



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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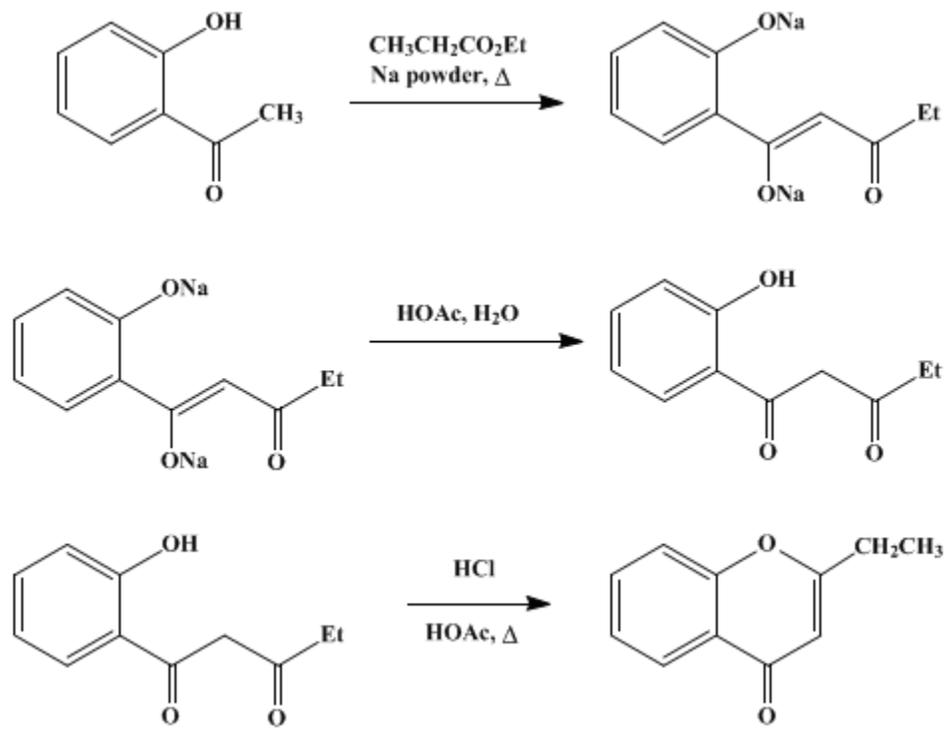
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.387 (1955); Vol. 21, p.42 (1941).

2-ETHYLCHROMONE

[Chromone, 2-ethyl-]



Submitted by Ralph Mozingo

Checked by Homer Adkins and Robert J. Gander.

1. Procedure

In a 1-l. three-necked flask fitted (Note 1) with a reflux condenser, a dropping funnel, and a stirrer (Note 2) are placed 24 g. (1.05 gram atoms) of oxide-free sodium and 200 ml. of xylene (Note 3). The condenser is protected by a drying tube containing soda-lime. The flask is surrounded by an oil bath which is heated until the sodium is melted. The stirrer is started, and, after the sodium is powdered, the oil bath is removed. When the contents of the flask have cooled to room temperature, the stirrer is stopped, the xylene decanted, and the sodium washed with 100 ml. of dry ether to remove traces of xylene.

The flask is replaced and completely surrounded by an ice bath (Note 4). A current of nitrogen is passed through the flask for 5 minutes by means of a rubber tube attached to the dropping funnel. The nitrogen inlet tube is removed, and a mixture of 60 g. (0.44 mole) of *o*-hydroxyacetophenone (Note 5) and 125 g. (140 ml., 1.2 moles) of ethyl propionate (Note 3) is placed in the dropping funnel and protected by a soda-lime tube. The ester-ketone mixture is dropped very slowly onto the powdered sodium. After a small amount (2–5 ml.) of the mixture has been added, the ice bath is removed and the flask warmed with the hand to make sure that the reaction has started (Note 6). When the reaction has started, the funnel is adjusted so that one-half of the ester-ketone mixture is added over a period of 1.5–2 hours. After half of the mixture has been added, the rate of addition is again regulated so that the remainder is added in 30 minutes.

After all the ester-ketone mixture has been added and the reaction has subsided, the ice bath is removed and replaced by a steam bath. The crust on the mixture is broken up and the mixture heated on a steam bath until all the sodium has reacted (30–60 minutes). The reaction mixture is allowed to cool

and is poured with stirring onto 300 g. of crushed ice. Ninety-five milliliters of glacial [acetic acid](#) in 350 ml. of water is added, and the mixture is stirred for 30 minutes. The organic layer which separates is removed by means of a separatory funnel, and the water layer is extracted three times with 200-ml. portions of [ether](#). The extracts are combined with the original organic material, and the [ether](#) is distilled from a steam bath. To the residue are added 150 ml. of glacial [acetic acid](#) and 10 ml. of concentrated [hydrochloric acid](#), and the solution is refluxed for 30 minutes, after which it is allowed to cool to room temperature ([Note 7](#)).

