ORGANIC SYNTHESES

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

VOL. 29

NEW YORK

JOHN WILEY & SONS, INC.

LONDON: CHAPMAN & HALL, LIMITED

ORGANIC SYNTHESES

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Uniform Size: 6 by 9 Inches. Cloth Binding

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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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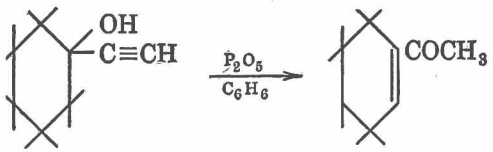
1-ACETYLCYCLOHEXENE

(Ketone, 1-cyclohexenyl methyl)



Submitted by J. H. SAUNDERS.[1]
Checked by E. L. JENNER and R. S. SCHREIBER.

1. Procedure

In a 500-ml. round-bottomed flask are placed 40 g. (0.32 mole) of 1-ethynylcyclohexanol (p. 47), 250 ml. of dry benzene, 10 g. of phosphorus pentoxide, and a boiling chip. A reflux condenser is attached to the flask, and the benzene solution is refluxed gently on a steam cone for 2.5 hours. At the end of that time the contents of the flask are cooled and the benzene is decanted from the phosphorus pentoxide, washed once with 100 ml. of 5% sodium bicarbonate solution, and dried over 15 g. of anhydrous sodium sulfate. The benzene is removed by distillation at atmospheric pressure, and the acetylcyclohexene is carefully fractionated at reduced pressure, through a 15-cm. helix-packed column. The yield of material boiling at 85–88°/22 mm., n_D^{20} 1.4892, is 22.5–28 g. (56–70%).

2. Methods of Preparation

1-Acetylcyclohexene has been prepared by treating cyclohexene with acetyl chloride and aluminum chloride,[2,3,4,5] by treating 1-ethynylcyclohexanol with oxalic acid [6] or 85% aqueous

formic acid,[5,7,8,9] and by the dehydrohalogenation and hydrolysis of ethylidenecyclohexane nitrosochloride.[10]

[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] Darzens, *Compt. rend.*, **150**, 707 (1910).

[3] Christ and Fuson, *J. Am. Chem. Soc.*, **59**, 895 (1937).

[4] Nightingale, Milberger, and Tomisek, *J. Org. Chem.*, **13**, 358 (1948).

[5] Hurd and Christ, *J. Am. Chem. Soc.*, **59**, 120 (1937).

[6] Levina and Vinogradova, *J. Applied Chem. U.S.S.R.*, **9**, 1299 (1936) [*C.A.*, **31**, 2587 (1937)].

[7] Rupe, Messner, and Kambli, *Helv. Chim. Acta*, **11**, 454 (1928).

[8] Fischer and Löwenberg, *Ann.*, **475**, 203 (1929).

[9] Chanley, *J. Am. Chem. Soc.*, **70**, 246 (1948).

[10] Wallach, *Ann.*, **360**, 46 (1908).

ACRYLIC ACID

I. PYROLYSIS METHOD

$$CH_2{=}CHCO_2C_2H_5 \xrightarrow{590^\circ} CH_2{=}CHCO_2H + CH_2{=}CH_2$$

Submitted by W. P. RATCHFORD.
Checked by ARTHUR C. COPE, WILLIAM R. ARMSTRONG, and JAMES J. RYAN.

1. Procedure

A 90-cm. length of 28-mm. (outside diameter) Pyrex tubing packed with pieces of Pyrex tubing (Note 1) is mounted vertically in an electric furnace (Note 2) capable of maintaining a temperature of 585–595°. A 250-ml. long-stemmed separatory funnel is connected to the upper end of the tubing with a stopper (Note 3), and the lower end is connected to a 500-ml. three-necked flask immersed in ice water. The flask, which serves as a receiver, is attached to a 50-cm. water-cooled reflux condenser, which in turn is connected by short lengths of rubber tubing to two traps in series which are immersed in a Dry Ice-trichloroethylene mixture. The exit tube of the second trap is vented to a hood. From 0.2 to 0.3 g. of hydroquinone is placed in the

receiver, together with a few pieces of Dry Ice which serve to displace air from the entire apparatus. The third neck of the receiver is stoppered.

