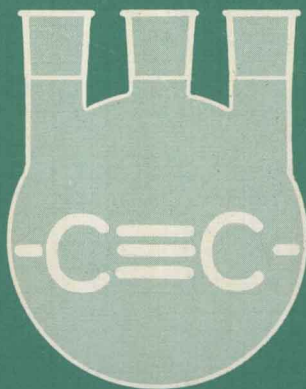


studies in organic chemistry 34

PREPARATIVE ACETYLENIC CHEMISTRY

SECOND EDITION

LAMBERT BRANDSMA



ELSEVIER

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SECOND EDITION

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PREPARATIVE ACETYLENIC CHEMISTRY

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Preface

"Preparative Acetylenic Chemistry", the first book of a series of laboratory manuals containing experimental procedures that are based upon the author's personal bench experience, appeared in 1971. The book has been frequently used by students during practical courses and their research period in our laboratory. Several procedures have been carried out one or more times by persons with a relatively limited bench experience. Discussions with them about their results were highly useful and have in many cases resulted in modified procedures or descriptions. These have been included in the present edition which is considerably different from the first one, *e.g.*:

1. A number of procedures have been omitted or replaced by others.
2. The subdivision and titling of the chapters and experiments have been changed.
3. Some new and attractive methods, for example eliminations under phase-transfer conditions and couplings under the influence of zero-valent palladium compounds, have been included.
4. In a number of cases additional experiments have been described in order to give a more complete picture of the scope of the concerned methods.
5. The indexes of the first edition have been replaced by a type-compound-method index.

The author is indebted to Mrs. Y.A. Heus-Kloos and Mr. D.M. Grove for helpful suggestions during the preparation of this edition.

Financial support and gifts of chemicals by AKZO-Chemie (Deventer), Andeno (Venlo), Chemetall GmbH (Frankfurt am Main, F.R.G.), Diosynth (Oss), DSM (Geleen), Quest International (Naarden) and Shell (Amsterdam) are gratefully acknowledged.

L. Brandsma, January, 1988

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Chapter I

General Practical Information

1. Introduction

With many chemists the word acetylenes evokes associations with vigorous explosions: they remember the stories with which their high-school chemistry teacher illustrated his lessons on the difference in stability of acetylenes and alkanes or alkenes. Indeed, accidents have occurred during welding with acetylene from inadequately equipped cylinders. Furthermore, attempts in the laboratory to prepare mono- and dichloroacetylene in an undiluted state are extremely risky and the structure of highly unsaturated, unsubstituted compounds such as $\text{HC}\equiv\text{CC}\equiv\text{CC}\equiv\text{CH}$, is in itself a sufficiently strong warning to be cautious during preparation. It is not justified, however, to consider acetylenic chemistry as the playground of reckless dare-devils*.

An important aim of this book, which complements a large number of books and reviews [3-32], is to make organic chemists familiar with the experimental methods (some being unconventional) that give access to a versatile and interesting class of compounds.

2. Laboratory Equipment and Techniques for the Procedures in this Book

2.1 General

By far the most of the syntheses described in this book are carried out in the **standard apparatus (fig. 1)**, a round-bottomed three-necked flask, equipped with a combination of a gas inlet and a dropping funnel, a mechanical stirrer and a thermometer-gas outlet combination. A flask with **slanting necks (fig.-1)**** is **extremely impractical** for the following reasons. First it is very difficult to place the thermometer (or a gas inlet tube) in such a position that contact with the stirrer during its motion is avoided. Secondly, in some reactions it is essential that the reagent added from the dropping funnel is distributed immediately over the liquid in the reaction flask and does not flow along the glass wall before it comes into contact with the bulk of the solution (*e.g.* Chap. IV, exps. 5 and 8).

In most procedures described in this book, stirring is carried out mechanically, using a **glass rod** (diameter not less than 5 mm) ending in or connected to a **paddle** (*e.g.* a piece of

*Many teachers in chemistry seem to know better what one should not do than what one has to do in order to carry out a synthesis in a successful way.

