Working with Hazardous Chemicals

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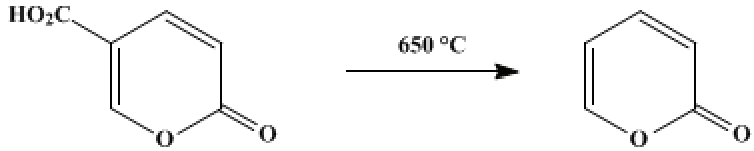
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.046.0101

Organic Syntheses, Coll. Vol. 5, p.982 (1973); Vol. 46, p.101 (1966).

α-PYRONE

[2-Oxo-1, 2H-pyrane-]



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Checked by E. J. Corey, W. H. Pirkle, and M. J. Haddadin.

1. Procedure

(Note 1)

A 37.5-g. (0.266-mole) sample of coumalic acid (Note 2) is placed in a 30 × 10 cm. cylindrical flask attached horizontally to a 55 × 3 cm. oven-heated Vycor tube (Note 3) *loosely* packed with 20 g. of fine copper turnings (Note 4). Following the Vycor tube successively are two ice-cooled 50-ml. receivers and a dry ice trap. The latter is connected to an efficient vacuum pump (Note 5). The system is evacuated, and the Vycor tube is heated to 650–670°. Then the flask containing the coumalic acid is heated with a nichrome wound heating jacket to 180°, and the temperature is allowed to rise slowly to 215°. During this time coumalic acid sublimes into the Vycor tube and α-pyrone distills into the ice-cooled receivers. The pressure is held below 5 mm. (Note 6). The yield of pale yellow crude material is 18–19.3 g. (70–75%). Distillation affords 16.9–18 g. (66–70%) of colorless oily α-pyrone. b.p. 110° (26 mm.), n^{25}D 1.5270.

2. Notes

1. Since this procedure was checked, a method[1] has been developed which uses a vertical arrangement of the oven together with a powder sifter placed above the oven. This allows the use of less pure starting material but with reduced yields. Also, it allows more rapid throughput. It is required that the top portion of the tube be filled with porcelain Berl saddles onto which the powder is sifted. The saddles then pick up any tarry residue which might clog the pyrolysis tube.
2. Coumalic acid, m.p. 206–209°, was prepared by the method of Wiley and Smith[2] and recrystallized from methanol as described. Starting material prepared in this way still contains impurities but is satisfactory for the preparation of α-pyrone. A purer grade of colorless coumalic acid, m.p. 206–208.5°, may be obtained by further recrystallization and a subsequent sublimation at 180–190° (0.5 mm.) (Precision Glass Macro Sublimator No. JM7410), and its use leads to higher yields of α-pyrone (80–85%) by the procedure given here. However, the losses of coumalic acid incurred in the purification (about 50%) and the time involved render this modification unprofitable. On the other hand, when unrecrystallized coumalic acid is used, the yields are generally somewhat lower (60–65%) and the results are slightly more variable.
3. The following apparatus was used by the submitters. The furnace was a Lindberg Model CF-1R High Temperature Combustion Furnace (Fisher Scientific Co. Catalog No. 10-467-1; E. H. Sargent Co. Catalog No. S-35955). This furnace has a hot zone of 8 3/4; in. and a maximum temperature of 1450°C. Because of the short heating length, the Vycor tube was packed with copper turnings over its entire length to prevent condensation of coumalic acid in the cooler parts of the tube. Glass wool insulation was used at both ends of the furnace to prevent heat loss.
The heater used for the sublimation vessel was made from a length of 15-cm. Pyrex tubing. The tube was covered partially with moistened asbestos fiber strips (*ca.* 1 mm. thick) which remain in place when dry. The tube was only partially covered with asbestos to allow visual inspection of the sublimation vessel. A sufficient length of nichrome wire (depending on the resistance of the wire) was wound over the asbestos base, and more asbestos was added over that already in place to hold the wire loops apart. During use, the open end was well stuffed with glass wool.

The sublimation vessel was made from 10-cm. Pyrex tubing sealed at one end and fitted with a standard taper 34/45 female joint at the other end.
The checkers used a Hoskins tube furnace, type FD303A (Central Scientific Co.), 17 in. long. The heater for the sublimation vessel was wound in two sections with heating wire in such a way that a decreasing temperature gradient in the direction of the pyrolysis oven was maintained. The open end of the heater was closed by an asbestos end plate which could be heated independently by a small nichrome coil.
4. Copper appears to function only as a surface heat transfer agent. Broken pieces of porous plate, for example, may also be used.
5. Better yields are obtained at low pressures (preferably below 5 mm.) because of more efficient sublimation of coumalic acid. The submitters report that a water aspirator could be used with crude (unrecrystallized) coumalic acid to avoid damage to the vacuum pump by untrapped corrosive vapors, and that yields of α-pyrone averaged 45% in this modification. The checkers used a mechanical pump with an efficient sodium hydroxide trap in all runs.
6. It is important that the melting of the coumalic acid be prevented during the sublimation process; hence maintenance of the lowest possible pressure is recommended. If the material in the sublimation vessel begins to melt, resinification occurs with no further sublimation and a correspondingly lower yield of product. The temperature of the sublimator should be maintained high enough to allow a maximum rate of sublimation of coumalic acid, but not so high as to cause melting. Increasing the scale of the preparation increases the possibility of resinification of coumalic acid in the sublimator before complete reaction. However, the submitters have successfully carried out the preparation of α-pyrone on twice the scale described here using the same procedure and apparatus (except that the collection flasks were 100-ml. size). On the larger scale it is advisable to use pure sublimed coumalic acid. In the experience of the checkers, larger-scale runs are much less readily reproducible.

3. Discussion

α-Pyrone has previously been prepared in low yield by the pyrolysis of heavy metal salts of coumalic acid[3] and by the small-scale pyrolysis of α-pyrone-6-carboxylic acid over copper.[4]

4. Merits of the Preparation

This method affords α-pyrone in quantity and in good yield not achieved previously.[3] The compound has considerable possibilities in Diels-Alder reactions, such as a decarboxylative double diene synthesis.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 462
- Org. Syn. Coll. Vol. 9, 28

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References and Notes

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2. H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *J. Am. Soc.*, **91**, 2330 (1969).
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4. H. von Pechmann, *Ann.*, **264**, 272 (1891).
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6. H. E. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960).

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

2-Oxo-1, 2H-pyrane-

methanol (67-56-1)

copper,
copper turnings (7440-50-8)

Coumalic acid (500-05-0)

α-pyrone-6-carboxylic acid

α-Pyrone (504-31-4)