

(dec.),<sup>1</sup> 149–151° (dec.),<sup>2</sup> 150–151° (dec.),<sup>3</sup> 139–141° (dec.),<sup>4</sup> and 220° (dec.).<sup>5,6</sup> have been reported. The capillary melting point is influenced by the rate of heating<sup>7</sup> and the temperature of the bath. To avoid these effects the melting point apparatus of Dennis and Shelton<sup>8</sup> was used in this work. With this apparatus, the melting point is the lowest temperature of instantaneous melting. The grand average of five melting point values on each of five samples was 240°, with a standard error of approximately  $\pm 1^\circ$ . (Capillary melting points of about 147° (dec.) were obtained by immersion in a bath at 145° with a rate of heating of 3° per minute.) The poor precision is caused by inadequate contact with the surface of the bar and by convection currents which disperse fine particles into the air. With samples of optimum particle size range, the lowest temperature of instantaneous melting obtained by testing at progressively increasing temperatures was the same as the lowest temperature of instantaneous melting obtained by testing at progressively decreasing temperatures.

These conclusions may be reached: (1) The most nearly correct melting point is about 240°. (2) The melting point is not a good criterion of purity. (3) The melting point reported by Seidel and Bittner of 220° (dec.) was probably obtained with aminosalicic acid, rather than with the hydrochloride, as some have assumed,<sup>9</sup> and must have been taken by some technique involving the observation of instantaneous melting.

- (1) Kolbe, U. S. Patent 427,564; German Patent 50,835.
- (2) Erlemeyer, *et al.*, *Helv. Chim. Acta*, **31**, 988 (1948).
- (3) O'Connor, *Lancet*, **254**, 191 (1948).
- (4) Whittet, *ibid.*, **254**, 268 (1948).
- (5) Seidel, *Ber.*, **34**, 4351 (1901).
- (6) Seidel and Bittner, *Monatsh.*, **23**, 415 (1902).
- (7) McAnnally and Seymour, *Lancet*, **254**, 303 (1948).
- (8) Dennis and Shelton, *THIS JOURNAL*, **52**, 3128 (1930).
- (9) Sheehan, *ibid.*, **70**, 1665 (1948).

CALCO CHEMICAL DIVISION  
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## A New Synthesis of Diethyl 1,1-Cyclobutanedicarboxylate

By HARRY M. WALBORSKY<sup>1</sup>

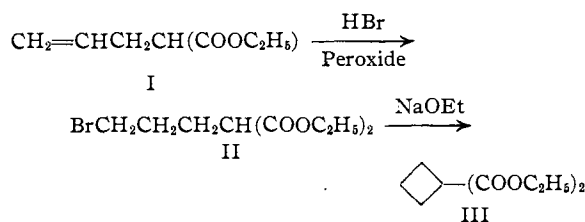
The standard method for preparation of diethyl 1,1-cyclobutanedicarboxylate (III), the reaction between trimethylene bromide and diethyl malonate, gives a yield of approximately 25%.<sup>2</sup> The major product is tetraethyl 1,1,5,5-pentanetetra-carboxylate formed by further reaction of the intermediate II with diethyl malonate. To eliminate this side reaction, II was independently prepared by the addition of hydrogen bromide to diethyl allylmalonate (I)<sup>3</sup> and then cyclized to

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(2) Heisig and Stodola, "Organic Syntheses," **23**, 16 (1943).

(3) Linstead and Rydon, *J. Chem. Soc.*, 582 (1933), report the preparation of I in 80% yield from allyl bromide and diethyl malonate.

III by treatment with sodium ethylate. The over-all yield from I is about 50%.



### Experimental

**Diethyl  $\gamma$ -Bromopropylmalonate (II).**—A solution of 67 g. of I in an equal volume of toluene containing a small amount of dibenzoyl peroxide was saturated at 0° with gaseous hydrogen bromide. After removal of excess hydrogen bromide and toluene, the residue was distilled *in vacuo*. A fraction, 75 g. (79%), boiling over a 6° range was collected, b. p. ca. 140° at 5 mm.,  $n_{25}^{25}D$  1.455. A portion of this material was allowed to stand for twelve hours with an excess of trimethylamine in benzene and the resulting quaternary salt was converted<sup>4</sup> to the picrate, m. p. 102.5–103.5° from ethanol.

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{28}\text{N}_4\text{O}_{11}$ : C, 46.7; H, 5.8. Found: C, 47.0; H, 5.9.

An authentic sample<sup>5</sup> of II, b. p. 139–141° at 5 mm.,  $n_{25}^{25}D$  1.455, gave the same quaternary picrate, m. p. and mixed m. p. 102.5–103.5°.

**Diethyl 1,1-Cyclobutanedicarboxylate (III).**—To the refluxing solution of 5.8 g. of sodium dissolved in 600 ml. of absolute ethanol was added slowly with stirring 72 g. of II. After refluxing for two and one-half hours the solvent was removed *in vacuo* and the residue was treated with water; the product was taken up in ether and distilled at 23 mm., b. p. 119–126°,  $n_{25}^{25}D$  1.433,<sup>6</sup> yield 38 g. (74%).

This work was performed under a contract between the Office of Naval Research and the California Institute of Technology.

(4) Cf. Howton, *THIS JOURNAL*, **69**, 2555 (1947), footnote 5.

(5) Willstätter and Etilinger, *Ann.*, **326**, 99 (1903).

(6) This is the value given in the literature for III, Gladstone cited by Perkin, *J. Chem. Soc.*, **51**, 4 (1887).

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## The Synthesis of Some 4-Alkoxy-7-chloroquinaldic Acid Derivatives

By ALEXANDER R. SURREY

Although the 2-alkoxycinchoninic acid derivatives<sup>1</sup> are known to possess strong local anesthetic activity, the corresponding quinoline derivatives in which substituents in the 2- and 4-positions are interchanged have not been reported in the literature. Inasmuch as a suitable starting material, ethyl 7-chloro-4-hydroxyquinaldate, was available in this Laboratory, it seemed desirable to prepare the 4-alkoxy derivatives in order to compare their physiological activity with the corresponding 2-alkoxy compounds.

Accordingly, 7-chloro-4-hydroxyquinaldic acid and its ethyl ester were treated with phosphorous oxychloride to give the corresponding 4-chloro compounds, I and II (Table I), respectively.

(1) Miescher, *Helv. Chim. Acta*, **15**, 163 (1932).