



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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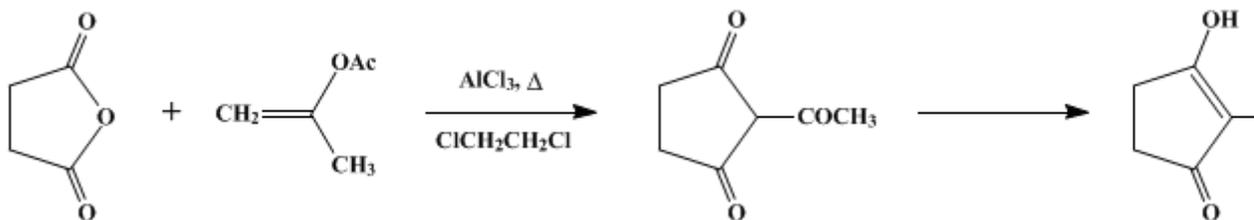
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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2-ACETYL-1,3-CYCLOPENTANEDIONE

[2-Acetyl-3-hydroxy-2-cyclopenten-1-one, (Note 1)]



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1. Procedure

Caution! Since hydrogen chloride is evolved in this reaction, it should be conducted in a hood.

A dry, 3-l., three-necked round-bottomed flask equipped with a sealed mechanical stirrer (all-glass or glass-Teflon), a reflux condenser fitted with a calcium chloride drying tube and a 100-ml. dropping funnel is charged with 50.0 g. (0.500 mole) of finely powdered succinic anhydride (Note 2), 133.4 g. (1.000 mole) of freshly crushed anhydrous aluminum chloride (Note 3), and 500 ml. of anhydrous 1,2-dichloroethane. The mixture is stirred vigorously at room temperature for about 2 hours to dissolve as much of the solid reactants as possible before 50.0 g. (0.500 mole) of isopropenyl acetate (Note 4) is added rapidly through the dropping funnel; the reaction starts immediately as indicated by a rise in temperature to about 60° to 70°. The mixture is refluxed for 15 minutes with continuous stirring. The hot reaction mixture, which contains a sticky oil, is poured into a stirred mixture of 200 ml. of 12 M hydrochloric acid and 1000 g. of crushed ice, and the reaction flask is rinsed with part of the acidic aqueous phase. When the dark mass has dissolved, 200 ml. of 12 M hydrochloric acid is added, and the mixture is stirred vigorously for about 3 hours (Note 5). The dichloroethane phase is separated, and the aqueous phase is extracted with eight 600-ml. portions of dichloromethane. The extracts are combined with the dichloroethane phase (Note 6) and extracted first with 600 ml. and then twice with 200-ml. portions of aqueous saturated sodium hydrogen carbonate solution. The combined sodium hydrogen carbonate extracts are washed with 200 ml. of dichloromethane and then cautiously acidified in a 3-l. beaker with 150 ml. of 12 M hydrochloric acid, with vigorous stirring. The acidic solution (Note 7) is extracted first with 600 ml. and then with four 400-ml. portions of dichloromethane. The bulk of the dichloromethane is removed by distillation at atmospheric pressure and water bath temperatures; however, the last 150 ml. of solvent is removed below room temperature under reduced pressure (about 20 mm.), leaving 24–27 g. of crude 2-acetyl-1,3-cyclopentanedione as a light brown solid, m.p. 68–71° (Note 8).

The crude product is purified by decolorization with charcoal and recrystallization from 100–150 ml. of diisopropyl ether, giving 19–21 g. (27–30%) of colorless needles, m.p. 70–72°. This material is sufficiently pure for most purposes. Further purification may be achieved by recrystallization from diisopropyl ether and/or sublimation at 60° (0.1 mm.) onto a cold-finger condenser, giving material melting at 73–74° (Note 9), (Note 10).

2. Notes

- 2-Acetyl-1,3-cyclopentanedione is completely enolized in the solid state as well as in solution.² Indirect evidence indicates that the carbon-carbon double bond of the enol is within the ring.
- The submitters used a practical grade of succinic anhydride obtained from Matheson, Coleman and Bell.