**Compare also H.J.E. Loewenthal, "A Guide to the Perplexed Organic Experimentalist", Heyden, 1978.



fig. -1 A negative start

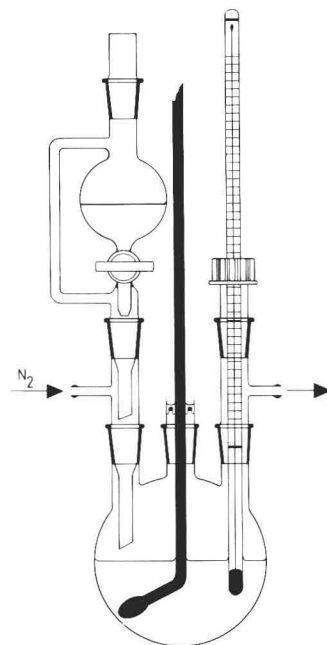


fig. 1



fig. 2

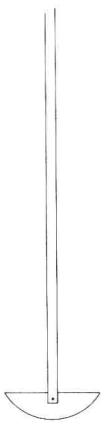


fig. 3

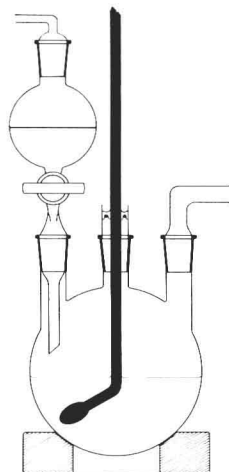


fig. 4

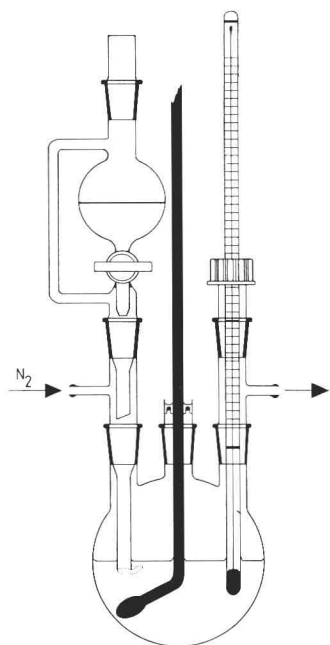


fig. 5

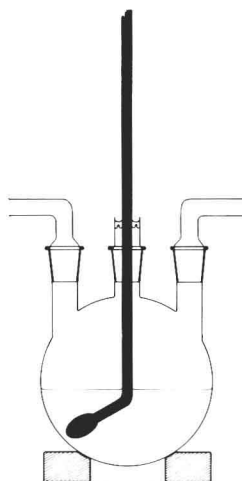


fig. 6

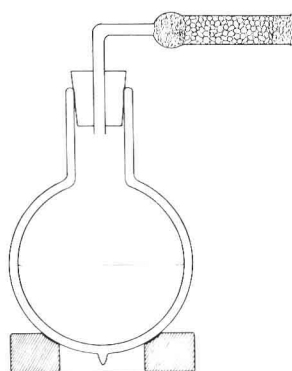


fig. 7

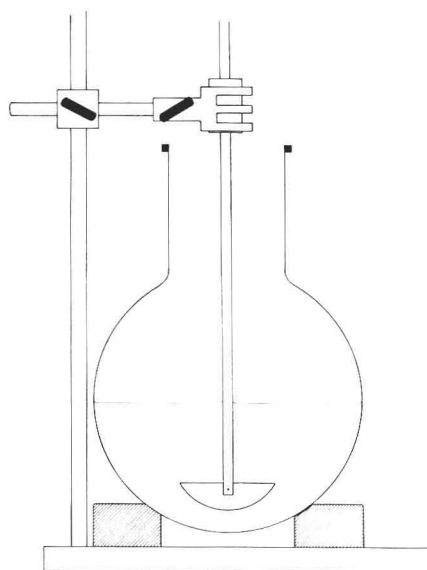


fig. 8



fig. 10

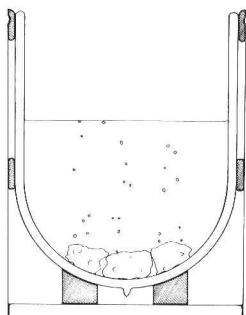


fig. 9

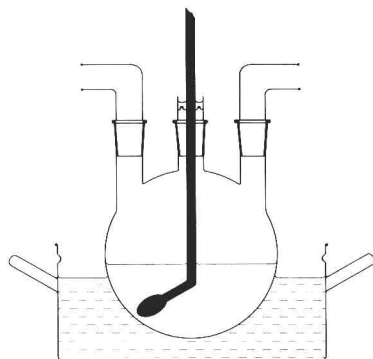


fig. 12

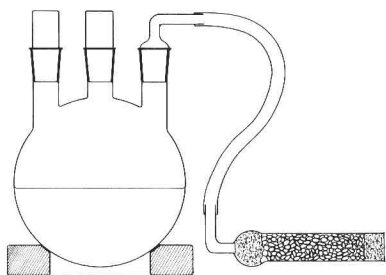


fig. 11

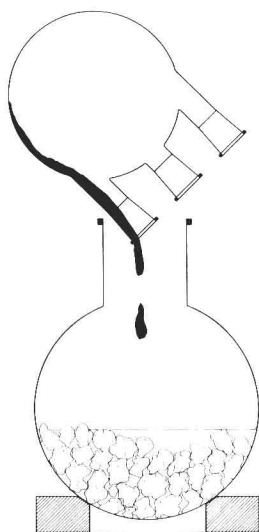


fig. 13

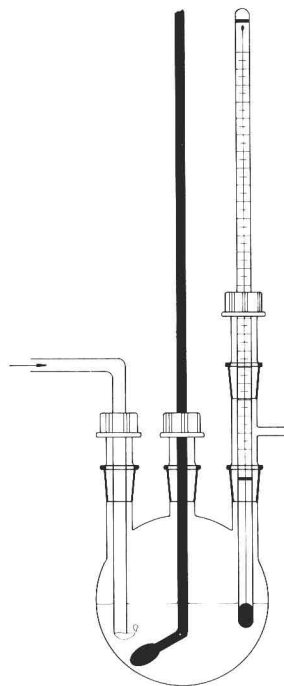


fig. 16

