the filtration, suction is applied gently and at intervals to avoid excessive cooling by evaporation in the lower part of the funnel. If the filtration is not performed rapidly and carefully, the crude product will crystallize in the funnel. The filtration can be omitted, but the presence of insoluble materials complicates the next step by making it difficult to determine when solution of the crude product is complete.

3. The amount of acid required varies with dryness of the filter cake. The acidification can be followed by observing the color of a thin layer of the solution splashed against the side of the container. The color changes from dark red to olive brown at the end point. Both colors are so deep that they are not easily distinguished except when thin layers are viewed. After the end point is observed, an additional 10 ml. of acetic acid is added.

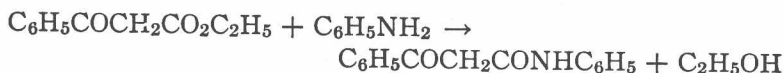
4. Unless properly dried the substance will melt at 80–90°, owing to the presence of water of crystallization.

3. Methods of Preparation

2-Amino-4-nitrophenol has been prepared by the partial reduction of 2,4-dinitrophenol chemically¹⁻⁵ and electrolytically,⁶ and by the action of sulfuric acid on 3-nitroazidobenzene.⁷

BENZOYLACETANILIDE

(Acetanilide, α -benzoyl)



Submitted by CHARLES J. KIBLER and A. WEISSBERGER.

Checked by R. L. SHRINER and FRED W. NEUMANN.

1. Procedure

A 250-ml. three-necked, round-bottomed flask is fitted with a dropping funnel, a mechanical stirrer, and a steam-jacketed column (15–20 cm. long) terminating in a still head. The still head carries a thermometer and is connected to a condenser set for downward distillation. In the flask are placed 42.2 g. (0.22 mole) of ethyl benzoylacetate¹ (Note 1) and 50 ml. of dry xylene, and the flask is immersed in an oil bath. The bath is heated to 145–150°, stirring is begun, and 18.2 ml. (18.6 g., 0.20 mole) of

¹ Laurent and Gerhardt, *Ann.*, **75**, 68 (1850).

² Post and Stuckenberg, *Ann.*, **205**, 72 (1880).

³ Auwers and Röhrig, *Ber.*, **30**, 995 (1897).

⁴ Pomeranz, Ger. pat. 289,454 [*Frdl.*, **12**, 117 (1914–1916)].

⁵ Gershzon, *J. Applied Chem. (U.S.S.R.)*, **9**, 879 (1936) [*C.A.*, **30**, 7554 (1936)].

⁶ Hofer and Jacob, *Ber.*, **41**, 3196 (1908).

⁷ Kehrmann and Idzkowska, *Ber.*, **32**, 1066 (1899).

¹ *Org. Syntheses*, **23**, 35 (1943).

aniline is added dropwise during 30 minutes. About 5 minutes after the addition has begun, the temperature in the still head rises to 75–78° as alcohol begins to distil. Approximately 12–14 ml. of distillate (Note 2) is collected in a 25-ml. graduate in about 1 hour; the end of the reaction is indicated by the fall of the temperature in the still head.

The reaction flask is removed from the oil bath, and the solution is poured into a 250-ml. beaker to crystallize; 10 ml. of benzene is used to rinse out the flask. When crystallization sets in, 50 ml. of petroleum ether (b.p. 35–55°) is added to the warm mixture with manual stirring. After the mixture has been chilled in an ice bath, the product is filtered by suction and washed with 100 ml. of a 1 : 1 petroleum ether-benzene mixture. It is then removed from the funnel, stirred into a slurry with 100 ml. of the mixed solvent, filtered, and again washed with 50 ml. of the solvent. These washings remove the bulk of the color, and a powdery white product remains. After standing overnight in a warm place, the product weighs 35.5–36.5 g. (74–76%) and melts at 104–105°. It may be purified further by recrystallization from benzene (3.7 ml. per g.). The yield of colorless benzoylacetanilide melting at 106–106.5° cor. is 32–34 g.

