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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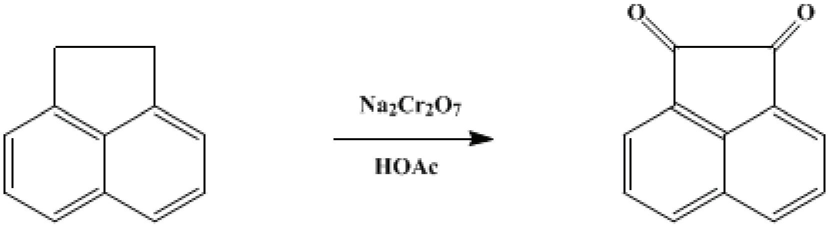
ACENAPHTHENEQUINONE



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1. Procedure

A mixture of 100 g. (0.65 mole) of a technical grade of acenaphthene, 5 g. of ceric acetate (Note 1), and 800 ml. of glacial acetic acid is placed in a 4-l. stainless-steel beaker arranged for external cooling with cold water (Note 2). A thermometer and a powerful stirrer are inserted, and 325 g. (1.1 mole) of sodium bichromate dihydrate is added over a period of 2 hours, the temperature being kept at 40° (Note 3). Stirring is then continued at room temperature for an additional 8 hours; during this time the reaction mixture becomes quite thick, owing to the separation of the quinone and chromium salts. The suspension is diluted with 1.5 l. of cold water, and the solid is collected on a 10-in. Büchner funnel and washed free from acid.

The solid is next digested on the steam bath for 30 minutes with 500 ml. of a 10% sodium carbonate solution, and is filtered and washed. The solid is then extracted for 30 minutes at 80° with 1 l. of 4% sodium bisulfite solution; at the end of this period 15 g. each of Filtercel and Norit are added, and the suspension is filtered. The extraction is repeated, and the combined filtrates are acidified at 80° with constant stirring (Note 4), to Congo red paper, with concentrated hydrochloric acid (50–60 ml.). The temperature is maintained at 80° for 1 hour with constant stirring. The acenaphthenequinone separates as a bright yellow crystalline solid; it is collected on a Büchner funnel and washed with water until free from acid. The yield is 45–70 g. (38–60%); m.p. 256–260°.

The crude quinone (50 g.) is recrystallized from 250 ml. of *o*-dichlorobenzene without filtering (Note 5); the crystals are rinsed with methanol. The recovery is 45 g., m.p. 259–260° (Note 6), (Note 7).

2. Notes

1. The checkers used Eastman Kodak white label acenaphthene. Cerium salts appear to have a beneficial effect. Probably any cerous salt will be satisfactory, it being oxidized in the reaction. The submitters have used cerous chloride, ceric carbonate, and ceric acetate; the last can be obtained in the form of a 50% mixture with other rare-earth acetates from the Lindsay Light and Chemical Company, West Chicago, Illinois. The checkers used cerous chloride.
2. The checkers found no need to cool the reaction; instead the bath was used to heat the reaction to 40°. With technical grade acenaphthene, cooling is necessary.
3. If the oxidation temperature has been allowed to rise to 50°, tar formation makes it necessary to do five or six treatments with sodium bisulfite. The extractions should be continued as long as the filtrate gives a precipitate on acidification.
4. The acidification should be performed in a hood; much sulfur dioxide is evolved.
5. The quinone crystallizes so rapidly that filtration is impossible; however, there is no insoluble material if mechanical dirt has been excluded.
6. This oxidation has been run using 80 times these amounts; the yield of recrystallized material drops to 38–40%.
7. The red color of acenaphthenequinone[1] is due to biacenaphthylidenedione, m.p. 295°. It is an appreciable contaminant in a hot oxidation; the product may also contain appreciable amounts of

naphthalic anhydride.

3. Discussion

Acenaphthenequinone has been prepared by oxidation of acenaphthene with chromic acid,[1,2,3,4,5,6,7,8,9,10] with calcium permanganate,[11] with air in the presence of catalysts in various solvents,[12,13,14,15] with 30% hydrogen peroxide in acetic acid,[16] by the formation of an oxime with an alkyl nitrite followed by hydrolysis,[17,18,19] and from oxalyl chloride and naphthalene.[20,21] This procedure is based on the disclosure in a P.B. report.[10]

References and Notes

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

chromium salts

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

methanol (67-56-1)

sodium carbonate (497-19-8)

sulfur dioxide (7446-09-5)

sodium bisulfite (7631-90-5)

Norit (7782-42-5)

chromic acid (7738-94-5)

Naphthalene (91-20-3)

hydrogen peroxide (7722-84-1)

naphthalic anhydride (5343-99-7)

acenaphthene (83-32-9)

Acenaphthenequinone (82-86-0)

ceric acetate

sodium bichromate dihydrate (10588-01-9)

cerous chloride (7790-86-5)

biacenaphthylidenedione

calcium permanganate

oxalyl chloride (79-37-8)

o-dichlorobenzene (95-50-1)

ceric carbonate

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