



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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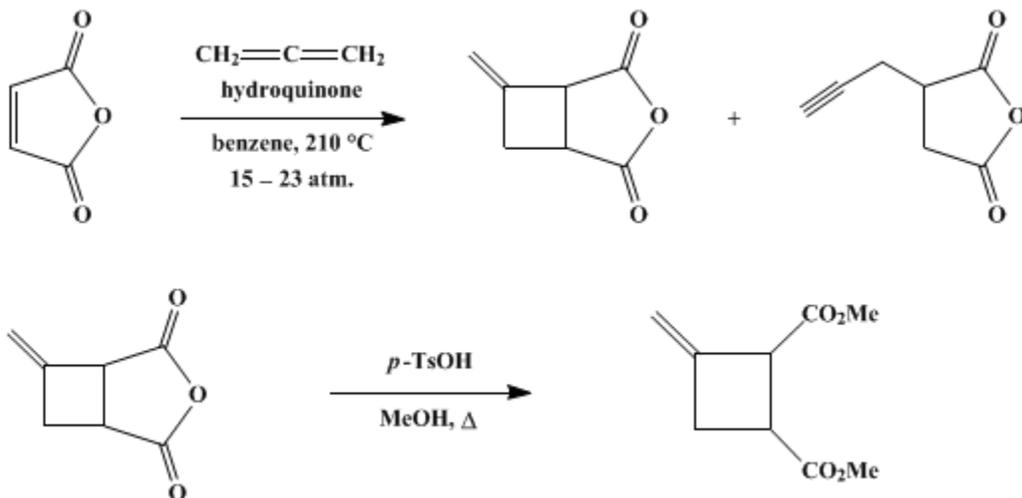
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.459 (1973); Vol. 43, p.27 (1963).*

## DIMETHYL 3-METHYLENECYCLOBUTANE-1,2-DICARBOXYLATE

### [3-Methylenecyclobutane-1,2-dicarboxylic acid, dimethyl ester]



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### 1. Procedure

A. *3-Methylenecyclobutane-1,2-dicarboxylic anhydride*. A 2-l. stainless steel autoclave equipped with stirrer, pressure gauge, and thermocouple is charged with 500 g. (5.1 moles) of *maleic anhydride*, 645 ml. of *benzene*, and 0.25 g. of *hydroquinone*. The autoclave is closed, cooled to  $-70^{\circ}$  with stirring, and evacuated to a pressure of about 20 mm. *Allene*<sup>3</sup> (100 g., 2.5 moles) (*Note 1*) is sucked into the autoclave, and the mixture is heated with stirring for 8–10 hours at  $200\text{--}210^{\circ}$ . During this time, the pressure drops from 23 atm. to 15 atm. The vessel is cooled to  $25^{\circ}$ , and unreacted *allene* (6–13 g.) is vented into a cold trap (*Note 2*). The *benzene* solution is decanted, and about 500 ml. of *acetone* is added to the autoclave and stirred until the dark viscous residue goes into solution. The *benzene* and *acetone* solutions are combined, filtered, and distilled through a 19-mm.  $\times$  1.8-m. Nester spinning-band still.<sup>4</sup> When the pot temperature reaches  $170^{\circ}$ , the pressure is reduced to 40 mm., and up to 250 g. of *maleic anhydride*, b.p.  $110\text{--}115^{\circ}/40$  mm., is recovered. Finally 119 g. of crude anhydride mixture, b.p.  $70\text{--}125^{\circ}/3$  mm. (*Note 3*), is collected.

The crude anhydride is carefully fractionated through a 13-mm.  $\times$  1.2-m. Nester still at a pressure of 25 mm. (*Note 4*) and a reflux ratio of at least 10:1. After a fore-run of *maleic anhydride*, b.p.  $50\text{--}100^{\circ}/25$  mm., and a small intermediate fraction, there is obtained 75–90 g. (22–26%) of *3-methylenecyclobutane-1,2-dicarboxylic anhydride*; b.p.  $155\text{--}159^{\circ}/25$  mm.;  $n_D^{25}$  1.4935–1.4952 (*Note 5*). This material is of sufficient purity for most uses, but it contains approximately 2–5% of *propargylsuccinic anhydride*. Redistillation through the Nester still gives 65–80 g. (19–23%) of *3-methylenecyclobutane-1,2-dicarboxylic anhydride*; b.p.  $155^{\circ}/25$  mm.;  $n_D^{25}$  1.4946–1.4955.

By continuing the distillation after removal of the cyclobutane anhydride, there is obtained 25–30 g. (7–9%) of *propargylsuccinic anhydride*; b.p.  $162\text{--}168^{\circ}/25$  mm.; m.p.  $63\text{--}68^{\circ}$ . The melting point is raised to  $69\text{--}70^{\circ}$  by one recrystallization from 100 ml. of *benzene* (80% recovery of purified product).

