Organic Syntheses

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). 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.

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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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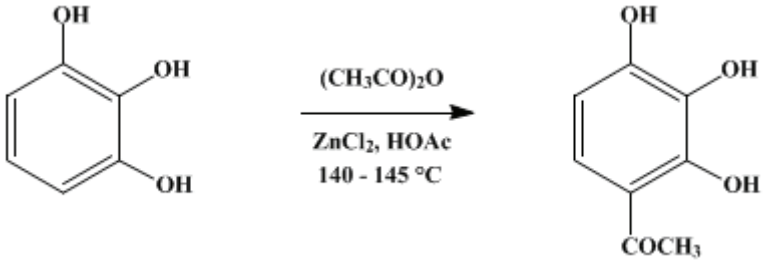
GALLACETOPHENONE



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1. Procedure

In a 250-cc. round-bottomed flask, fitted with a reflux condenser to which is attached a calcium chloride tube, 28 g. (0.21 mole) of freshly fused and finely powdered zinc chloride (Note 1) is dissolved in 38 cc. of glacial acetic acid by heating in an oil bath at 135–140°. Forty grams (0.37 mole) of 95 per cent acetic anhydride is then added to the clear, pale brown liquid, followed by the addition in one lot of 50 g. (0.4 mole) of distilled pyrogallol (Note 2). The mixture is heated at 140–145° (Note 3) for forty-five minutes with frequent and vigorous shaking. The unused acetic anhydride and acetic acid are removed by distilling under reduced pressure. The red-brown cake is broken up by the addition of 300 cc. of water with mechanical stirring for a few minutes. The mixture is cooled in ice water, filtered with suction, and washed with cold water. The crude material, 45–50 g., is crystallized from 500 cc. of boiling water saturated with sulfur dioxide. The yield of straw-colored needles melting at 171–172° is 36–38 g. (54–57 per cent of the theoretical amount). On saturating the mother liquor with salt and cooling to 10°, 4–5 g. of crude material is obtained, which on recrystallization yields 3–4 g. of pure material (Note 4).

2. Notes

1. A good quality of zinc chloride must be used, and it is an advantage to fuse it immediately before use.
2. Variations in the proportions of acetic acid, acetic anhydride, and zinc chloride did not result in increased yields.
3. The temperature must be carefully regulated and must not exceed 150°. In this preparation, as well as in the preparation of other ketones by the Nencki reaction, higher temperatures lead to the formation of a highly colored and resinous product which probably contains a little diketone.
4. This method has been used for the preparation of other phenolic ketones such as resacetophenone, 2-acetyl-1-naphthol,[1] 2-phenylacetyl-1-naphthol, and 2-phenylpropionyl-1-naphthol.[2]

3. Discussion

The method described above is a modification of the process of Nencki and Sieber.[3] Gallacetophenone has also been prepared by treating pyrogallol with acetyl chloride,[4] and from 2-formyl-4-acetylresorcinol by treatment with hydrogen peroxide and alkali.[5]

References and Notes

1. Witt and Braun, Ber. **47**, 3227 (1914).
2. Cheema and Venkataraman, J. Chem. Soc. **1932**, 919.
3. Nencki and Sieber, J. prakt. Chem. (2) **23**, 151, 538 (1881); Nencki, Ber. **27** 2737 (1894). Crabtree and Robinson, J. Chem. Soc. **121**, 1038 (1922).

4. Einhorn and Hollandt, Ann. **301**, 107 (1898); Fischer, Ber. **42**, 1020 (1909).
5. Nakazawa, J. Pharm. Soc. Japan **59**, 297 (1939) [C. A. **33**, 8186 (1939)].

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

Resacetophenone

acetic acid (64-19-7)

acetic anhydride (108-24-7)

acetyl chloride (75-36-5)

sulfur dioxide (7446-09-5)

zinc chloride (7646-85-7)

hydrogen peroxide (7722-84-1)

Gallacetophenone (528-21-2)

pyrogallol (87-66-1)

2-acetyl-1-naphthol (711-79-5)

2-phenylacetyl-1-naphthol

2-phenylpropionyl-1-naphthol

2-formyl-4-acetylresorcinol