



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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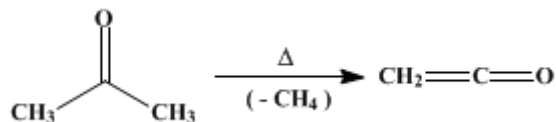
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.330 (1941); Vol. 4, p.39 (1925).

KETENE

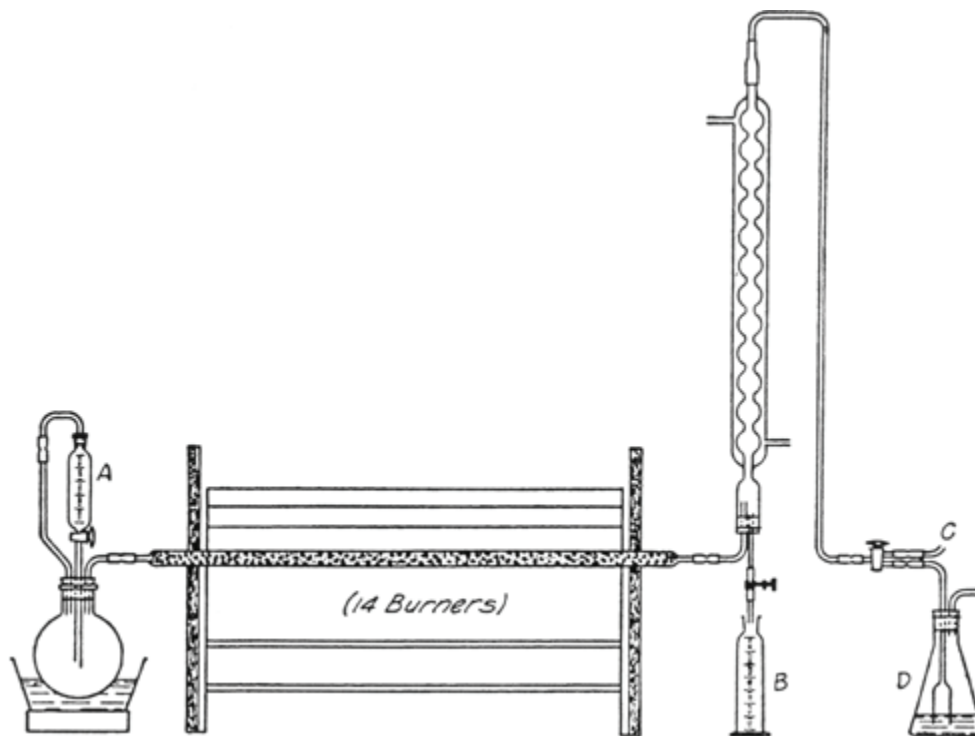


Submitted by C. D. Hurd
Checked by Oliver Kamm

1. Procedure

(A) *Preparation of Ketene.*—The arrangement of the apparatus is shown in Fig. 19 (Note 1). The graduated separatory funnel, shown in the diagram, filled with 100 g. (126 cc., 1.7 moles) of commercial acetone, leads into a 500-cc. round-bottomed flask which, in turn, is connected by gas-tight joints (Note 2) to a glass combustion tube filled with broken porcelain, a spiral or bulb condenser, a three-way stopcock, and a reaction flask. In the reaction flask is placed the material with which the ketene is to react (Note 3). A second reaction flask may be placed in series, if desired, to ascertain if any ketene escaped reaction in the first flask.

Fig. 19.



Prior to either of these steps, fourteen of the twenty burners of the combustion furnace are lighted (Note 4) and tiles are placed over the lighted burners, which finally must be adjusted to yield a maximum temperature. The first two and last four burners are unused.

When the furnace is fully heated, boiling water is placed beneath the round-bottomed flask and cold water passed through the condenser. Acetone is now dropped in at the rate of 3–4 cc. per minute. About one-half the acetone should be recovered as distillate in cylinder B (Note 5). Ketene, admixed with methane, carbon monoxide, and ethylene, passes into the reaction flasks (Note 6) in 25–29 per cent yields of the theoretical amount. The flow may be interrupted at will by checking the acetone flow (Note 7).