The entire reaction mixture is then subjected to fractional distillation through a Widmer column ([Note 8](#)). The material boiling up to 120° is removed at atmospheric pressure and discarded. The contents of the flask are cooled and the pressure reduced to 7 mm. The fraction up to 80°/7 mm. is removed and discarded. The material boiling at 80–90°/7 mm. is collected, and, after the contents of the flask have been cooled, the pressure is reduced to 2 mm. and all the material boiling up to 110°/2 mm. is collected and combined with the 80–90°/7 mm. fraction. The next fraction, boiling at 110–138°/2 mm., is collected separately. On refractionation of the lower fraction (b.p. 80°/7 mm.–110°/2 mm.) there is obtained 13–15 g. of [o-hydroxyacetophenone](#) (b.p. 87–88°/7 mm.). To the residue after recovery of the [o-hydroxyacetophenone](#) is added the fraction boiling at 110–138°/2 mm. The pressure is again reduced to 2 mm. and the fraction boiling at 124–126°/2 mm. collected. This fraction is pure [2-ethylchromone](#) and weighs 42–45 g. (70–75% based on the ketone not recovered) ([Note 9](#)).

2. Notes

1. All the stoppers used should be rubber ones that have been boiled for 2 hours in 10% [sodium hydroxide](#) and thoroughly washed and dried before use.
2. A convenient stirrer may be made by fitting a ¼-in brass rod with a disk 1 in. in diameter. Four holes are drilled through the disk, and through each hole is placed a loop of 18-gauge Nichrome wire. The loops are each turned so that the twisted end is next to the stirrer shaft and each is twisted in the middle to give a double loop. The stirrer shaft is then passed through a 4-in. length of glass tubing which fits tightly about the shaft. A rubber seal is made by slipping a piece of rubber tubing over the brass rod and glass tubing. The rubber tubing extends about 3 mm. up onto the stirrer shaft, over which it fits rather tightly. A drop of [glycerol](#) placed on the stirrer shaft just above the rubber sleeve serves as a lubricant for the seal. The seal is similar to that described for the preparation of [dypnone](#) (p. 368, [Note 1](#)).
3. The [xylene](#) is dried over [sodium](#) and distilled from it. The [ethyl propionate](#) is dried over [phosphorus pentoxide](#), more of the drying agent being added from time to time until some solid [phosphorus pentoxide](#) remains. The ester is then decanted into a flask containing fresh [phosphorus pentoxide](#) and fractionated. The fraction boiling at 98–99°/745 mm. is collected.
4. An ice bath is used to keep the reaction from becoming too violent. An ice-salt bath must not be used or the reaction may be delayed in starting.
5. The [o-hydroxyacetophenone](#) was made as described by Miller and Hartung [*Org. Syntheses Coll. Vol. 2, 543 (1943)*] for *o*- and *p*-hydroxypropiophenone except that the procedure for isolating the product was modified as follows. The cold, partly solidified oil, separating after acidification, was diluted with [benzene](#) and the water layer extracted with [benzene](#). After distillation of the [benzene](#), the residue was distilled at 17 mm. until the solid *p*-isomer began to collect in the condenser. The distillate was then fractionated through a Widmer column, and the fraction boiling at 90–110°/17 mm. was saved. Refractionation gave [o-hydroxyacetophenone](#) boiling at 105–106°/20 mm. or 87–88°/7 mm. in a yield of 30% based upon the [phenyl acetate](#).
6. It is *very important* that the operator assure himself that the reaction has started before more of the ester-ketone mixture is added, and that the first half of the mixture be added slowly, or the reaction may proceed with *explosive violence*. It is usually possible to tell when the reaction has started by the local evolution of heat when the ice bath is removed and by the appearance of the yellow salt of the diketone.
7. The preparation should be carried as far as this point without interruption.
8. The Widmer column had a spiral 15 cm. in length, and had an electrically heated jacket.¹
9. The submitter carried out this preparation with twice the quantities recommended here. The yield was 68–77 g. (56–64%).

3. Discussion

This chromone has been prepared by the condensation of ethyl propionate with *o*-hydroxyacetophenone using sodium.^{2,3}

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 478](#)

References and Notes

1. Smith and Adkins, *J. Am. Chem. Soc.*, **60**, 662 (1938).
 2. Heilbron, Hey, and Lowe, *J. Chem. Soc.*, **1934**, 1312.
 3. Mozingo and Adkins, *J. Am. Chem. Soc.*, **60**, 669 (1938).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

oxide-free sodium

o- and *p*-hydroxypropiophenone

[hydrochloric acid \(7647-01-0\)](#)

[acetic acid \(64-19-7\)](#)

[Benzene \(71-43-2\)](#)

[ether \(60-29-7\)](#)

[sodium hydroxide \(1310-73-2\)](#)

[glycerol \(56-81-5\)](#)

[nitrogen \(7727-37-9\)](#)

[sodium \(13966-32-0\)](#)

[xylene \(106-42-3\)](#)

[ethyl propionate \(105-37-3\)](#)

[2-Ethylchromone,
Chromone, 2-ethyl- \(14736-30-2\)](#)

[phenyl acetate \(122-79-2\)](#)

[phosphorus pentoxide \(1314-56-3\)](#)

[o-Hydroxyacetophenone \(118-93-4\)](#)

Dynnone (495-45-4)

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