



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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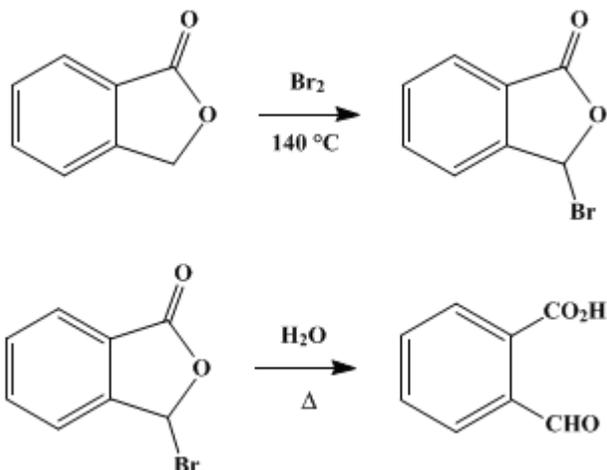
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.737 (1955); Vol. 23, p.74 (1943).

PHTHALALDEHYDIC ACID



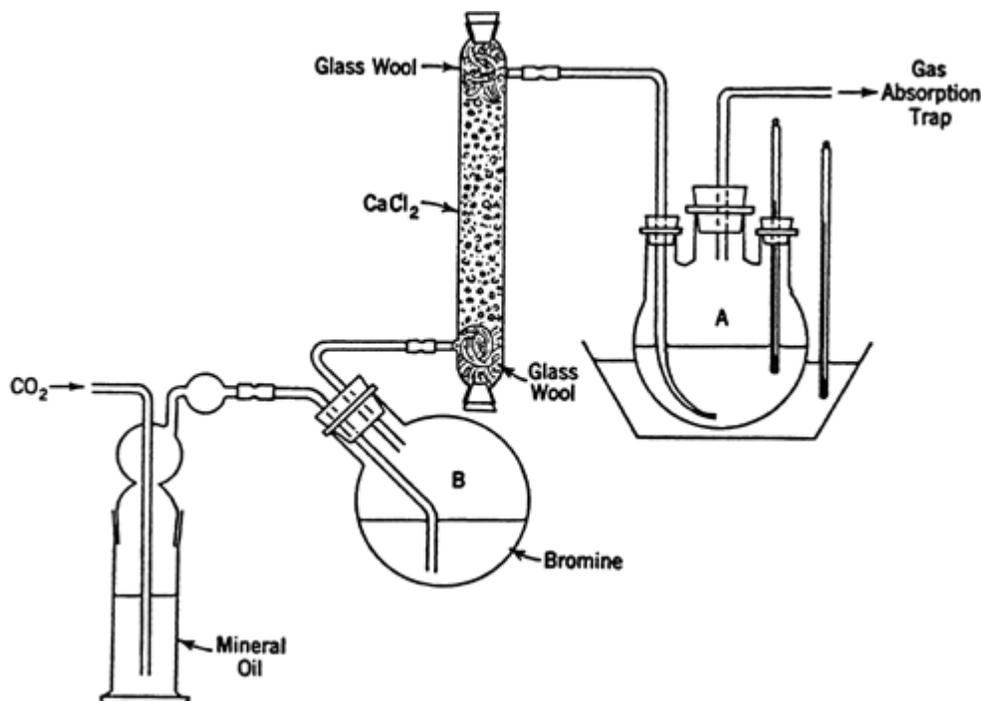
Submitted by R. L. Shriner and F. J. Wolf.

Checked by Lee Irvin Smith, R. T. Arnold, and Walter Frajola.

1. Procedure

A. *2-Bromophthalide*. The apparatus shown in Fig. 26 is used for the bromination. Flasks *A* and *B* are of 200-ml. capacity. Bromine is introduced by means of a current of carbon dioxide, which passes through mineral oil or sulfuric acid in the bubble counter, then through the bromine in flask *B*, and finally through the drying tower. The tower is conveniently made from a condenser jacket and is filled with anhydrous calcium chloride. Flask *A* is surrounded by an oil bath and is equipped with a thermometer, an outlet tube of wide bore connected to a gas-absorption trap, and a gas-inlet tube having an inside diameter of 2 mm. The inlet tube reaches to the bottom of the flask.

Fig. 26.



In the reaction flask *A* is placed 134 g. (1 mole) of [phthalide](#) (Note 1). In flask *B* is placed 160 g. (53.5 ml., 1 mole) of [bromine](#). The oil bath is maintained at 140–155°, and the stream of [carbon dioxide](#) is started when the temperature of the [phthalide](#) has reached 140°. The temperature inside flask *A* is maintained at 135–150° (oil bath 140–155°) during the course of the reaction (Note 2). [Carbon dioxide](#) is introduced at such a rate that no [bromine](#) vapor is observed in the outlet tube (5–8 bubbles per second). The stream of [carbon dioxide](#) is continued for 30 minutes after all the [bromine](#) color has disappeared from the train. The reaction is complete in 10–13 hours, depending upon the rate at which the [bromine](#) has been introduced into the reaction mixture.

