Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Org. Synth. **1928**, *8*, 10
DOI: 10.15227/orgsyn.008.0010

APPARATUS FOR CATALYTIC REDUCTION

Submitted by Roger Adams and V. Voorhees.
Checked by Henry Gilman and S. A. Harris.

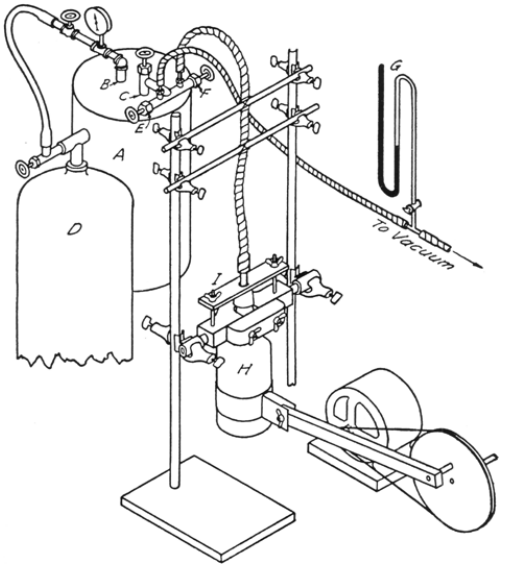
1. Procedure

(*A*) *Apparatus* (Fig. 5).—A Prest-o-lite tank A from which the filling has been removed (Note 1), or any other similar tank of about 8- to 10-l. capacity, may be conveniently used as a container for hydrogen. The top of the tank contains two openings B and C. In B is welded a tube holding a gauge and valve, and through this tube the hydrogen from a large cylinder D is introduced into the tank. In C is welded another tube controlled by a needle valve. E is used for the vacuum, a manometer G being introduced into this system, and F for a tube leading to the reaction bottle H. These outlets are so arranged that it is possible to shut off the tank from either outlet and also to make a direct connection between the vacuum and the bottle H, leaving tank A out of the circuit. The connection between the tank A and the bottle H is a heavy taped rubber tube (Note 2) which is in turn connected to a glass tube inserted through the stopper of the bottle. The rubber tube and stopper should be of high grade and must be carefully boiled with alkali before being used (Note 3). The arrangement for shaking the bottle is shown in the diagram (Note 4). The driving pulley is connected to the reaction bottle by a wooden or preferably a metal rod. The rod in turn is attached by a yoke to a metal ring which circles the bottom of the bottle. The ring opens on the back side of the bottle and is held together by a wing-nut and bolt. In order to hold the stopper in the bottle when the latter is filled with hydrogen under pressure, a metal strip I is clamped tightly over the stopper. This strip is screwed to the long wooden bottle holder which extends between the bearings, and a short wooden piece which fits around the neck of the bottle is attached to the longer one by means of screws held by wingnuts. This arrangement permits removal of the bottle from the apparatus without detaching the metal strip.

The chief precautions in setting up this reduction outfit are, first, to have every piece free from catalytic poisons, and second, to be certain that there are no leaks (Note 5). The latter are sometimes an annoying factor, and the complete apparatus should be carefully tested before attempting any reductions for standardizing the hydrogen tank. The apparatus is put together in final form with the empty reduction bottle attached to the hydrogen tank exactly as it is arranged in a reduction. The tank is then filled with hydrogen until the gauge reads 2.5–3 atm. (40–45 lb.) and the temperature of the tank recorded. The reading of the gauge is observed as soon as equilibrium is reached and the bottle is then shaken for six to eight hours. Observations are made of the drop in pressure, taking into account any change of temperature which may occur during this time. In general if the drop in pressure is less than 0.03 atm. (0.5 lb.) in the time indicated the apparatus may be considered sufficiently free from leaks for ordinary work.

For some reactions it is advantageous to heat the mixture, and the following arrangement is very satisfactory for this purpose. The bottle H is wrapped with moistened asbestos paper to a thickness of about 3 mm. and the paper is then allowed to dry. When the asbestos is thoroughly dry the bottle is wound with a coil of No. 24 Nichrome wire, beginning the coil at the bottom of the bottle and making the turns about 9 mm. apart. The wire is then covered with a 3-mm. layer of asbestos, which is moistened and allowed to dry, after which the wire is wound around the bottle in another coil from top to

Fig. 5.



bottom. The second coil is covered with asbestos as before, and the ends of the wire are connected to the terminal wires from a source of current. These wires are led along the bottle to the neck and held by means of tape in order to avoid excessive shaking. A variable resistance in the circuit is used to regulate the temperature.

