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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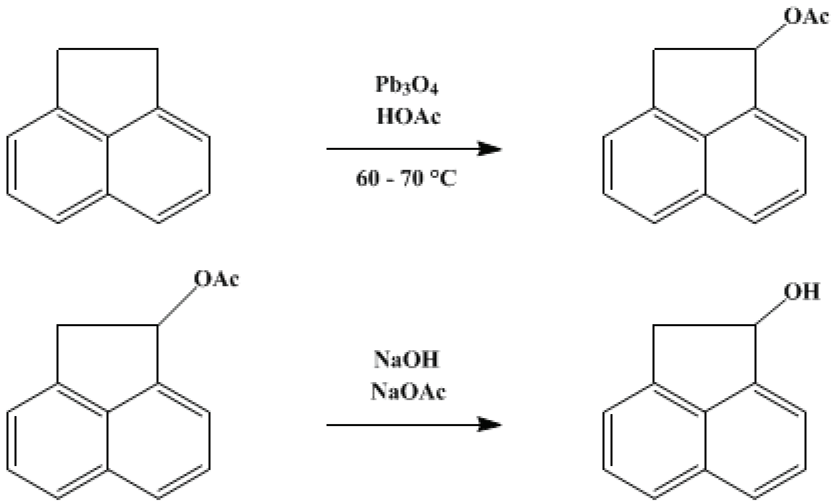
ACENAPHTHENOL-7

[1-Acenaphthenol]



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1. Procedure

A. *Acenaphthenol acetate*. In a 2-l. round-bottomed flask are placed 154 g. (1 mole) of acenaphthene (Note 1) and 1.1 l. of glacial acetic acid (Note 2). The flask is fitted with a tantalum or Nichrome wire stirrer[1] and a thermometer extending below the surface of the liquid. The solution is stirred and heated to 60°, at which point the source of heat is removed and 820 g. of red lead (Note 3) is added in portions of about 50 g., each portion being added as soon as the color due to the previous portion has been discharged. During this operation, which requires 30–40 minutes, the temperature is maintained at 60–70 (Note 4) by external cooling. The reaction is complete when a portion of the solution gives no test for lead tetraacetate (Note 5). The dark red syrupy solution (which may contain a few suspended particles of red lead and lead dioxide) is poured into 2 l. of water contained in a 4-l. separatory funnel. The acetate is extracted with a 350-ml. portion of ether and then with a 250-ml. portion. The total extract is washed first with 100 ml. of water, then with 300 ml. of saturated sodium chloride solution and is finally dried over 50 g. of anhydrous sodium sulfate. The sodium sulfate is removed by filtration and washed colorless with three 50-ml. portions of dry ether. The combined filtrate and washings are placed in a 500-ml. Claisen flask with an inset side arm, and, after distillation of the solvent, the acetate is distilled under reduced pressure. The acetate distils almost entirely at 166–168°/5 mm. (bath temperature 180–185°, raised to 220° at the end) as a mobile yellow oil. The yield is 170–175 g. (80–82%) (Note 6).

B. *Acenaphthenol*. The acetate obtained as above is dissolved in 275 ml. of methanol in a 2-l. round-bottomed flask, and a solution of 40 g. (1.2 equiv.) of sodium hydroxide in 400 ml. of water is added (Note 7). This mixture is refluxed for 2 hours (Note 7) and then cooled below 20°. The yellow crystalline acenaphthenol is collected on a filter and washed well with about 1.5 l. of water. The crude product is air-dried (138–143 g.) and then dissolved in 2 l. of boiling benzene. The solution is treated with 6–8 g. of decolorizing carbon (Note 8) and filtered through a heated funnel. The orange-red filtrate is concentrated to about 1 l., and the acenaphthenol is allowed to crystallize. After filtering with suction and washing with cold benzene (about 500 ml.) until the wash solvent is colorless, the acenaphthenol is obtained as practically colorless needles, m.p. 144.5–145.5° (cor.) (Note 9). It weighs 117–121 g. From the filtrate may be obtained an additional quantity of material which on one recrystallization gives only 3–5 g. of pure acenaphthenol. The total yield amounts to 120–126 g. (70–74% based on the acenaphthene).

2. Notes

1. The "95% acenaphthene" sold by Reilly Tar and Chemical Corporation melts at 92.5–93.5° (cor.) and is quite satisfactory for use in this reaction. A recrystallized sample of this acenaphthene (m.p. 93–93.5°) or acenaphthene from the Gesellschaft für Teerverwertung (m.p. 93–93.5°) gives no better yield of pure acenaphthenol.
2. The glacial acetic acid should be purified by distillation from potassium permanganate. About 30–50 g. of potassium permanganate for each 1.5 l. of acetic acid should be used.
3. Mallinckrodt's analytical reagent red lead (assay 85–90%) was used. Merck's and Baker's N.F. V red lead are also quite satisfactory. Previously prepared lead tetraacetate is in no way preferable to red lead for this oxidation.
4. If the oxidation is carried out at 50° the yield is unaffected, but several hours are required to complete the addition. At 40°, the reaction is very slow and the yield is lowered.
5. A drop of the reaction mixture is placed on a moist piece of starch-iodide paper. The development of a blue color shows the presence of lead tetraacetate.
6. The acenaphthenol acetate contains small amounts of acenaphthene and acenaphthenone but is pure enough for the next step.
7. The dark violet color appearing on addition of the alkali is probably due to the presence of acenaphthenone. Crystalline acenaphthenol begins to separate almost immediately after the alkali has been added. Care must be taken in heating to refluxing because when heated too rapidly the acenaphthenol crystallizes suddenly from solution and the heat evolved may blow part of it out through the condenser.
8. If the charcoal treatment is omitted, the acenaphthenol obtained is light yellow but practically pure.
9. Marquis[2] reported the melting point as 148°; von Braun and Bayer[3] reported it as 146°.

3. Discussion

Acenaphthenol has been prepared in poor yield by the oxidation of acenaphthene with lead dioxide;[2] and it is among the products obtained by hydrogenation of acenaphthene quinone.[3] The above procedure is essentially that described more briefly in the literature.[4]

References and Notes

1. Hershberg, *Ind. and Eng. Chem., Anal. Ed.*, **8**, 313 (1936); *Org. Syntheses* Coll. Vol. **2**, 117 (1943).
2. Marquis, *Compt. rend.*, **182**, 1227 (1926).
3. von Braun and Bayer, *Ber.*, **59**, 920 (1926).
4. Fieser and Cason, *J. Am. Chem. Soc.*, **62**, 432 (1940).

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

red lead

acetic acid (64-19-7)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

potassium permanganate (7722-64-7)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

carbon (7782-42-5)

acenaphthene (83-32-9)

acenaphthene quinone (82-86-0)

ACENAPHTHENOL-7

1-Acenaphthenol,
acenaphthenol (6306-07-6)

Acenaphthenol acetate (14966-36-0)

acenaphthenone (2235-15-6)

lead dioxide

lead tetraacetate (546-67-8)