While still warm, the reaction mixture is transferred to a 250-ml. modified Claisen flask fitted for distillation under reduced pressure. Any [hydrogen bromide](#) remaining in the reaction mixture is removed by heating at 120° under the vacuum of a water pump. The product is then distilled under reduced pressure. The fore-run of less than 15 g. is largely [phthalide](#) (Note 3). The [2-bromophthalide](#), which distils at 138–142°/4 mm. (128–132°/2 mm.), weighs 175–178 g. (82–83% based on the [phthalide](#)) (Note 4). It is water-clear and solidifies to a solid which melts at 69–73°.

The distilled product is pure enough for use in the subsequent hydrolysis, but it may be purified by recrystallization from 100 ml. of [carbon tetrachloride](#). Upon cooling, 100 g. of pure [2-bromophthalide](#) melting at 75° is obtained. An additional 30–40 g. of slightly yellow material is obtained by concentrating the mother liquor.

B. [Phthalaldehydic acid](#). The entire distillate is placed in a 500-ml. flask and covered with 230 ml. of water. The flask is equipped with a mechanical stirrer and is heated on a steam cone. The hydrolysis is complete when the layer of [2-bromophthalide](#) has disappeared (about 30 minutes). The reaction mixture is then placed in a refrigerator overnight, during which time the entire mass solidifies. The product is filtered, washed with two 50-ml. portions of ice water, and dried in the air. The yield of crude product melting at 60–65° (Note 5) is 140–160 g.

The crude product is recrystallized from 400 ml. of hot water and dried in the air. The recrystallized product is white, melts at 95–96°, and weighs 97–102 g. (78–83% based on the bromo compound or 65–68% based on the [phthalide](#)).

2. Notes

1. The [phthalide](#) used by the submitters and by the checkers was a commercial product, obtained from E. I. du Pont de Nemours and Company, Wilmington, Delaware. This product is no longer available. [Phthalide](#) may be prepared in 82.5% yield by hydrogenation of [phthalic anhydride](#) in [benzene](#) at 270° under 3000 lb. pressure in the presence of [copper chromite](#)¹ or, in yields of 61–71%, from [phthalimide](#) according to the procedure given in *Org. Syntheses Coll. Vol. 2, 526* (1943).
2. At a temperature below 135°, bromination does not take place readily. Above 155°, the reaction mixture becomes considerably darker, and the yield is lower.
3. A change in crystalline structure of the distillate is observed when all the [phthalide](#) has been removed.
4. The checkers consistently obtained yields of at least 87%, and in one run the yield of product melting at 78° was 95%.
5. In one run, the checkers obtained 180 g. of product which melted at 67°. This, after recrystallization, melted at 94.5–95° and weighed 121 g. This yield is 84.9% of the theoretical amount based on the bromo compound, or 80% based on the [phthalide](#). The crude product holds water tenaciously, but this is removed by allowing the product to stand in a vacuum desiccator over Drierite.

3. Discussion

To the methods listed in *Org. Syntheses Coll. Vol. 2, 523* (1943) may be added the hydrolysis of [2-chlorophthalide](#);² the action of [carbon dioxide](#) and [sodium](#), under pressure, upon [o-chlorobenzaldehyde](#);³ and from the hydrolysis of [methyl phthalaldehydate](#), obtained by the Rosenmund reduction of the acid chloride of methyl hydrogen phthalate.⁴ The procedure described above is essentially that of Racine.⁵

This preparation is referenced from:

References and Notes

1. Austin, Bousquet, and Lazier, *J. Am. Chem. Soc.*, **59**, 864 (1937).
 2. Austin and Bousquet, U. S. pat. 2,047,946 [*C. A.*, **30**, 6011 (1936)].
 3. Morton, LeFevre, and Hechenbleikner, *J. Am. Chem. Soc.*, **58**, 754 (1936).
 4. Eliel and Burgstahler, *J. Am. Chem. Soc.*, **71**, 2251 (1949).
 5. Racine, *Ann.*, **239**, 79 (1887).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Drierite

acid chloride of methyl hydrogen phthalate

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

carbon dioxide (124-38-9)

phthalic anhydride (85-44-9)

sodium (13966-32-0)

Phthalimide (85-41-6)

COPPER CHROMITE

Phthalaldehydic acid (119-67-5)

2-chlorophthalide

Phthalide (87-41-2)

2-bromophthalide (6940-49-4)

[methyl phthalaldehyde \(4122-56-9\)](#)

[o-chlorobenzaldehyde \(89-98-5\)](#)

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