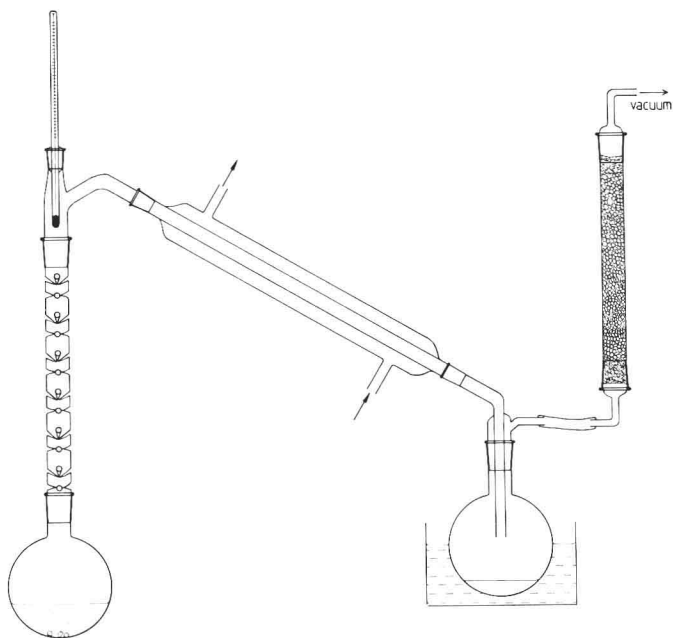


fig. 14

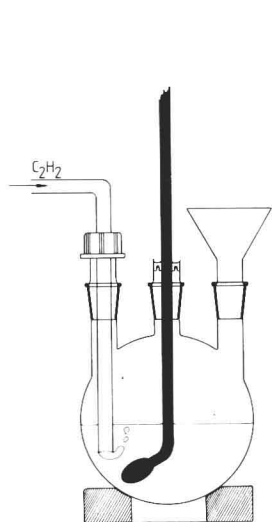


fig. 15

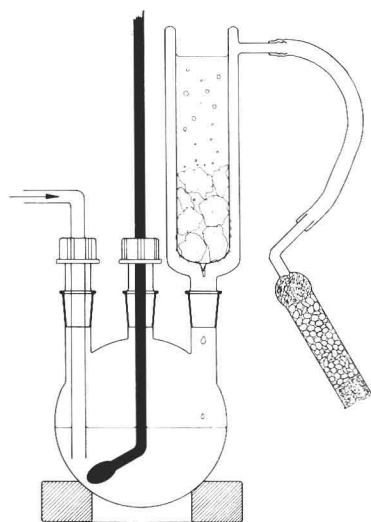


fig. 17

the rod that is flattened, surface $\sim 1 \text{ cm}^2$) with the upper side of the rod being connected to the stirring motor. The stirring rod passes through a ground glass-joint with a gas-tight O-ring seal (**fig. 2**). This hockey-stick like stirrer does not suffice when the reaction mixture has a high "viscosity" (e.g. thick suspension) or when the volume to be stirred is larger than 3 l. In such cases a **metal rod** equipped with a **chromium-plated paddle** may be used (**fig. 3**).

The various types of reaction flasks and auxiliary equipment are shown in the **figs. -1 to 17** and/or described in the experiments.