(B) *Preparation of Acetanilide*.—Since *ketene* is a highly reactive gas, it is usually prepared for immediate consumption instead of being isolated as such. It reacts with various groups which contain *hydrogen*, such as hydroxyl, amino, mercaptan, hydroxylamino, etc., forming acetyl derivatives.

Twenty-five grams (0.27 mole) of *aniline* is placed in the reaction flask, D, and 50 cc. of dry *ether* added as solvent (Note 8). A second reaction flask is connected at C, in which is placed 5 g. of *aniline*, dissolved in 20 cc. of dry *ether*. This prevents the escape of *ketene* vapor at the beginning and at the close of the operation (Note 5). In all, 85 cc. of *acetone* is passed through the apparatus, 39 cc. of which is recovered as distillate. Therefore, 44 cc. (or 35 g.) of *acetone* is decomposed. The duration of the run is about thirty minutes. Twenty-one grams of *acetanilide*, which corresponds to a yield of 25.8 per cent of the theoretical amount, based upon the amount of *acetone* decomposed, is isolated from the reaction mixture (Note 9).

2. Notes

1. *Apparatus*. A graduated dropping funnel and a graduated cylinder for the distillate are chosen because of convenience in determining the volume of decomposed *acetone*.

The bulb (or spiral) condenser is chosen because of its efficiency. With an ordinary condenser, it is necessary to insert two U-tubes, cooled by ice, between the condenser and the reaction flask, to remove all the *acetone* from the *ketene*. In many reactions, however, this admixed *acetone* will do no harm. This part of the apparatus is designed to eliminate the loss of *ketene* by solvent action, prior to its entry into the reaction flask.

A wide-mouthed delivery tube in the reaction flask is essential to prevent clogging, when a solid product is formed. Automatic stirring in the reaction flask may be used to advantage in certain instances. There is constant agitation, of course, as the gaseous decomposition products bubble through. Either Scotland glass or Pyrex is satisfactory for the combustion tube. An estimate of the temperature is 650° (Note 4). The life of the tube is lengthened if it rests upon a layer of thin asbestos paper. The tube is filled with pieces of broken porcelain, to serve as a "heat reservoir"; there is no catalytic effect. The porcelain blackens during the reaction.

2. *Care in Assembly*.—Since this is a gaseous reaction, it is essential that the apparatus be free from leaks; thus, corks are eliminated wherever possible. The ends of the combustion tube and the top of the condenser are drawn to the diameter of the connecting tubes and joined by a piece of thick-walled rubber tubing. Care should be taken to have the ends of the glass tubes come into contact. The rubber tube situated between the furnace and condenser is protected by the asbestos screen, but a further essential precaution is taken, namely, that this end of the combustion tube extend a considerable distance from the furnace.

The stoppers in the reaction flask and at the top of the dropping funnel are of rubber; the other two are well-selected corks, bored perfectly and painted both inside and out with water-glass, one day previous to being used.

3. The apparatus may be calibrated by allowing the *ketene* to react with 5 *N* alkali and titrating the excess alkali with acid.

4. With an electric combustion furnace, wherein a temperature of 695–705° is maintained, consistent yields of 35–40 per cent *ketene* are produced. The best rate of flow in such a case is 4–6 cc. per minute, with recovery of 60–80 per cent of the original *acetone* as distillate. Although yields of *ketene* ranging above 45 per cent have been obtained frequently with this apparatus, they could not be duplicated consistently.

5. The thermal decomposition of *ketene* into *carbon monoxide* and *ethylene* is prevented, as far as possible, by the rapid removal of *ketene* from the hot tube, which is accomplished by the undecomposed *acetone* vapor. About half the *acetone* originally used should be collected unchanged as distillate by the vertical condenser. The yield of *ketene* will fall considerably if less distillate is formed.

6. *Ketene* gas is very irritant when inhaled, and hence proper cautions should be taken to avoid inhalation.

7. The generator, Fig. 19, is easily assembled from apparatus which can be found in almost every laboratory. Offsetting these advantages is the low yield of *ketene* obtained. If the necessary equipment is available, the generator described by Williams and Hurd¹ is recommended in place of the one shown above. With the Williams and Hurd generator, the yield of *ketene* is 80–90 per cent based on the *acetone* decomposed, and the output is 0.45 mole of *ketene* per hour. The generator may be run

intermittently, or continuously for a period of twenty-four hours, and requires a minimum of attention (Jonathan L. Williams and Charles D. Hurd, private communication checked by N. L. Drake).