2. Notes

1. The ethyl benzoylacetate, aniline, and xylene should be redistilled before use. It is necessary that the flask and reagents be free from moisture. Impure starting materials and particularly traces of acids lower the yields. The submitters obtained 82–83% yields of benzoylacetanilide by using Eastman xylene (histological).

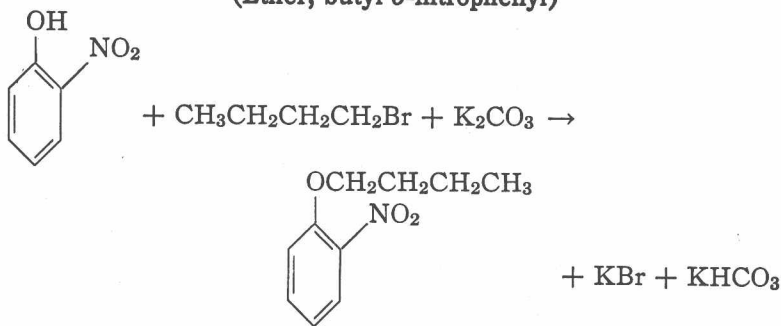
2. The distillate consists of a mixture of xylene and alcohol. By adding 100 ml. of water, the xylene layer can be separated and measured. Of 14 ml. of distillate, about 3.5 ml. is xylene and the balance, 10.5 ml. (89% of the theoretical amount), is alcohol.

3. Methods of Preparation

Benzoylacetanilide has been made by heating aniline and methyl benzoylacetate in an autoclave at 150°² and by heating the anil $C_6H_5NHCOCH_2C(=NC_6H_5)C_6H_5$ with dilute acid.²

o-n-BUTOXYNITROBENZENE

(Ether, butyl *o*-nitrophenyl)



Submitted by C. F. H. ALLEN and J. W. GATES, JR.
 Checked by W. E. BACHMANN and G. DANA JOHNSON.

1. Procedure

A mixture of 28 g. (0.2 mole) of *o*-nitrophenol (Note 1), 30 g. (0.22 mole) of *n*-butyl bromide, 28 g. (0.2 mole) of anhydrous potassium carbonate, and 200 ml. of dry acetone in a 1-l. round-bottomed flask is refluxed on a steam bath for 48 hours (Note 2). At the end of this time the acetone is distilled from the mixture, 200 ml. of water is added to the residue, and the product is extracted with two 100-ml. portions of benzene. The combined benzene extracts are washed with three 100-ml. portions of 10% sodium hydroxide, the benzene is removed by distillation at

² Knorr, *Ann.*, **245**, 372 (1888).

ordinary pressure, and the residual oil is distilled under reduced pressure. The yield of product boiling at 118–121°/1 mm. (Note 3) is 29–31 g. (75–80%) (Notes 4 and 5).

2. Notes

1. A technical grade of *o*-nitrophenol was used; the yield is no better with the pure material. In place of *n*-butyl bromide, a corresponding amount (36.8 g.) of the iodide can be used with no change in yield.

2. The checkers shook the flask occasionally during the first 1.5 hours in order to prevent caking of the contents.

3. The boiling point is 126–129° at 2 mm. and 171–172° at 19 mm.

4. Other nitrophenyl ethers can be prepared in a similar manner and in essentially the same yields. When the size of the run was increased to 2 moles, the yields were increased to 85–90%. The hexyl derivatives require 72 hours for reaction.

The boiling points of some ethers prepared by the present procedure are as follows: *m-n*-butoxynitrobenzene, 120–124°/2 mm.; *p-n*-butoxynitrobenzene, 150–154°/5 mm.; *p*-isopropoxynitrobenzene, 283–286°/760 mm.; *o-n*-hexoxynitrobenzene, 145–148°/1 mm.; *p-n*-hexoxynitrobenzene, 170–174°/5 mm.

5. The alkoxyanilines are obtained readily by reduction of the alkoxynitrobenzenes in alcohol in the presence of Raney nickel catalyst.¹ The boiling points of some of these are as follows: *m-n*-butoxyaniline, 120–124°/2 mm.; *p-n*-butoxyaniline, 135–138°/5 mm.; *p*-isopropoxyaniline, 145–147°/20 mm.; *p-n*-hexoxyaniline, 155–158°/5 mm.