The furnace is heated to 590° (Note 4), and after the air has been displaced 200 g. (216 ml., 2 moles) of ethyl acrylate (Note 5) is placed in the separatory funnel and admitted to the reaction tube at a rate of about 90 drops a minute (Note 3), so that the addition requires about 2 hours. At the end of the addition the contents of the receiver and the small amount of liquid in the traps are combined. The total weight of crude acrylic acid containing some ethyl acrylate is 126–136 g.

The crude product is placed in a 250-ml. flask containing a capillary inlet tube through which carbon dioxide is admitted. Ten grams of hydroquinone and 15 g. of diphenyl ether are added, and the flask is attached to a suitable fractionating column (Note 6). The product is fractionated carefully (Note 7) at 135 mm. pressure. The pressure is lowered gradually when most of the ethyl acrylate has distilled, and at about 70°/90 mm. the receiver is changed. The first fraction (mostly ethyl acrylate) amounts to 9–10 g. The pressure is lowered further to 50 mm., and the acrylic acid is distilled fairly rapidly, without reflux, at 69–71°/50 mm. The acrylic acid fraction weighs 108–116 g. and is 95–97% pure according to acidimetric titration. The yield is 68–75% based upon 100% acrylic acid content (Notes 8 and 9).

If the acrylic acid is not to be used at once, it is stabilized by the addition of hydroquinone and is stored in a refrigerator.

2. Notes

1. The middle third of the Pyrex tube should be packed with 20-mm. lengths of fire-polished 7-mm. Pyrex tubing. The lower end of the tube is drawn out to a size that permits attachment to the receiver with a rubber stopper.

2. A type FD303 combustion furnace (made and sold by the Hoskins Manufacturing Company, Detroit, Michigan) or any similar furnace is satisfactory.

3. A groove filed in the stopcock of the separatory funnel aids in controlling the rate of addition. If available, a small constant-

feed pump may be used to introduce the ester into the pyrolysis tube. The rate of addition of the ester is not critical, but at high rates cracking is incomplete and at low rates the yield is reduced. A slow stream of nitrogen (100 bubbles per minute) flowing through the tube reduces refluxing and makes the feed rate easier to observe. The nitrogen may be introduced through a tube in the stopper holding the separatory funnel or through a side arm sealed near the upper end of the pyrolysis tube.

4. The temperature is measured by a movable Chromel-Alumel thermocouple located in the furnace by the side of the tube and connected to a potentiometer or millivoltmeter. The thermocouple junction is adjusted so that during the run it is at the hottest point in the furnace. For the Hoskins Company furnace this point is about 9 in. from the top of the furnace. The temperature is controlled manually to 590 ± 5° by means of an autotransformer (Variac) rated at 5 amperes, 110 volts.

5. Commercial ethyl acrylate, containing hydroquinone inhibitor, may be used directly if it is of good quality.

6. The submitter used an insulated column with a 38 by 1.1 cm. section packed with ⅛-in. copper helices made of No. 26 B & S gauge copper wire. He states that a column packed with glass helices is unsatisfactory. The checkers used a 100 by 1.7 cm. Vigreux column. Either type of column should be equipped with a total condensation, partial take-off head.

7. Ethyl acrylate and acrylic acid polymerize easily, and overheating must be avoided in the distillation. The flask is heated in an oil bath which is not permitted to rise above 115°. The diphenyl ether which is added serves to expel the acrylic acid at the end of the distillation.

8. The submitter states that the product may be purified by freezing and decanting the supernatant liquid several times. The acrylic acid may be obtained in 97% purity by this method, but it has a faint yellow color. The yield is 50 to 60%.

9. The submitter states that methacrylic acid may be prepared in a similar manner by pyrolyzing ethyl methacrylate. Under the same conditions of temperature and feed rate, the conversion is slightly higher and the yield is about the same.

