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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 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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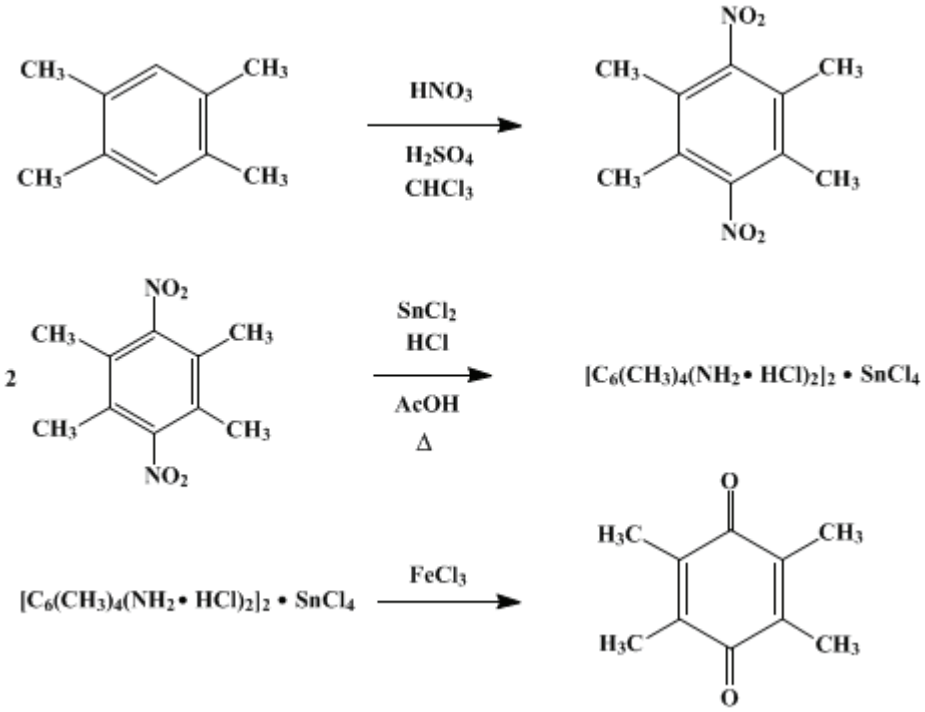
DUROQUINONE



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1. Procedure

(*A*) *Dinitrodurene*.—A solution of 13.4 g. (0.1 mole) (Note 1) and (Note 2) of durene (p. 248) in 100 cc. of chloroform is added to 75 cc. of concentrated sulfuric acid in an 800-cc. beaker provided with a thermometer and an efficient mechanical stirrer. The mixture is cooled to 10°, and 16 g. (10.7 cc.) of fuming nitric acid (sp. gr. 1.5) (Note 3) is added drop by drop, with stirring, from a 125-cc. separatory funnel, the mixture being cooled in an ice-salt bath and the nitric acid added at such a rate that the temperature does not rise above 50° (about fifteen minutes is required for the addition). As soon as all the acid has been added the mixture is poured into a separatory funnel, the sulfuric acid layer is removed, and the upper chloroform layer is immediately (Note 4) run into 500 cc. of 10 per cent sodium carbonate solution. The sulfuric acid layer is discarded because it contains very little dinitrodurene. Four portions are nitrated, and the combined chloroform solutions are washed twice with 2.5 per cent sodium carbonate solution, dried overnight with 30 g. of anhydrous calcium chloride, filtered, and the chloroform distilled until crystals of dinitrodurene begin to appear. At this point four times the volume of hot 95 per cent ethyl alcohol is added (about 500 cc.), and the resulting mixture is cooled to 10°. The solid is filtered and washed twice with 50 cc. of cold (10°) 95 per cent ethyl alcohol. The yield from four nitrations is 82.5–84 g. (92–94 per cent of the theoretical amount) of a product melting at 207–208° (Note 5).