(*B*) *Use of Apparatus*.—The tank A is filled with hydrogen to a pressure of 3–3.5 atm. from the cylinder D (Note 6). The solution in a suitable solvent, of the substance to be reduced is poured into the bottle H and the platinum oxide (p. 463) is added (Note 7) and (Note 8). The bottle is attached to the apparatus and evacuated by opening valves E and F and closing C. In the case of low-boiling solvents, the evacuation is continued only until the solvent begins to boil; in other cases it is continued until the pressure as recorded by the manometer remains fairly constant. The valve E is then closed and hydrogen is admitted to the bottle H from the tank A by opening valve C (Note 9) and (Note 10). When the pressure in the bottle has become adjusted the pressure of the hydrogen and the temperature of the tank A are recorded. Shaking is started. Within a few minutes the brown platinum oxide turns black (see Note 6 on p. 467), and the absorption of hydrogen begins. The shaking is continued until the theoretical amount of hydrogen has been absorbed.

The hydrogen remaining in the bottle is removed, air is admitted and the mixture allowed to stand or, if necessary, shaken for a few minutes in order to aid the settling of the catalyst. In certain cases where the catalyst settles spontaneously at the end of the reduction it is not necessary to shake the mixture with air. The solution may be decanted from the main portion of the catalyst and a second reduction carried out. In cases where the catalyst cannot be used directly for another reduction (see Note 9 on p. 468) the solution is filtered, preferably through an asbestos filter (Note 11), and fresh solvent is used for washing. The reduction product is isolated from the filtrate, usually by distilling off the solvent. The reduction of ethyl *p*-nitrobenzoate to ethyl *p*-aminobenzoate (p. 240) and benzalacetophenone to benzylacetophenone (p. 101) is described in detail.

(*C*) *Standardization of Apparatus*.—After making certain that there are no leaks in the apparatus (Note 5) the hydrogen tank may be standardized by reducing 11.6 g. (0.1 mole) of pure maleic acid (Note 12) dissolved in 150 cc. of 95 per cent alcohol using 0.1 g. of catalyst (p. 463). The reduction is carried out according to the procedure described in part (*B*). Shaking of the mixture is continued until no more hydrogen is absorbed; the theoretical amount is absorbed by 0.1 mole of maleic acid within twenty or thirty minutes. The temperature of the tank is recorded. The decrease in pressure corresponds to 0.1 mole of hydrogen at the observed temperature.

If the succinic acid is desired it may be recovered merely by filtering the platinum, evaporating the alcohol and crystallizing from about 10–15 cc. of boiling water. The yield of product is 10–11.5 g. (84–98 per cent of the theoretical amount) depending on the care used in crystallization.

2. Notes

1. The bottom of the tank is cut off, the filling removed, and the bottom welded on again.

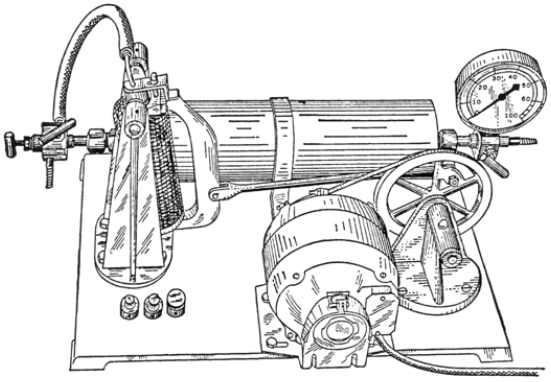
2. A copper tube may be used for this connection but is less satisfactory since the shaking tends to wear it out at the joints.

3. It is advisable to boil the tube and stopper with several portions of 20 per cent sodium hydroxide until the solution is no longer colored yellow, after which the boiling is carried out several times with distilled water.

4. The motor, pulley and the supports for the reaction vessel must be attached firmly to a heavy wooden stand which will allow as little motion as possible in the apparatus during shaking, thus reducing to a minimum the possibility of the gradual formation of leaks.

The arrangement for shaking should be so made that the reaction bottle is agitated at a rate above which no difference in the speed of reduction is observed. A suitable motor is a 1/30 h.p., 1760 r.p.m., the pulley on the motor 2.5 cm. in radius, and the wooden driving pulley 7.5 cm. in radius. The distance from the center of the pulley to the hole for attaching the rod to the reaction bottle is 3.2 cm.; the distance from the center of the pulley on the motor to the center of the driving pulley to the bottle attachment is 30 cm. Considerable latitude is possible in these measurements. Although the apparatus in Fig. 5 is readily set up in any laboratory, a more compact and more stable form is shown in Fig. 6. An apparatus similar to this can be purchased complete from the Parr Instrument Co., Moline, Ill.

Fig. 6.



