



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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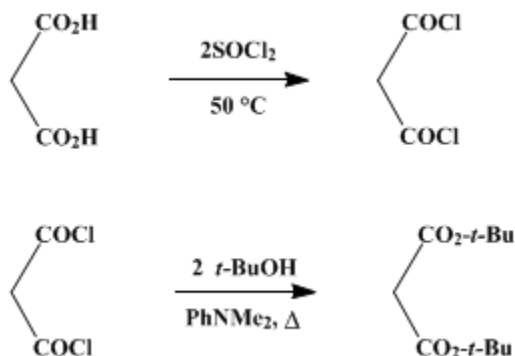
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

## DI-*tert*-BUTYL MALONATE

[Malonic acid, di-*t*-butyl ester]



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Checked by William S. Johnson and Rudolph W. Kluiber.

### 1. Procedure

#### 2.

A. *Malonyl dichloride*. In a 250-ml. Erlenmeyer flask (Note 1) fitted by a ground-glass joint to a reflux condenser capped with a calcium chloride drying tube are placed 52 g. (0.5 mole) of finely powered, dry *malonic acid* (Note 2) and 120 ml. (about 1.65 mole) of *thionyl chloride* (Note 3). The flask is warmed for 3 days in a heating bath kept at  $45\text{--}50^\circ$  (Note 4). During this period the mixture, which is agitated occasionally by gentle swirling, gradually darkens to a deep brownish red or sometimes a blue color. Finally the mixture is heated at  $60^\circ$  for 5–6 hours. After cooling, it is transferred to a 125-ml. modified Claisen flask and distilled at reduced pressure (water aspirator). A calcium chloride guard tube is inserted between the vacuum line and the apparatus, and the flask is heated with a bath rather than a free flame. After a small fore-run of *thionyl chloride*, the malonyl chloride distils at  $58\text{--}60^\circ/28\text{ mm}$ . The pale yellow product amounts to 50.5–60 g. (72–85% yield),  $n_D^{29}$  1.4572.

B. *Di-tert-butyl malonate*. A 1-l. three-necked flask is fitted with a thermometer, a mercury- or rubber sleeve-sealed mechanical stirrer, a reflux condenser protected by a calcium chloride guard tube, and a dropping funnel (either pressure-equalized or protected by a calcium chloride guard tube). A mixture of 100 ml. (about 1 mole) of *tert*-butyl alcohol, dried by distillation from *sodium* and 80 ml. (0.63 mole) of dry *dimethylaniline* (Note 5) is placed in the flask, the stirrer is started, and a solution of 28.0 g. (0.2 mole) of *malonyl dichloride* in about 60 ml. of dry, alcohol-free *chloroform* (Note 6) is added slowly from the dropping funnel while the reaction flask is cooled in an ice bath. The reaction is strongly exothermic, and the rate of dropping is regulated so that the temperature of the mixture does not exceed  $30^\circ$ . After the addition is complete (about 30 minutes) the light-greenish mixture is heated under reflux for 4 hours. The mixture is then cooled, 150 ml. of ice-cold 6*N* *sulfuric acid* is added with stirring, and the product is extracted with three 250-ml. portions of *ether* (Note 7). The combined *ether* extracts are washed once with 6*N* *sulfuric acid*, twice with water, twice with 10% *potassium carbonate*, and once with saturated *sodium chloride*, and are finally dried over anhydrous *sodium sulfate* to which a small amount of *potassium carbonate* is added. The *ether* is removed by distillation at reduced pressure (water aspirator), and the residue (to which a pinch of *magnesium oxide*

is added) is distilled at reduced pressure from a modified Claisen flask ([Note 8](#)). The yield of colorless [di-tert-butyl malonate](#), distilling at 65–67°/1 mm., 110–111°/22 mm., is 35.8–36.2 g. (83–84%),  $n_D^{25}$  1.4159, m.p. about –6°.

## 2. Notes

1. Better results are obtained by using a flat-bottomed flask, which permits the insoluble [malonic acid](#) to be distributed over a greater surface.
2. The reaction mixture is heterogeneous at first, and if the acid is not finely powdered, some of it remains unreacted. Attempts to carry out the reaction on a larger scale resulted in some charring and lower yields.
3. Eastman Kodak Company white label quality [thionyl chloride](#) is satisfactory.
4. The temperature range is critical, and yields are lower if it is not controlled carefully. The use of [pyridine](#) as a catalyst is not recommended as it produces charring even after relatively short reaction periods.
5. J. T. Baker [dimethylaniline](#) (purified grade) is satisfactory without distillation.
6. The [chloroform](#) was dried over and distilled from anhydrous [calcium chloride](#) just before use.
7. The [dimethylaniline](#) may be recovered from the aqueous layer where it is dissolved as the salt.
8. [Di-tert-butyl malonate](#), like most *tert*-butyl esters, decomposes readily on heating in the presence of traces of acids. It is therefore desirable to give all glassware to be used for distillation of the material an alkali rinse before use. The addition of a small amount of [magnesium oxide](#) also helps to inhibit the decomposition during distillation.<sup>2</sup> When decomposition starts, foaming is generally observed. In this event the addition of glass wool to the distillation flask helps to keep the product from foaming over.

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## 3. Discussion

Procedure I is a modification<sup>2</sup> of the method of Altschul<sup>3</sup> for preparing *tert*-butyl esters. [Di-\*tert\*-butyl malonate](#) also has been prepared by the reaction of [malonyl dichloride](#) and [tert-butyl alcohol](#) in the presence of a base,<sup>4,5</sup> and by the reaction of carbon suboxide with [tert-butyl alcohol](#).<sup>6</sup> Procedure II is based on the former<sup>4</sup> method and developed from studies initiated by P. C. Mukharji of the University College of Science and Technology, Calcutta.

[Malonyl dichloride](#) has been prepared from [malonic acid](#) and [thionyl chloride](#),<sup>4,7,8,9,10,11</sup> and from carbon suboxide and anhydrous [hydrogen chloride](#).<sup>12</sup> The present procedure is adapted from that of Staudinger and Bereza<sup>9</sup> and of Backer and Homan.<sup>4</sup>

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### References and Notes

1. Rose Research Institute, Calcutta, India.
  2. Fonken and Johnson, *J. Am. Chem. Soc.*, **74**, 831 (1952).
  3. Altschul, *J. Am. Chem. Soc.*, **68**, 2605 (1946).
  4. Backer and Homan, *Rec. trav. chim.*, **58**, 1048 (1939).
  5. Backer and Lolkema, *Rec. trav. chim.*, **57**, 1234 (1938).
  6. Hagelloch and Feess, *Chem. Ber.*, **84**, 730 (1951).
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  8. Asher, *Ber.*, **30**, 1023 (1897).
  9. Staudinger and Bereza, *Ber.*, **41**, 4463 (1908).
  10. von Auwers and Schmidt, *Ber.*, **46**, 477 (1913).
  11. McMaster and Ahmann, *J. Am. Chem. Soc.*, **50**, 145 (1928).
  12. Diels and Wolf, *Ber.*, **39**, 696 (1906).
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### Appendix

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

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

thionyl chloride (7719-09-7)

sodium sulfate (7757-82-6)

dimethylaniline (121-69-7)

Malonyl dichloride (1663-67-8)

Malonic acid (141-82-2)

*tert*-butyl alcohol (75-65-0)

Di-*tert*-butyl malonate,

Malonic acid, di-*t*-butyl ester (541-16-2)