II. ACIDOLYSIS METHOD

$$CH_2{=}CHCO_2CH_3 + HCO_2H \xrightarrow{H_2SO_4} CH_2{=}CHCO_2H + HCO_2CH_3$$

Submitted by C. E. REHBERG.
Checked by ARTHUR C. COPE and ELBERT C. HERRICK.

1. Procedure

One hundred and eighty-four grams (151 ml., 4 moles) of formic acid (Note 1), 1032 g. (1060 ml., 12 moles) of methyl acrylate (Note 2), 30 g. of hydroquinone, and 2 ml. of sulfuric acid are mixed in a 2-l. two-necked round-bottomed flask fitted with a capillary inlet tube. The flask is attached to a 100 by 1.7 cm. Vigreux column (Note 3) and is heated in an oil bath at 85–95°. The mixture is heated under total reflux until the temperature of the vapor at the still head falls to 32° (after 1–3 hours). Methyl formate then is distilled slowly at 32–35° as long as it is formed (8–10 hours). A reflux ratio of about 5 to 1 is maintained during the first part of the distillation, which is decreased to total take-off at the end. When no more methyl formate is produced, the excess methyl acrylate is distilled at 32–35°/140 mm. with the bath temperature at 60–65°. During the distillation, a slow stream of carbon dioxide is admitted through the capillary inlet. When all the methyl acrylate has been removed, the acrylic acid is distilled at 53–56°/25 mm. Upon redistillation through the same column (Note 4) acrylic acid of 97% purity (by acidimetric titration) is obtained in a yield of 220–230 g. (74–78% based upon 100% acrylic acid content), b.p. 54–56°/25 mm.

2. Notes

1. Acetic acid may be used, but it reacts much less rapidly and less completely, and fractionation of the reaction mixture is more difficult. Pure formic acid (98–100%) is preferred.

2. Commercial methyl acrylate may be used without purification if it is of good quality.

3. Either a Vigreux column or a column containing an open

spiral of copper or Nichrome wire is satisfactory. The column should be jacketed and fitted with a total condensation, variable take-off head.

4. Hydroquinone or another polymerization inhibitor should be added before distillation of acrylic acid or its esters.

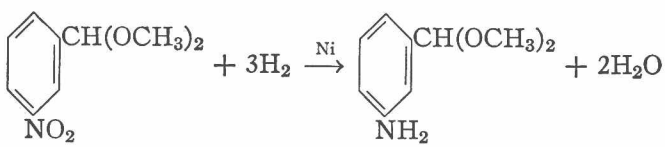
3. Methods of Preparation

Acrylic acid free of water has been prepared by treating lead acrylate with hydrogen sulfide;[1,2] by heating α,β-dibromopropionic acid with copper;[3] by dry distillation of a mixture of equivalent amounts of sodium acrylate and β-chloropropionic acid,[4] and by the two methods described in these preparations.[5]

[1] Caspary and Tollens, *Ann.*, **167**, 252 (1873).
[2] Wohlk, *J. prakt. Chem.*, (2) **61**, 212 (1900).
[3] Biilmann, *J. prakt. Chem.*, (2) **61**, 491 (1900).
[4] Riiber and Schetelig, *Z. physik. Chem.*, **48**, 348 (1904).
[5] Ratchford, Rehberg, and Fisher, *J. Am. Chem. Soc.*, **66**, 1864 (1944).

m-AMINOBENZALDEHYDE DIMETHYLACETAL

(Benzaldehyde, m-amino-, dimethylacetal)



Submitted by Roland N. Icke, C. E. Redemann, Burnett B. Wisegarver, and Gordon A. Alles.
Checked by H. R. Snyder and Frank X. Werber.

