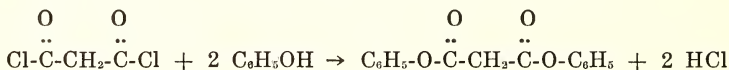


## The Preparation of Aromatic Esters of Malonic Acid<sup>1</sup>

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The preparations of four aromatic esters of malonic acid have been described in the literature. These are the diphenyl-, di- $\beta$ -naphthyl-, di-*p*-tolyl-, and di-*p*-nitrophenyl malonates.

The preparation of diphenyl malonate by Bischoff and von Hedenström (5) in 1902 illustrates one of the synthetic methods employed. Phenol and malonyl chloride were warmed on a water bath for a short time; hydrogen chloride was evolved and the solid ester crystallized on cooling.



These workers tried without success to prepare this ester from malonic acid, phenol, and thionyl chloride. However, Auger and Billy (1) were able to synthesize diphenyl malonate from malonic acid, phenol, and phosphorus oxychloride.

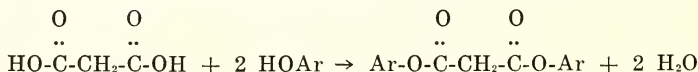
Guia (6) obtained di- $\beta$ -naphthyl malonate rather than the desired coumarin-type compound when he heated  $\beta$ -naphthol, malonyl chloride, and aluminum chloride in carbon disulfide. Backer and Lolkema (2) synthesized di-*p*-tolyl malonate and di-*p*-nitrophenyl malonate from malonyl chloride according to the above equation. The latter ester was also prepared by these investigators by treatment of the diphenyl malonate with nitric acid at 0°.

Since carbon suboxide has been reported (7) to react with alcohols to yield dialkyl malonates, it seemed of interest to attempt to extend the reaction to phenols.



Five phenols were successfully esterified with carbon suboxide, with sulfuric acid or *p*-toluenesulfonic acid present at catalyst. Salicylic acid did not esterify and was quantitatively recovered.

As a check on their structure it seemed desirable and of interest to prepare some of these diaryl malonates directly from malonic acid.



Sulfuric acid or *p*-toluenesulfonic acid was used as a catalyst. The reaction was carried out in refluxing toluene so as to remove the water as it formed. By this second method, four aromatic esters of malonic

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acid were prepared. These esters were identical with esters prepared from carbon suboxide (Table I).

TABLE I. Diaryl Malonates

Phenol	Method	Catalyst	Ester m.p., °C	Yield %
Phenol	I	H <sub>2</sub> SO <sub>4</sub>	49-50	90.0
o-Cyclohexylphenol	I	pTSA <sup>b</sup>	134-135	37.6
	II	H <sub>2</sub> SO <sub>4</sub>	134-135	5.1
β-Naphthol	I	H <sub>2</sub> SO <sub>4</sub>	142-142.5	94.0
	II	H <sub>2</sub> SO <sub>4</sub>	144-145 <sup>c</sup>	3.4
p-Nitrophenol	II	H <sub>2</sub> SO <sub>4</sub>	198.5-200 <sup>d</sup> dec	1.2
	I	H <sub>2</sub> SO <sub>4</sub>		87.6
p-Phenylpherol	I	pTSA	199-200 <sup>e</sup>	5.5
	II	pTSA	199-200	21.5
	II	H <sub>2</sub> SO <sub>4</sub>	199-200	8.8

<sup>b</sup>pTSA—p-Toluenesulfonic acid. Analysis of ester Calcd. for C<sub>27</sub>H<sub>32</sub>O<sub>4</sub>: C, 77.11; H, 7.67. Found: C, 77.09; H, 7.10.

<sup>c</sup>Giua (6) found 146-147°.

<sup>d</sup>Backer and Lolkema (2) 202-203° dec.

<sup>e</sup>Analysis of ester Calcd. for C<sub>27</sub>H<sub>26</sub>O<sub>4</sub>: C, 79.40; H, 4.94. Found: C, 79.44; H, 5.16.

### Experimental

*Carbon Suboxide.* This reagent was prepared by the pyrolysis of diacetyltartaric anhydride similar to the procedure reported in a previous publication (3). However, the apparatus was improved by the inclusion of an electrical condenser-precipitator as described by the authors (4). The carbon suboxide produced was carefully distilled and collected in anhydrous ether in a flask surrounded by dry-ice and acetone. The concentration, as shown by the weight of malonanilide precipitated from an aliquot portion of the solution, corresponded to one gram of carbon suboxide per 4.3 ml. of solution. From 635 grams of diacetyltartaric anhydride, 69 grams (34%) of carbon suboxide were obtained.

*Diaryl Malonates (Method I).* Each phenol (0.044 mole) was dissolved in as little anhydrous ether as was needed for solution, and either four drops of concentrated sulfuric acid or a pea-size crystal of p-toluenesulfonic acid was added to this solution in a pressure bottle. After the sealed bottle had been cooled in the refrigerator, 1.5 grams (0.022 mole) of carbon suboxide in 6.5 ml. of the ether solution was added from a buret. The buret was kept cold by a jacket containing an ice-salt mixture, and the ether solution was added to the buret by means of a siphon. The sealed pressure bottle was kept in the refrigerator for three days and then permitted to warm to room temperature.

No odor of carbon suboxide was observed when the bottle was opened. The ether was allowed to evaporate, and the residue was dissolved in hot 95% ethanol. A few drops of water were added and the solution cooled. The solid which separated was recrystallized from toluene or a second time from aqueous ethyl alcohol.

*Diaryl Malonates (Method II).* The apparatus consisted of a 500-ml. round-bottom flash, surmounted by a Dean-Stark tube and a water-cooled reflux condenser. All connections were by means of ground glass joints. A plug of absorbent cotton was placed in the open end of the condenser tube to exclude atmospheric moisture. The flask was heated over a hot-plate.

In the flask were placed 10.4 grams (0.1 mole) of malonic acid, the required weight (0.22 mole) of the phenol, and 300 ml. of anhydrous toluene. The mixture was refluxed briefly to dissolve the solids, and then the catalyst (four drops of concentrated sulfuric acid or a small crystal of p-toluenesulfonic acid) was added. Refluxing was continued (several days) until the water level in the Dean-Stark tube no longer rose. The solution was then concentrated to about 75 ml. and cooled. The solid product which separated was washed with ether and recrystallized from toluene, adding a small volume of petroleum ether after the material had dissolved. Two or three such recrystallizations were required. The di-p-nitrophenyl malonate was recrystallized from glacial acetic acid.

### Summary

Two new methods have been developed for the synthesis of aryl esters of malonic acid. One method employs carbon suboxide and a phenol; the other malonic acid and a phenol. The carbon suboxide method produces the esters in high yields.

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