2.2 Reactions in Liquid Ammonia

A large number of acetylenic compounds can be prepared with excellent results using **anhydrous liquid ammonia** as the solvent. The conversions can be performed under normal pressure at the boiling point (-33°C) of ammonia or, if necessary, at a lower temperature. The usual apparatus is a **three-necked round-bottomed flask**, equipped with a **mechanical stirrer** (see **fig. 4**). The liquid ammonia is obtained directly from the cylinder which, if it is equipped with a dip tube, can remain in an upright position during tapping or otherwise is placed on a stand at an angle of about 30° to the floor with the tap pointing down (see A.I. Vogel, A textbook of Practical Organic Chemistry, 4th ed. (Longmans), p. 98). On opening the tap, liquid ammonia flows through the plastic tube connected to the cylinder. Since this tube may contain some moisture, a volume of 100 to 150 ml should first be allowed to flow into the hood before the end of the tube is placed into one of the open necks of the reaction flask. Several liters of liquid ammonia can be obtained within a few minutes. The losses due to evaporation during tapping are relatively small (20% or less). After the required volume of ammonia has been obtained, the tap is closed and the necessary equipment is **immediately** placed on the flask (or plugs of cotton wool are temporarily placed on the necks). In view of the possibility of splashing or frothing while carrying out the synthesis, the flask should **never** be filled more than 50% (preferably only $\sim 35\%$). It is completely unnecessary to fill the flask by condensing ammonia into it, unless extremely careful working conditions with small amounts of NH_3 are required or the water content of the ammonia is greater than 0.2%. The **water content** of the liquid ammonia is readily checked. This can be done semi- quantitatively by gently stirring in small pieces of alkali metal ($\sim 0.1 \text{ g}$ of Na or 0.02 g of Li) preferably under a nitrogen atmosphere. The next piece of metal is added after the blue colour has disappeared completely. The weight of the metal required to obtain a persisting blue colour, gives a fairly good impression of the water content. Too large an amount of water in the ammonia may give rise to frothing during the preparation of Li- or $\text{NaC}\equiv\text{CH}$ from the alkali metals and acetylene: the solutions of the alkali acetylides in these cases are turbid due to the presence of alkali hydroxide.

Introduction of **alkali metal** into the flask containing liquid ammonia is most easily done with a **powder funnel**, which temporarily replaces a part of the equipment. The cleaned lumps of metal are held above the funnel and cut into pieces (for handling alkali metals see our previous book "Preparative Polar Organometallic Chemistry", Springer-Verlag, 1987.)

Thanks to the relatively high heat of evaporation of ammonia, many reactions can be carried out at **its boiling point, -33°C** . The use of a dry ice-acetone reflux condenser is absolutely unnecessary. Losses due to evaporation are easily compensated by adding ammonia from the cylinder. The rate of evaporation can be limited by insulating the flask with cotton wool; the ice which forms on the outside of the flask as a result of condensation can, to some extent, have a similar function.

If a **volatile compound** is to be prepared in liquid ammonia, it is desirable to **cool** the flask to a temperature **below the b.p.** (-33°C) of ammonia. To prevent introduction of air and moisture during cooling, nitrogen is led through the apparatus (see **fig. 1**).

In the case of **slow reactions** it is inconvenient trying to maintain a sufficiently low temperature throughout the conversion in a normal flask, even with the use of a dry ice-acetone condenser. It is much easier to allow the reaction to proceed in a **round-bottomed Dewar flask** (**fig. 7**, a flask with an evacuated space between the two walls). The rate of evaporation is reduced to a minimum (10 g/h or less) if the inner wall is covered with a silver mirror (covering the flask with aluminum foil is a good alternative). An example of a reaction in a Dewar flask is the conversion of $\text{LiC}\equiv\text{CH}$ with oxirane to $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{OLi}$ (Chap. III, exp. 23). The ammoniacal solution of $\text{LiC}\equiv\text{CH}$ is first prepared in the usual apparatus and then transferred (by pouring) into the Dewar flask. The oxirane is subsequently added over a short period and a stopper with a drying tube is placed on the flask. After 24 h the solution is poured into a normal round-bottomed flask and the ammonia is removed by evaporation.

This book contains a few procedures that are preferably carried out in a big (5-10 l) **round-bottomed flask with one, wide neck** (**fig. 8**). The stirring rod is then placed centrally and the reagent is added portion-wise through the neck.

If, during the addition of a reagent **contact with ammonia vapour has to be avoided**, the reagent is added through a tube ending a few cm above the surface of the liquid ammonia, while a vigorous stream of **nitrogen** is passed through the tube, (**fig. 5**). Relatively small amounts may also be introduced by means of a syringe, being careful to keep the injection needle a few cm above the surface of the liquid.

2.3 Reactions in Other Solvents

Several acetylenic derivatives are prepared by dehydrohalogenation of vicinal dibromo compounds, which are obtained by adding bromine to olefinic compounds.

Addition reactions of halogens to double bonds are usually carried out in carbon tetrachloride. Textbook knowledge about radical substitutions makes some chemists hesitant in using **chloroform** (CHCl_3) or **dichloromethane** (CH_2Cl_2), which in fact are easily removable substances. Halogenation of CHCl_3 and CH_2Cl_2 only occurs under forcing conditions, so that addition reactions with Br_2 and even Cl_2 can be carried out in CH_2Cl_2 (with Cl_2 below 0°C) if they are sufficiently fast. The use of **diethyl ether** in additions of Br_2 to olefins may be advantageous, because in many cases removal of the ether before carrying out the subsequent reaction is not necessary.