1. Procedure

In a 1-l. steel bomb [1] are placed 295 g. (1.5 moles) of *m*-nitrobenzaldehyde dimethylacetal (p. 72), 250 ml. of technical anhydrous methanol, and 1 tablespoon of Raney nickel catalyst.[2] Hydrogen is introduced until the pressure is about 1000 lb. (Note 1). The bomb is heated to about 40°, at which point the heating is discontinued and the shaker is started. The hy-

drogenation soon becomes rapid as the temperature rises to about 70° (Note 2). The bomb is refilled with hydrogen as many times as necessary (Note 3). The theoretical amount of hydrogen (4.5 moles) is absorbed in about 1.5 hours.

The bomb is cooled, the remaining hydrogen is discharged, and the bomb is opened. The solution is transferred to a beaker, and the bomb is rinsed with a little methanol which is added to the solution. The catalyst is removed by filtration (*Caution! The catalyst may be pyrophoric*), and most of the filtrate is transferred to a 500-ml. Claisen flask set on a steam bath for distillation of the methanol; the remainder of the filtrate is introduced into the Claisen flask when the volume of the first portion has been reduced sufficiently by distillation. After all the methanol has been removed the aminoacetal is distilled under diminished pressure. The yield of *m*-aminobenzaldehyde dimethylacetal, a light-yellow liquid boiling at 123–124°/4 mm. or 110–112°/1.5 mm., is 168–196 g. (67–78%).

2. Notes

1. The hydrogenation is similar to one described earlier.[1] As the bomb does not contain enough hydrogen to complete the reduction, more hydrogen should be admitted whenever the pressure drops below 300 lb.

2. Because of the high heat capacity of the bomb the internal temperature continues to rise (to about 70°) after the heater is turned off. As the exothermic hydrogenation begins the temperature rises to about 80°. The temperature should be kept below 85° to prevent hydrogenolysis of the acetal.

3. If the hydrogenation is started at a pressure of about 1500 lb. in a 2.5-l. bomb it will not be necessary to introduce more hydrogen. However, it may be necessary to stop the shaker occasionally to prevent a temperature rise beyond 85°.

3. Methods of Preparation

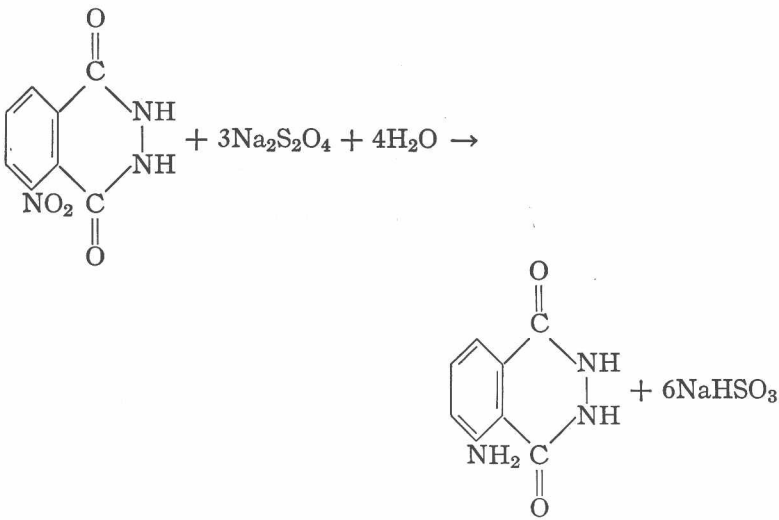
This acetal has not been described previously. The corresponding diethylacetal has been prepared by the reduction of

m-nitrobenzaldehyde diethylacetal with sodium sulfide [3] and by the reaction of the anhydro compound of *m*-aminobenzaldehyde with ethanolic hydrogen chloride and ethyl orthoformate.[4]

[1] *Org. Syntheses*, **22**, 9 (1942).
[2] *Org. Syntheses*, **21**, 15 (1941).
[3] Haworth and Lapworth, *J. Chem. Soc.*, **121**, 76 (1922).
[4] Bottomley, Cocker, and Nanney, *J. Chem. Soc.*, **1937**, 1891.

