



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](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.

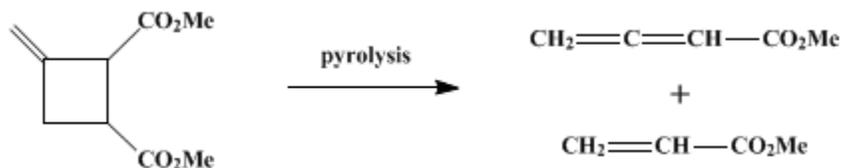
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

*Organic Syntheses, Coll. Vol. 5, p.734 (1973); Vol. 43, p.71 (1963).*

## METHYL BUTADIENOATE

[Butadienoic acid, methyl ester]



Submitted by H. B. Stevenson and W. H. Sharkey<sup>1</sup>.

Checked by R. D. Birkenmeyer, W. E. Russey, and F. Kagan<sup>2</sup>.

### 1. Procedure

A "Vycor" tube 550 mm. long and 25 mm. in outside diameter is packed for 500 mm. of its length with 6-mm. × 6-mm. quartz rings and mounted vertically so that the upper section is encased in a tube furnace 150 mm. long and the lower section is encased in a tube furnace 300 mm. long. The upper furnace, which serves as a preheater, is monitored by a thermocouple placed between the tube and the furnace heating elements. The temperature of the lower furnace is monitored by a thermocouple located in the center of the lower packed section. The upper end of the pyrolysis tube is fitted with a Y-tube carrying the thermocouple well and a graduated addition funnel with a pressure-equalizing arm. The lower end is attached through one 500-ml. trap and two 200-ml. traps, each immersed in a mixture of solid carbon dioxide and acetone, to a regulated vacuum source. One gram of hydroquinone is placed in the first trap.

The pyrolysis tube is flushed with nitrogen, the lower section is heated to 600° and the upper section to 300° (Note 1), and the pressure is regulated at 25 mm. Then 184 g. (1.00 mole) (Note 2) of dimethyl 3-methylenecyclobutane-1,2-dicarboxylate<sup>3</sup> is admitted over a period of 3 hours (Note 3). The product, which amounts to 172–177 g., collects in the traps. It is distilled through a 13-mm. × 1.2-m. Nester spinning-band still.<sup>4</sup> First there is 41–47 g. (48–55%) of methyl acrylate,  $n_D^{25}$  1.4010, b.p. 34–36°/150 mm., then 39–43 g. (40–44%) of methyl butadienoate,  $n_D^{25}$  1.4635 (Note 4), b.p. 59–60°/52 mm. or 48–49°/26 mm. By continuing the distillation, 20–30 g. of starting material, b.p. 125–150°/25 mm., can be recovered.

### 2. Notes

1. The temperature of the lower section is quite critical and should be maintained within the range 590–610°. However, the preheater section is needed only to volatilize the ester, so any temperature between 200° and 400° is satisfactory.
2. Since an estimated 3–5 g. of carbon is deposited in the tube during the pyrolysis, it is advisable to pyrolyze only 1 mole of ester at a time and to burn out the carbon with a slow stream of air at 600° between pyrolyses.
3. The space velocity is approximately 125 l. of standard gas per l. of free space per hour, and the contact time is approximately 0.3 second.
4. The checkers used a 10-mm. × 0.76-m. Nester spinning band still and obtained material having  $n_D^{25}$  1.4620 that could not be purified by redistillation. Analysis by vapor-phase chromatography (silicone gum rubber, 20% w/w on firebrick, 120-cm. × 6-mm. outside diameter column at 125°) showed this material to be 95% methyl butadienoate contaminated by small amounts of two other materials.

### 3. Discussion

The method used is described by Drysdale, Stevenson, and Sharkey.<sup>5</sup> The methyl ester of butadienoic acid has not been described previously, but the free acid contaminated by 2-butynoic acid has been prepared by Wotiz, Matthews, and Lieb<sup>6</sup> by carbonation of propargylmagnesium bromide.

Ethyl butadienoate has been prepared by Eglinton, Jones, Mansfield, and Whiting<sup>7</sup> by alkali-catalyzed isomerization of ethyl 3-butynoate prepared from 3-butynol by chromic acid oxidation and esterification.

#### 4. Merits of the Preparation

This procedure gives a product free of acetylenic groups. It illustrates the synthesis of an olefinic compound by cracking a cyclobutane into two fragments.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 459
- Org. Syn. Coll. Vol. 9, 28

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#### References and Notes

1. Contribution No. 568 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Delaware.
2. Upjohn Co., Kalamazoo, Michigan.
3. H. B. Stevenson, H. N. Cripps and J. K. Williams, *this volume*, p. 459.
4. R. G. Nester, *Anal. Chem.*, **28**, 278 (1956).
5. J. J. Drysdale, H. B. Stevenson, and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 4908 (1959).
6. J. H. Wotiz, J. S. Matthews, and J. A. Lieb, *J. Am. Chem. Soc.*, **73**, 5503 (1951).
7. G. Eglinton, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 3197 (1954).

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

hydroquinone (123-31-9)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

acetone (67-64-1)

carbon (7782-42-5)

chromic acid (7738-94-5)

methyl (2229-07-4)

methyl acrylate (96-33-3)

cyclobutane (287-23-0)

Dimethyl 3-methylenecyclobutane-1,2-dicarboxylate (53684-52-9)

Methyl butadienoate,

Butadienoic acid, methyl ester (18913-35-4)

butadienoic acid

2-butynoic acid (590-93-2)

propargylmagnesium bromide

Ethyl butadienoate

ethyl 3-butynoate

3-butynol (927-74-2)