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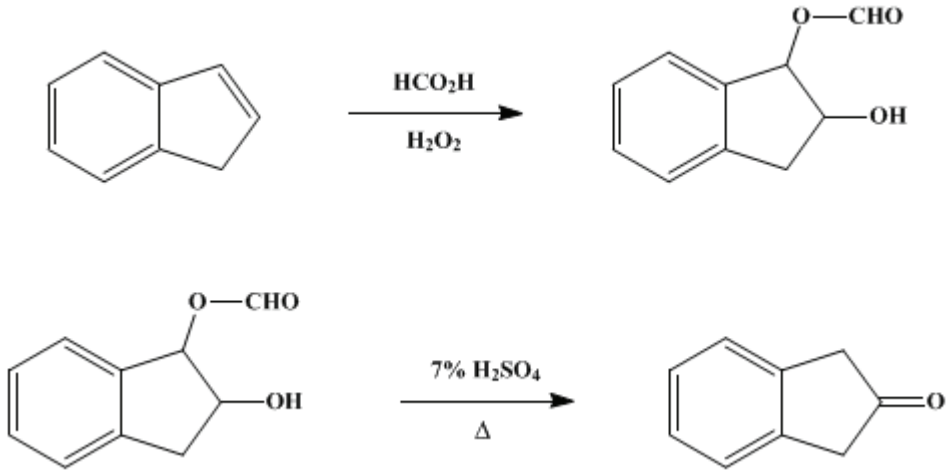
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.041.0053

Organic Syntheses, Coll. Vol. 5, p.647 (1973); Vol. 41, p.53 (1961).

2-INDANONE



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1. Procedure

In a 2-l. three-necked flask fitted with stirrer, dropping funnel, and thermometer are placed 700 ml. of formic acid (88%) and 140 ml. of hydrogen peroxide (30%, 1.37 moles). While the temperature is kept at 35–40° (Note 1), 116.2 g. (117.3 ml., 1.00 mole) of indene (98%) (Note 2) is added dropwise, with stirring, over a period of 2 hours. An additional 100 ml. of formic acid is used to rinse the last of the indene from the dropping funnel into the reaction flask. The reaction solution is stirred at room temperature for 7 hours to ensure complete reaction (Note 3). The solution is transferred to a 2- or 3-l. Claisen flask, and the formic acid is removed under aspirator pressure (b.p. 35–40°/20–30 mm.), care being taken to maintain the boiler temperature below 60° (Note 4). The residue, after being cooled to room temperature, is a yellowish brown crystalline solid (Note 5), the color being due to contamination by a small amount of brownish oil.

In a 5-l. flask fitted with a long condenser (about 40 cm.) connected to an ice-cooled receiver is placed 2 l. of 7% (by volume) sulfuric acid. The solution is heated to boiling, and the crude monoformate of 1,2-indanediol is added. Steam is introduced and the mixture is steam distilled, while external heat is applied with a flame in order to maintain the boiler contents at a constant volume of 2 l. The steam distillation is carried out at the rate of about 1 l. per hour until 5–6 l. of distillate have been collected and the 2-indanone has stopped distilling (Note 6). The dark-brown oily residue becomes semisolid at room temperature.

The cold distillate is filtered with suction, and the white crystalline solid is sucked thoroughly dry on the filter (Note 7). The crystals are dried further in a vacuum desiccator (at about 1 mm.) at room temperature or below for about 12 hours. The melting point of the 2-indanone is 57–58° (Note 8). The yield is 90–107 g. (69–81%).

2. Notes

1. This is the best temperature at which to control the reaction. At higher temperatures, the reaction becomes too vigorous. The stirrer must be sufficiently powerful to thoroughly mix the phases or a very low yield will result. A Hershberg stirrer has been found to be very effective in this preparation (private communication from H. E. Baumgarten).
2. The indene ($n_D^{25.5}$ 1.5698, b.p. 74–76°/24 mm.) was obtained from Rütgerswerke, A. G., West Germany, through Terra Chemicals, Inc., 500 Fifth Avenue, New York 36, N. Y. It was faintly yellow, but was used without distillation, since distillation, although it removed the yellow color, did not change

the refractive index. When Matheson, Coleman and Bell technical grade indene was used (redistilled, $n_D^{25.5}$ 1.5606, b.p. 177–179°), a 45% yield of 2-indanone was obtained.
3. The reaction mixture can be left overnight at this point with no adverse effect upon yield.
4. A higher temperature should be avoided at the start to prevent boilover, and later to reduce side reactions and eliminate danger from possible residual peroxides.
5. The reaction can be interrupted at this point and the formate ester stored for several weeks, if desired.
6. The rate of flow of cooling water through the condenser must be regulated so that the condenser does not become clogged with 2-indanone. The end point of the distillation can be recognized by lack of turbidity in the condensate or of solidification in the condenser when cold water is passed rapidly through the condenser.
7. The steam distillate, with the 2-indanone under water, can be kept for as long as a week in the refrigerator. In the dry state, 2-indanone is unstable to air at room temperature but can be kept in a closed vessel for several days at room temperature and for longer periods (several weeks or more) in a refrigerator.
8. The ultraviolet spectrum in the 300–350 mμ region showed that less than 1% of 1-indanone was present. If the 2-indanone darkens on standing, it can be repurified by steam distillation or by crystallization from ethanol.

3. Discussion

2-Indanone was first prepared by distillation of the calcium salt of *o*-phenylenediacetic acid[2,3] and, more recently, by the action of acetic anhydride on its potassium salt.[4] It has been obtained by the dilute sulfuric acid-catalyzed hydrolysis and decarboxylation of 2-iminoindan-1-carboxylate[5] and ethyl 2-indanone-1-carboxylate.[6] 2-Indanone is commonly obtained by acid-catalyzed dehydration of an indene glycol,[7,8] as illustrated in this preparation. Indene glycol has been obtained from indene via the bromohydrin.[9,10,11,12] The most recent preparation of 2-indanone is by Curtius degradation of 2-indenecarboxylic acid.[13]

References and Notes

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

calcium salt of o-phenylenediacetic acid

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic anhydride (108-24-7)

formic acid (64-18-6)

hydrogen peroxide (7722-84-1)

1-Indanone (83-33-0)

indene (95-13-6)

2-Indanone (615-13-4)

monoformate

1,2-indanediol

2-iminoindan-1-carboxylate

ethyl 2-indanone-1-carboxylate

indene glycol

2-indenecarboxylic acid