8. An ice bath surrounding the reaction flask is usually employed not only to prevent the vaporization of the solvent, but also to promote a greater solubility of *ketene*.

It has been found that the formation of *acetanilide* from *ketene* and *aniline* takes place more satisfactorily if the *ketene* is passed directly into excess *aniline* without any dry ether present. The excess *aniline* may then be removed by distillation under reduced pressure until the temperature of the vapors is 10–15° higher than the boiling point of *aniline*. An alternative plan is to remove excess *aniline* by dilute *hydrochloric acid*, to filter the *acetanilide*, and to wash with water.

9. It is suggested that improved yields of *ketene* may be obtained by directly dropping the *acetone* in at a rate of about 2 cc. per second instead of slowly distilling it into the hot tube (C. D. Hurd, private communication).

3. Discussion

Ketene can be prepared by the pyrogenic decomposition of *acetic anhydride*,² *triacetin*,³ *acetone*,⁴ and other ketones;⁵ and by the action of *zinc* on an ethereal solution of *bromoacetyl bromide*.⁶ The procedure described is based on work of Schmidlin and Bergmann⁴ as modified by Hurd and Cochran.⁴ The preparation of *ketene* from *acetone* has been the subject of numerous articles and patents.⁷ The more recent work usually involves either the use of hot metallic filaments or of metallic oxide catalysts.⁸

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 2*, 102
- *Org. Syn. Coll. Vol. 3*, 508
- *Org. Syn. Coll. Vol. 5*, 679
- *Org. Syn. Coll. Vol. 9*, 28

References and Notes

1. Williams and Hurd, *J. Org. Chem.* **5**, 122 (1940).
2. Wilsmore, *J. Chem. Soc.* **91**, 1938 (1907); Deakin and Wilsmore, *ibid.* **97**, 1968 (1910); Peytral, *Compt. rend.* **193**, 1199 (1931).
3. Ott, *Ber.* **47**, 2393 (1914).
4. Schmidlin and Bergmann, *Ber.* **43**, 2881 (1910); Hurd and Cochran, *J. Am. Chem. Soc.* **45**, 515 (1923); Hurd and Tallyn, *ibid.* **47**, 1427 (1925); Hurd, *ibid.* **45**, 3095 (1923); Biltz, *Z. angew. Chem.* **36**, 232 (1923); Ketoid Co., *Brit. pat.* 237,573 [*C. A.* **20**, 1415 (1926)]; Clarke and Waring, *U. S. pat.* 1,723,724 [*C. A.* **23**, 4485 (1929)]; Goldschmidt and Orthner, *Z. angew. Chem.* **42**, 40 (1929); Mitchell and Reid, *J. Am. Chem. Soc.* **53**, 332 (1931); Rice, Greenberg, Waters, and Vollrath, *ibid.* **56**, 1763 (1934).
5. Hurd and Kocour, *J. Am. Chem. Soc.* **45**, 2167 (1923).
6. Staudinger and Klever, *Ber.* **41**, 594 (1908).
7. The following references are representative, not complete. Ott, Schröter, and Packendorff, *J. prakt. Chem.* **130**, 177 (1931); Röhm and Haas Co., *U. S. pat.* 1,879,497 [*C. A.* **27**, 313 (1933)]; Al, *Angew. Chem.* **45**, 545 (1932); Berl and Kullmann, *Ber.* **65**, 1114 (1932); Berl, *Ger. pat.* 536,423 [*C. A.* **26**, 999 (1932)].
8. Herriott, *J. Gen. Physiol.* **18**, 69 (1934); Morey, *Ind. Eng. Chem.* **31**, 1129 (1939); Williams and Hurd, *J. Org. Chem.* **5**, 122 (1940).

Appendix

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

hydrochloric acid (7647-01-0)

ether (60-29-7)

acetic anhydride (108-24-7)

aniline (62-53-3)

hydrogen (1333-74-0)

Acetanilide (103-84-4)

carbon monoxide (630-08-0)

acetone (67-64-1)

methane (7782-42-5)

zinc (7440-66-6)

ethylene (9002-88-4)

Ketene (463-51-4)

triacetin (102-76-1)

bromoacetyl bromide (598-21-0)