5-AMINO-2,3-DIHYDRO-1,4-PHTHALAZINEDIONE

(1,4-Phthalazinedione, 5-amino-2,3-dihydro-)



Submitted by CARL T. REDEMANN and C. ERNST REDEMANN.
Checked by CLIFF S. HAMILTON and C. W. WINTER.

1. Procedure

In a 1-l. conical flask are placed 52 g. (about 0.15 mole) of the equimolecular mixture of 5-nitro-2,3-dihydro-1,4-phthalazinedione (p. 78) and sodium sulfate (Note 1), 200 ml. of water, and 75 ml. of 15 *N* ammonium hydroxide solution (sp. gr. 0.90). The flask is stoppered and shaken until all, or very nearly all, of

the solid has dissolved, and 84 g. (0.4 mole) of sodium hydrosulfite dihydrate (Note 2) is added in three portions. The solution becomes hot, the temperature sometimes reaching the boiling point, and the dark orange-red color begins to fade. After the spontaneous reaction has subsided the solution is boiled gently for a few minutes and filtered to remove any insoluble impurities. The filtrate is heated on a steam bath or over a small flame for 30 minutes. During this time the 5-amino-2,3-dihydro-1,4-phthalazinedione begins to separate as a light-yellow flocculent precipitate or as a crust adhering to the walls of the flask. The hot solution is made distinctly acid to litmus paper with glacial acetic acid and allowed to stand overnight. The yellow precipitate is separated by filtration, washed well with cold water, and dried in a hot-air oven at 110° or below. The dry material weighs 25–27 g. and melts with decomposition at 301–305° (Note 3).

This material is sufficiently pure for most purposes. The chief impurities are small amounts of inorganic salts and a trace of the unreduced nitro compound. If a purer product is desired the crude material (5 g. per 100 ml.) is dissolved in hot 3 *N* hydrochloric acid, decolorizing carbon is added, the solution is filtered promptly (Note 4), and the filtrate is made just faintly acid to Congo red paper with concentrated ammonium hydroxide. After the mixture has cooled to room temperature the pale yellow flocculent precipitate is separated by filtration, washed well with cold water, and dried in the oven at 100° or below. The recovery in the crystallization is 70–75% (Note 5), and the product melts at 329–332° (Note 4).

2. Notes

1. No advantage is gained by using the purified nitro compound.

2. The success of this reduction depends upon the quality of the sodium hydrosulfite. The reagent should be taken from a fresh bottle; material which has stood in the laboratory for a long time probably has undergone oxidation.

3. The submitters used a Kullmann copper block for the

melting-point determinations. The melting point of the pure material has been reported in the literature at various values between 319° and 333°.

4. The 5-amino-2,3-dihydro-1,4-phthalazinedione should not be exposed to the hot hydrochloric acid longer than necessary since some hydrolysis appears to take place.

5. The percentage yield cannot be calculated with precision, since the exact quantity of nitro compound in the mixture taken for the reduction is unknown. The quantity of sodium hydrosulfite dihydrate employed is sufficient for the reduction of only 0.133 mole of nitro compound; the weight of the purified amino compound corresponds to about 80% of the theoretical yield calculated on the assumption that the hydrosulfite is the limiting reagent.

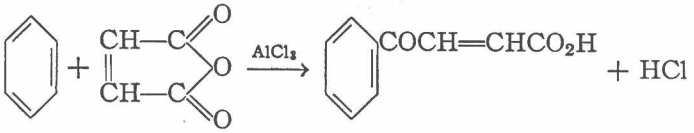
3. Methods of Preparation

5-Amino-2,3-dihydro-1,4-phthalazinedione, also called luminol and 3-aminophthalhydrazide, has been prepared from 5-nitro-2,3-dihydro-1,4-phthalazinedione by reduction with ammonium sulfide [1] or stannous chloride [2] and by catalytic hydrogenation over palladium on charcoal in alkaline solution [3] and by the reaction of 3-aminophthalimide [2] with hydrazine hydrate.