3. The submitters used anhydrous, sublimed **aluminum chloride** obtained from E. Merck AG, Darmstadt, Germany. The checkers used analytical reagent grade material obtained from Mallinckrodt Chemical Works.
4. The submitters used either a pure grade (more than 98.5%) of **isopropenyl acetate** or a practical grade (95–98%) from Fluka AG, Buchs SG, Switzerland. Generally, it was not essential to distill the material before use.
5. This treatment increases the amount of product which can be extracted from the aqueous solution.
6. Evaporation of the solvents at this stage gives an oily product which may be decolorized with charcoal and then recrystallized from **diisopropyl ether** to give **2-acetyl-1,3-cyclopentanedione**, m.p. 68–71°. However, the extraction with **sodium hydrogen carbonate** is preferred.
7. Decolorization of the acidic aqueous solution with charcoal at this stage improves the quality of the product.
8. **2-Acetyl-1,3-cyclopentanedione** is quite volatile and appreciable losses may occur if the evaporation of the concentrated solution is continued at elevated temperature.
9. Further amounts of **2-acetyl-1,3-cyclopentanedione** can be obtained by continuous extraction of the original aqueous phase with **dichloromethane**. The submitters have obtained total yields of product as high as 41–43%. **2-Acetyl-1,3-cyclopentanedione** is sparingly soluble in **diethyl ether** and is not extracted very efficiently from aqueous solution with **ether**.
10. **2-Acetyl-1,3-cyclopentanedione** can be hydrolyzed to **1,3-cyclopentanedione**.^{3,4} The preferred method⁴ is to keep a 0.1 M solution of **2-acetyl-1,3-cyclopentanedione** in 0.1 M aqueous **acetic acid** at 100° for 24 hours. The solvent is then evaporated at 40° with a water pump and the yellow solid is recrystallized from **butanone** (with charcoal) to give **1,3-cyclopentanedione**, m.p. 148–150°, in 65–80% yield.

3. Discussion

2-Acetyl-1,3-cyclopentanedione has been obtained in small amounts from the aluminum chloride-catalyzed reactions of **vinyl acetate** and **succinyl chloride** in **1,1,2,2-tetrachloroethane**.⁵ **2-Acetyl-1,3-cyclopentanediones** have been prepared via Dieckmann condensation of 1,4-bis(ethoxycarbonyl)-3,5-hexanediones.⁶ The present procedure is essentially that of Merényi and Nilsson⁷ with some modifications.

The diacylation of **isopropenyl acetate** with anhydrides of dicarboxylic acids is applicable to the synthesis of several other cyclic β -triketones in moderate yield.^{3,7} It has been used for the synthesis of **2-acetyl-1,3-cyclohexanedione** (40% yield), **2-acetyl-4-methyl-1,3-cyclopentanedione** (10% yield), **2-acetyl-4,4-dimethyl-1,3-cyclopentanedione** (10% yield), **2-acetyl-5,5-dimethyl-1,3-cyclohexanedione** (10% yield), **2-acetyl-1,3-cycloheptanedione** (12% yield), and **2-acetyl-1,3-indanedione** (25% yield). Maleic anhydrides under more drastic conditions give acetyl-1,3-cyclopent-4-enediones in yields from 5 to 12%.⁸ The corresponding acylation of the enol acetate of 2-butanone with **succinic anhydride** has been used to prepare **2-methyl-1,3-cyclopentanedione**, an important intermediate in steroid synthesis.^{9,10}

References and Notes

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

2-acety-1,3-indanedione

hydrogen chloride,
hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ether,
diethyl ether (60-29-7)

sodium hydrogen carbonate (144-55-8)

1,2-dichloroethane (107-06-2)

aluminum chloride (3495-54-3)

dichloromethane (75-09-2)

Succinic anhydride (108-30-5)

butanone (78-93-3)

succinyl chloride (543-20-4)

diisopropyl ether (108-20-3)

isopropenyl acetate (108-22-5)

vinyl acetate (108-05-4)

dichloroethane (75-34-3)

1,1,2,2-tetrachloroethane (79-34-5)

2-Methyl-1,3-cyclopentanedione (765-69-5)

2-Acetyl-1,3-cyclopentanedione (3859-39-0)

2-Acetyl-3-hydroxy-2-cyclopenten-1-one

1,3-cyclopentanedione (3859-41-4)

2-acetyl-1,3-cyclohexanedione (4056-73-9)

2-acetyl-4-methyl-1,3-cyclopentanedione

2-acetyl-4,4-dimethyl-1,3-cyclopentanedione

2-acetyl-5,5-dimethyl-1,3-cyclohexanedione

2-acetyl-1,3-cycloheptanedione