5. It is quite necessary that the welding of the tank be perfect and free from pin holes. Leaks frequently appear where the tubes are welded in the top of the tank. These may be eliminated by brazing the joints. A less satisfactory way is to use a cement of litharge and glycerol. This cement may also be used with success on leaky valves. Occasionally leaks occur in the rubber tubing or its connections with the bottle or tank, but these are unusual.

6. Electrolytic hydrogen was used in all experiments. This hydrogen is essentially free from all impurities except oxygen. Since oxygen in general has no harmful effect upon the reduction, no purification is necessary. If, however, oxygen-free hydrogen is needed, it must be passed over heated platinized asbestos.

7. This procedure may be varied in certain cases where it seems advantageous to reduce the platinum oxide to platinum black in the presence of the solvent alone (see Note 12 on p. 469).

8. During the course of the catalytic hydrogenation of carotin, using hexahydrobenzene and acetic acid as the solvent, it became necessary to add fresh platinum oxide catalyst. The reaction bottle was opened and immediately the powdered catalyst was added. As soon as the catalyst came in contact with the gas in the bottle an explosion resulted (H. A. Spoehr, private communication).

The above experience warrants precaution during addition of the catalyst. However, the experience of the editors in hundreds of catalytic reduction operations extending over more than ten years shows that such explosions are extraordinarily rare.

9. During the reductions it is usually advisable not to allow the pressure in the tank A to drop below about 2 atm. if the reduction is to be carried out in minimum time. When the gauge registers 2 atm. the tank is closed off from the reducing bottle and the pressure is increased to about 3–3.5 atm. by the admission of more hydrogen from D.

10. Ordinarily traces of air in the hydrogen have no deleterious effect upon the reductions. If, in any experiment, absolute freedom from air is desired the bottle may be evacuated and refilled with hydrogen two or more times. In this way the air is all washed out of the bottle.

11. When paper filters are used, the rapid suction of air through the paper in the presence of the catalyst often causes spontaneous combustion of the filter. Paper filters may be used, however, if care is taken to keep the filter covered with solvent while suction is being applied; just before the last portion of solvent has run through, the suction is stopped.

12. Instead of pure maleic acid, 10.6 g. (0.1 mole) of pure benzaldehyde may be used for the standardization. In this case 1 cc. of 0.1 molar ferrous sulfate is added to the mixture of benzaldehyde, alcohol and catalyst before the reduction is started (see Note 13 on p. 469). The reduction is complete in fifteen to thirty minutes.

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. Organic Syntheses, Inc., its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

The paragraphs above were added in September, 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

3. Discussion

Other forms of catalytic reduction apparatus which may be used in the laboratory are described in the following articles.[1]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 101
- Org. Syn. Coll. Vol. 1, 240

- Org. Syn. Coll. Vol. 1, 463
- Org. Syn. Coll. Vol. 2, 191
- Org. Syn. Coll. Vol. 2, 566
- Org. Syn. Coll. Vol. 3, 63
- Org. Syn. Coll. Vol. 3, 501
- Org. Syn. Coll. Vol. 3, 519
- Org. Syn. Coll. Vol. 4, 304
- Org. Syn. Coll. Vol. 4, 603
- Org. Syn. Coll. Vol. 4, 928
- Org. Syn. Coll. Vol. 5, 60
- Org. Syn. Coll. Vol. 5, 239
- Org. Syn. Coll. Vol. 5, 346
- Org. Syn. Coll. Vol. 5, 552

References and Notes

1. Paal and Amberger, Ber. **38**, 1390 (1905); Paal and Gerum, Ber. **41**, 813 (1908); Waser, Ueber Derivate des Cyclooctans (Promotionsarbeit), Zürich, 1911, p. 54; Willstätter and Hatt, Ber. **45**, 1472 (1912); Skita and Meyer, Ber. **45**, 3594 (1912); Stark, Ber. **46**, 2335 (1913); Böeseken, Van der Weide and Mom, Rec. trav. chim. **35**, 267 (1916); Rosenmund and Zetzsche, Ber. **51**, 580 (1918); Adams and Voorhees, J. Am. Chem. Soc. **44**, 1403 (1922); Klimont, Chem. Ztg. **46**, 275 (1922); Escourrou, Parfums France **26**, 88 (1925).

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

carotin

alcohol (64-17-5)

acetic acid (64-19-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

glycerol (56-81-5)

oxygen (7782-44-7)

ferrous sulfate (13463-43-9)

platinum oxide

Benzalacetophenone (94-41-7)

Benzylacetophenone (1083-30-3)

maleic acid (110-16-7)

Succinic acid (110-15-6)

platinum (7440-06-4)

copper (7440-50-8)

hexahydrobenzene (110-82-7)

benzaldehyde (100-52-7)

Ethyl p-aminobenzoate (94-09-7)

ethyl p-nitrobenzoate (99-77-4)