[1] Huntress, Stanley, and Parker, *J. Am. Chem. Soc.*, **56**, 241 (1934).
[2] Drew and Pearman, *J. Chem. Soc.*, **1937**, 30.
[3] Wegler, *J. prakt. Chem.*, **148**, 135 (1937)

β-BENZOYLACRYLIC ACID

(Acrylic acid, β-benzoyl)



Submitted by OLIVER GRUMMITT, E. I. BECKER, and C. MIESSE.
Checked by ARTHUR C. COPE and CLAUDE F. SPENCER.

1. Procedure

In a 1-l. three-necked round-bottomed flask fitted with a mercury-sealed stirrer and a reflux condenser are placed 34 g. (0.347 mole) of maleic anhydride (Note 1) and 175 g. (200 ml., 2.24 moles) of dry, thiophene-free benzene. Stirring is started, and, when the maleic anhydride has dissolved, 100 g. (0.75 mole) of anhydrous reagent grade aluminum chloride powder is added in 6–8 portions through the third neck of the flask at a rate so that the benzene refluxes moderately. The addition requires about 20 minutes. The mixture is then heated under reflux on a steam bath and stirred for 1 hour. The reaction flask is cooled thoroughly in an ice bath, a 250-ml. dropping funnel is attached to the third neck, and the mixture is hydrolyzed by adding 200 ml. of water with stirring and cooling (the first 50 ml. during 15–20 minutes and the balance in about 10 minutes), followed by 50 ml. of concentrated hydrochloric acid (Note 2). Stirring is continued for an additional 40 minutes, during which time it may be necessary to use a spatula to scrape adhering particles of the red-brown aluminum chloride addition compound from the walls of the flask.

The hydrolyzed mixture is transferred to a 1-l. Claisen flask, the transfer of material being completed by rinsing with about 50 ml. of warm water. The flask is heated in a water bath at 50–60°, and the benzene and some water are distilled at 20–30 mm. pressure (Note 3). While the residue is still molten, it is

transferred to a 1-l. beaker, and the flask is rinsed with 50 ml. of warm water. After standing at 0–5° for 1 hour, the yellow solid is collected on a suction filter and washed with a solution of 25 ml. of concentrated hydrochloric acid in 100 ml. of water and then with 100 ml. of water. The washing is done most efficiently by suspending the solid in the wash liquid, cooling to 0–5° with stirring, and then filtering with suction. The preparation should not be interrupted before this point (Note 3), at which stage the crude acid may be air-dried overnight at room temperature if desired. The crude product is dissolved in a solution of 40 g. of anhydrous sodium carbonate in 250 ml. of water by warming to 40–50° (Note 4), 2 g. of Celite or other filter aid is added, and the solution is filtered with suction while warm. After the filter has been washed with two 30-ml. portions of warm water, 2 g. of Norite is added to the combined filtrates and the mixture is heated at 40–50° for 10–15 minutes with frequent stirring, then filtered with suction. The clear, yellow filtrate is transferred to a 1-l. beaker and cooled to 5–10°, and 70 ml. of concentrated hydrochloric acid is added dropwise with stirring. Efficient cooling and stirring are necessary to avoid the precipitation of the acid as an oil. After being cooled to 0–5°, the mixture is filtered with suction; the solid is washed with two 50-ml. portions of cold water and then is dried in the oven at 50° for 12–36 hours to give 56–63 g. of light-yellow anhydrous β-benzoylacrylic acid, m.p. 90–93° (Note 5). The crude acid may be crystallized from benzene, using 12–15 ml. of benzene per 5 g. of acid and cooling at 5–10° (Note 6) to give 44–47 g. of β-benzoylacrylic acid, m.p. 94–96° (Note 7). Concentration of the filtrate to one-fourth to one-fifth of its original volume gives an additional 3–6 g., melting in the range 92–96°. The total yield is 49–52 g. (80–85%).

2. Notes

1. A good grade of commercial maleic anhydride was used, m.p. 52–54°.

2. When β-benzoylacrylic acid is heated with dilute hydrochloric acid, β-benzoyllactic acid is formed, which makes the purification of the product very difficult.[1] For this reason the