



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

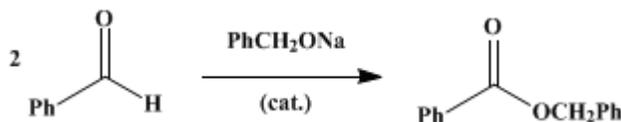
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## BENZYL BENZOATE

[Benzoic acid, benzyl ester]



Submitted by O. Kamm and W. F. Kamm.

Checked by Roger Adams and R. L. Jenkins.

### 1. Procedure

Three grams (0.13 atom) of **metallic sodium** is dissolved by warming for one-half hour in 70 g. (0.65 mole) of pure **benzyl alcohol** (Note 1), and after the mixture has cooled to room temperature the solution is added gradually, with thorough mixing, to 454 g. (4.3 moles) of c.p. **benzaldehyde** (which must contain *less* than 1 per cent of **benzoic acid**) (Note 2). The reaction mixture has a tendency to become warm, but the temperature should be kept slightly below 50–60° by cooling, if necessary (Note 3). A pasty gelatinous mass results. After about one-half hour the temperature of the mixture no longer rises; it is then warmed on the water bath for about one or two hours, with occasional shaking (Note 4).

The cooled reaction product is treated with 200 cc. of water (Note 5), the layer of oil separated, washed once with a second portion of water, and subjected to distillation under reduced pressure. The first fraction of the distillate contains **benzyl alcohol** together with unchanged aldehyde (Note 6), as well as a small quantity of water. The temperature then rises rapidly to the boiling point of **benzyl benzoate**, when the receiver is changed. The product boils at 184–185° /15 mm., and analysis by saponification shows it to consist of 99 per cent ester. The yield is 410–420 g. (90–93 per cent of the theoretical amount). This **benzyl benzoate** supercools readily, but after solidifying melts within one degree of the highest recorded value (19.4°) and therefore need not be refractionated, unless material of exceptional purity is required.

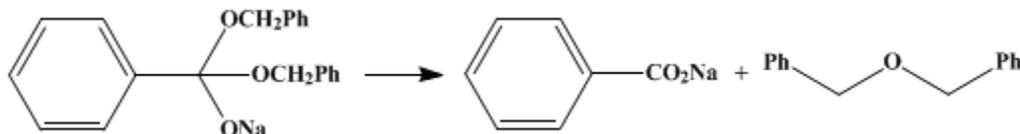
### 2. Notes

1. The **benzyl alcohol** used in this preparation must be free from impurities, especially aldehyde. One cubic centimeter dissolved in 50 cc. of water and treated with a freshly prepared clear solution of **phenylhydrazine acetate** should give no appreciable precipitate. If it is not pure, it must first be treated with alkali as described in (Note 6).

2. The **benzaldehyde** should be titrated in order to determine its acidity. If it is found to contain sufficient **benzoic acid** to react with a considerable proportion of the sodium alcoholate, a poor yield of ester will be obtained. Less than 1 per cent of **benzoic acid** will not interfere seriously with the yields obtained, but the presence of larger quantities of acid will be found to be detrimental and must be removed by washing the **benzaldehyde** with a **sodium carbonate** solution and redistilling with the precautions necessary to prevent too free an access of air to the distillate.

3. The order of mixing the reagents and the temperature of the ingredients at the time of mixing are the most important factors in the experiment.

In the presence of sodium benzoate two molecules of **benzaldehyde** react with the alkoxide to form an addition product. When the reaction mixture is overheated an important side reaction may occur, as follows:



Dibenzyl ether no doubt forms the chief impurity in benzyl benzoate. Since the boiling point of the former lies near that of the ester, it is not removed during the process of purification by distillation. The causes of variations in yield by the use of the older methods can now be explained. When benzaldehyde is added to the alkoxide, and especially when the latter is still warm, local overheating results; in fact, the temperature may rise far above 100° with the result that benzyl ether is formed. Simultaneously, the sodium benzoate is converted into sodium benzoate, which is of no value for inducing the desired reaction, and consequently very little benzyl benzoate is obtained. The same side reactions explain the failure of this experiment when the benzyl alcohol used in preparing the catalyst (sodium benzoate) is contaminated with benzaldehyde.

4. The temperature at which the reaction mixture is maintained after mixing, provided that it is held below 100°, has no great effect on the purity of product.

5. The reaction mixture is not treated with acetic acid, as usually recommended, for the reason that such a procedure yields a final product contaminated with benzoic acid, unless an alkaline wash is applied subsequently.

6. The recovered benzyl alcohol can be used for the preparation of a second lot of benzyl benzoate only after it has been boiled with strong sodium hydroxide to remove all traces of benzaldehyde.

### 3. Discussion

Benzyl benzoate can be prepared by the action of benzyl chloride on sodium benzoate, even in aqueous solution,<sup>1</sup> and by the action of alkoxides on benzaldehyde.<sup>2</sup> The sodium alkoxide method, used in the procedure described, is most convenient and practical. Unfortunately, it has been found to be extremely erratic in regard to yield (10–95 per cent), as well as in regard to the purity of the product (87–97 per cent ester).<sup>3</sup> As a result of the present study,<sup>4</sup> causes for variations are accounted for and the procedure has been converted into a satisfactory method of preparation.

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### References and Notes

1. Gomberg and Buchler, J. Am. Chem. Soc. **42**, 2059 (1920); Scelba, Boll. chim. farm. **62**, 33 (1923) [C. A. **17**, 2166 (1923)].
2. Claisen, Ber. **20**, 649 (1887); Kohn and Tranton, J. Chem. Soc. **75**, 1155 (1899); Matheson, Brit. pat. 270,651 [C. A. **22**, 1597 (1928)]; Grignard and Fluchaire, Ann. chim. **9**, 19 (1928).
3. Anon., Rep. Lab. Am. Med. Assoc. **12**, 84 (1919) [C. A. **14**, 3500 (1920)].
4. Kamm and Matthews, J. Am. Pharm. Assoc. **11**, 599 (1922).

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### Appendix

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

sodium alcoholate

sodium benzoate

acetic acid (64-19-7)

sodium hydroxide (1310-73-2)

sodium carbonate (497-19-8)

Benzoic acid (65-85-0)

benzaldehyde (100-52-7)

metallic sodium (13966-32-0)

sodium benzoate (532-32-1)

benzyl chloride (100-44-7)

BENZYL BENZOATE,  
Benzoic acid, benzyl ester (120-51-4)

Benzyl alcohol (100-51-6)

phenylhydrazine acetate

Dibenzyl ether,  
benzyl ether (103-50-4)