(*B*) *Reduction of Dinitrodurene*.—A solution of 90 g. of dinitrodurene in 1 l. of glacial acetic acid is boiled in a 12-l. flask (Note 6); 700 g. of stannous chloride is dissolved in 800 cc. of concentrated hydrochloric acid and heated to boiling. The heat is removed from the acetic acid solution of the nitro compound, and the stannous chloride solution is poured very carefully (during about ten minutes) into the dinitrodurene solution. The reaction is complete in fifteen minutes, and, as the solution cools, the stannic chloride compound of the diamine begins to crystallize. The reaction mixture is cooled to 10° in an ice-water bath, and the solid is filtered by suction, washed twice with 50 cc. of 95 per cent ethyl alcohol and twice with 50 cc. of ether, and dried. The filtrates from the tin compound contain very little

of the reduction product and may be discarded. The composition of this compound is $[C_6(CH_3)_4(NH_2{\cdot}HCl)_2]_2{\cdot}SnCl_4$, and it crystallizes from the reaction mixture in fine, glistening plates which are almost colorless. The yield is 145 g. (97 per cent of the theoretical amount).

(*C*) *Duroquinone*.—A suspension of 100 g. of the tin compound in a solution of 300 g. of ferric chloride crystals in a mixture of 150 cc. of water and 20 cc. of concentrated hydrochloric acid is allowed to stand overnight at about 30°, and is then filtered. The product is dissolved in 150 cc. of hot 95 per cent ethyl alcohol. The solution is filtered and allowed to stand overnight at 30°. The yield is 40 g. of duroquinone (90 per cent of the theoretical amount) melting at 109–110°.

2. Notes

1. It is better to nitrate the durene in small batches, for a high yield and pure product are obtained only with a minimal contact of the reaction mixture and the nitric acid.
2. Pure durene is absolutely essential for good results. Durene should be recrystallized from methyl alcohol until the melting point is 79–80°.
3. A large excess of nitric acid is undesirable, since it lowers the yield. The concentration of the nitric acid is also of importance, and, to obtain the best results, it should have a specific gravity of 1.5 or more.
4. It is important that the chloroform layer be run into the carbonate solution as quickly as possible, for continued standing in contact with even small amounts of acid leads to the formation of considerable amounts of red, tarry material. This renders the subsequent purification of the nitro compound much more difficult.
5. No mononitrodurene is ever obtained in this process. Either the dinitro compound results, or else unchanged material and oxidation products.
6. A large flask is necessary because the reduction is vigorous and the reaction mixture will boil up and practically fill the flask of the size recommended.

3. Discussion

Duroquinone has been prepared by the action of alkalies on 2,3-diketopentane[1] or 3,3-dichloro-2-pentanone;[2] from durenol by coupling with diazotized sulfanilic acid, reducing the azo dye, and oxidizing the resulting aminophenol to the quinone;[3] and from durene by the series of reactions used above,[4] which is due originally to Nef.[5] The method of nitration used in preparing dinitrodurene is a modification of a method introduced by Willstätter and Kubli.[6]

References and Notes

1. von Pechmann, Ber. **21**, 1420 (1888).
2. Faworsky, J. prakt. Chem. (2) **51**, 538 (1895).
3. Smith, Opie, Wawzonek, and Prichard, J. Org. Chem. **4**, 318 (1939).
4. Smith and Dobrovolny, J. Am. Chem. Soc. **48**, 1420 (1926).
5. Nef, Ber. **18**, 2806 (1885); Ann. **237**, 5 (1887).
6. Willstätter and Kubli, Ber. **42**, 4151 (1909).

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

tin compound

ethyl alcohol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

methyl alcohol (67-56-1)

ether (60-29-7)

chloroform (67-66-3)

nitric acid (7697-37-2)

sodium carbonate (497-19-8)

aminophenol (95-55-6)

stannous chloride

ferric chloride (7705-08-0)

Quinone (106-51-4)

stannic chloride (7646-78-8)

sulfanilic acid (121-57-3)

Durene (95-93-2)

Duroquinone (527-17-3)

Dinitrodurene (5465-13-4)

mononitrodurene

2,3-diketopentane (600-14-6)

3,3-dichloro-2-pentanone (57856-10-7)

durenol