B. *Dimethyl 3-methylenecyclobutane-1,2-dicarboxylate*. One liter of *methanol* is added cautiously with occasional shaking to 276 g. (2.00 moles) of *3-methylenecyclobutane-1,2-dicarboxylic anhydride* ( $n_D^{25}$  1.4946–1.4955; (*Note 6*)) and 5 g. of *p-toluenesulfonic acid* in a 2-l. three-necked flask fitted with

a thermometer, a condenser, and a dropping funnel. Refluxing starts after about two-thirds of the [methanol](#) has been added. The remainder is added at a rate that maintains vigorous boiling. The solution is refluxed for 30–40 hours with the pot temperature increasing from 67° to 68° ([Note 7](#)). The mixture is cooled to 15°, and [methanol](#) and water are removed by distillation under reduced pressure at temperatures below 15°, using a large receiver cooled with a mixture of solid [carbon dioxide](#) and [acetone](#). When the pressure goes below 1 mm., the temperature is increased to 50° until the distillation is completed. One liter of [methanol](#) ([Note 8](#)) is added to the residue, and the solution is heated under reflux for an additional 30–40 hours, during which time the pot temperature increases from 67° to 67.5°. The solution is cooled to 15°, 1.7 g. of finely powdered anhydrous [sodium carbonate](#) is added to neutralize the [p-toluenesulfonic acid](#), and the [methanol](#) and water are removed as before. Crude [dimethyl 3-methylenecyclobutane-1,2-dicarboxylate](#) is distilled rapidly at 65–85°/1 mm. through a 30-cm. Vigreux column ([Note 9](#)). The ester can be purified by redistillation through a 13-mm. × 1.2-m. Nester still, with the main fraction boiling at 134–137°/25 mm.; weight 297–338 g. (81–92%);  $n_D^{25}$  1.4624–1.4630.

## 2. Notes

1. Freshly distilled [allene](#) should be used. It should be free of [2-chloropropene](#), usually present in [allene](#) prepared by zinc dehalogenation of [2,3-dichloropropene](#),<sup>3</sup> to avoid formation of chlorine-containing products that liberate [hydrogen chloride](#) on distillation.
2. The impurities present in the original [allene](#) are concentrated in the recovered material. If recovered [allene](#) is to be reused, it should be fractionated first.
3. The checkers isolated 167 g. of crude anhydride mixture boiling at 70–125°/3 mm. The large tarry residue contains [allene](#) polymers and small amounts of [1,2,3,4,5,6,7,8-octahydronaphthalene-2,3,6,7-tetracarboxylic dianhydride](#), which can be recovered by diluting the residue with [benzene](#) and filtering.
4. Pot temperatures above 175°, which result from use of pressures above 25 mm., cause formation of high-boiling by-products.
5. Collection of the product fraction should begin after a few milliliters of an intermediate fraction has been collected at 155°/25 mm. This material has a low index of refraction.
6. The checkers found that the use of anhydride with  $n_D^{25}$  1.4937–1.4945 led to a product with a low index of refraction ( $n_D^{25}$  1.4616).
7. The temperature rises because of disappearance of [methanol](#) by conversion to the methyl ester. Attainment of equilibrium is signified by the pot temperature reaching a constant temperature.
8. The second treatment with [methanol](#) increases the yield from 60% to 90%.
9. Rapid distillation from the neutralized catalyst results in much smaller loss of ester than is encountered in the more usual procedure that includes washing with water and drying.

## 3. Discussion

The procedure used is essentially that described by Cripps, Williams, and Sharkey.<sup>5</sup> The anhydride has been prepared in a similar manner by Alder and Ackermann.<sup>6</sup> No other methods have been described for the preparation of these materials.

## 4. Merits of the Preparation

The first step of this procedure illustrates a general reaction, the addition of allenes to alkenes to form methylenecyclobutanes. The reaction has been reviewed recently.<sup>7</sup>

Since [3-methylenecyclobutane-1,2-dicarboxylic anhydride](#) is easily converted to [3-methyl-2-cyclobutene-1,2-dicarboxylic acid](#),<sup>8</sup> it is an intermediate to a variety of cyclobutenes. The [dimethyl ester of 3-methylenecyclobutane-1,2-dicarboxylic acid](#) is also a versatile compound; on pyrolysis it gives the substituted allene, [methyl butadienoate](#),<sup>9</sup> and on treatment with amines it gives a cyclobutene, [dimethyl 3-methyl-2-cyclobutene-1,2-dicarboxylate](#).<sup>8</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 734](#)

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## References and Notes

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  3. H. N. Cripps and E. F. Kiefer, *this volume*, p. 22.
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  6. K. Alder and O. Ackermann, *Ber.*, **90**, 1697 (1957).
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## Appendix

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

cyclobutene, dimethyl 3-methyl-2-cyclobutene-1,2-dicarboxylate

hydrogen chloride (7647-01-0)

Benzene (71-43-2)

methanol (67-56-1)

hydroquinone (123-31-9)

sodium carbonate (497-19-8)

carbon dioxide (124-38-9)

acetone (67-64-1)

2,3-dichloropropene (78-88-6)

Allene (463-49-0)

maleic anhydride (108-31-6)

2-chloropropene (557-98-2)

Dimethyl 3-methylenecyclobutane-1,2-dicarboxylate,  
3-Methylenecyclobutane-1,2-dicarboxylic acid, dimethyl ester,  
dimethyl ester of 3-methylenecyclobutane-1,2-dicarboxylic acid (53684-52-9)

3-Methylenecyclobutane-1,2-dicarboxylic anhydride

propargylsuccinic anhydride

1,2,3,4,5,6,7,8-octahydronaphthalene-2,3,6,7-tetracarboxylic dianhydride

3-methyl-2-cyclobutene-1,2-dicarboxylic acid

Methyl butadienoate (18913-35-4)

p-toluenesulfonic acid (104-15-4)