3. Methods of Preparation

The present procedure, which avoids the preparation of the salts of the phenols, is of general utility. It was first used by Claisen² for allyl ethers. *o-n*-Butoxynitrobenzene has been

¹ *Org. Syntheses*, **22**, 9 (1942).

² Claisen and Eisleb, *Ann.*, **401**, 39, 59 (1913).

prepared in a similar manner previously.³ The *m*-nitro- and *p*-nitrobutoxybenzenes have been obtained by alkylation of the phenol salts.^{4,5} The corresponding amines have been prepared previously by reduction of the nitro compounds by means of iron and water³ and by stannous chloride and hydrochloric acid.⁵

n-BUTYLBENZENE

(Benzene, butyl-)



Submitted by R. R. READ, L. S. FOSTER, ALFRED RUSSELL, and V. L. SIMRIL.

Checked by C. F. H. ALLEN and JAMES VAN ALLAN.

1. Procedure

A dry, 3-l., three-necked, round-bottomed flask (Notes 1 and 2) is fitted with an efficient reflux condenser (Note 3) protected by a drying tube, a dropping funnel, and a thermometer which extends well into the reaction mixture (Note 4); the flask is arranged so that it can be cooled externally (Note 5). In the flask is placed 161 g. (7 gram atoms) of sodium cut into shavings 1–2 mm. in thickness (Notes 6 and 7); the sodium is just covered with dry ether (about 300 ml.) (Note 8). A mixture of 411 g. (321 ml., 3 moles) of *n*-butyl bromide and 471 g. (315 ml., 3 moles) of bromobenzene (Note 9) is added slowly from the dropping funnel over a period of about 2.5 hours, the temperature being kept as near 20° as possible; the mass acquires a bluish color.

After the flask and contents have been allowed to stand at room temperature for 2 days with occasional shaking, the liquid is decanted (Note 10). Three hundred milliliters of methanol is then added carefully, and the mixture is refluxed on a steam bath

³ Li and Adams, *J. Am. Chem. Soc.*, **57**, 1567 (1935).

⁴ Hodgson and Clay, *J. Chem. Soc.*, **1933**, 661.

⁵ Gutekunst and Gray, *J. Am. Chem. Soc.*, **44**, 1742 (1922).

for 4 hours. Then 800 ml. of water is added to dissolve the salt, and the hydrocarbon layer is separated and added to the decanted liquid. The aqueous layer is extracted once with 250 ml. of ether (Note 11), and the combined hydrocarbon fraction, decanted solution, and ether extract are dried over 40 g. of calcium chloride. Most of the ether is removed on a steam bath, and the residual liquid is distilled through an electrically heated, jacketed column (Note 12). The fraction which boils at 180–182.5°/750 mm. is collected as *n*-butylbenzene (Notes 13 and 14); the yield is 261–281 g. (65–70%) (Note 15).

2. Notes

1. The size of the pieces of sodium, the control of temperature, and the use of an electrically heated, jacketed fractionating column are important factors in the successful preparation of the compound.

2. A copper flask and copper condenser reduce the hazard from breakage but are not essential and are less convenient with the quantities indicated.

3. Unless the reaction gets out of hand, the only function of the condenser is to prevent loss of ether. If the temperature gets above 30°, the reaction becomes violent and cannot be controlled by a single condenser.

4. A thermometer on which the scale is well above the surface of the reaction mixture is advisable; one reading from –50° to 50° is convenient.

5. The temperature range is critical. Below 15° reaction is extremely slow, but in time a vigorous reaction suddenly sets in and blows a good part of the reactants out through the condenser. Above 30° the reaction gets out of hand (Note 3).

6. This is a very tedious task. It is best accomplished by flattening the usual bars of sodium with a hammer and cutting the flattened strips with scissors. Alternatively the sodium, in 1-lb. lots, can be rolled under a heavy lawn roller (Read and Foster).

7. If the sodium is too thick, much of it fails to react, whereas