Organic Syntheses

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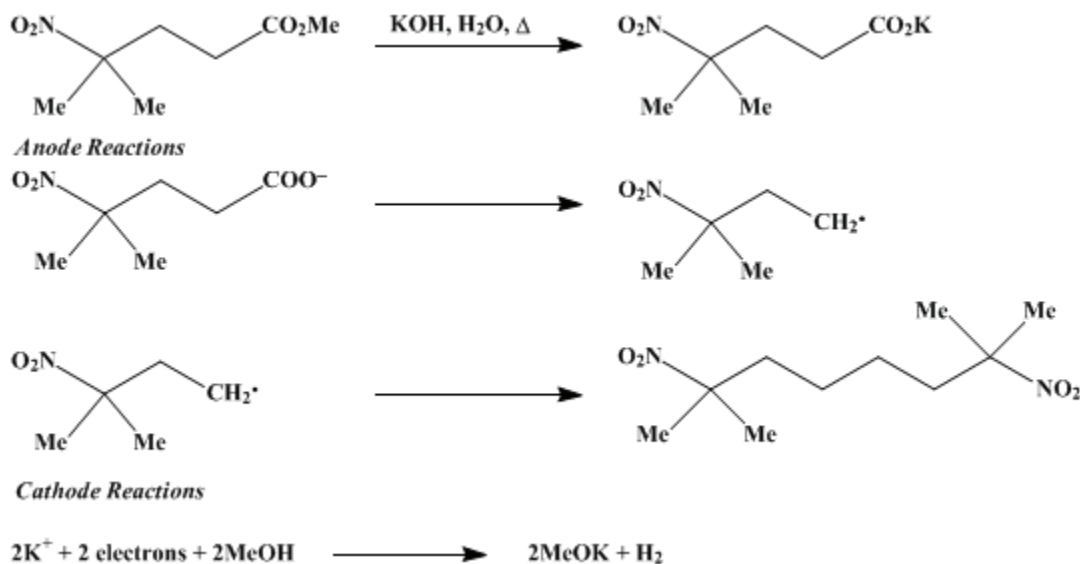
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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2,7-DIMETHYL-2,7-DINITROÖCTANE

[Octane, 2,7-dimethyl-2,7-dinitro-]

Submitted by W. H. Sharkey and C. M. Langkammerer[1].
Checked by Masaaki Takahashi, Marjorie C. Caserio, and John D. Roberts.

1. Procedure

A. *4-Methyl-4-nitrovaleric acid*. In a 2-l. three-necked flask equipped with a stirrer and reflux condenser is placed a solution prepared from 118 g. (1.78 moles) of 85% potassium hydroxide pellets and 500 ml. of water. A thermometer may be so placed in the third neck that the bulb extends below the surface of the solution. To this solution is added 300 g. (1.71 moles) of methyl 4-methyl-4-nitrovalerate.[2] The mixture is stirred and gently heated (Note 1) and (Note 2). After hydrolysis has started, as indicated by changes in appearance of the hazy reaction mixture, the external source of heat is removed. The reaction is complete when the cloudy mixture has changed to a clear solution. This requires about 20–25 minutes (Note 3).

The reaction mixture is cooled to room temperature, and a saturated solution of potassium permanganate is added in an amount sufficient for a violet color to persist for about 1 minute before turning green (Note 4). About 100–110 ml. is required. Manganese dioxide is removed by filtration, and the filtrate is extracted with methylene chloride to remove non-acidic organic material. The aqueous layer is acidified with 18% hydrochloric acid, whereupon a pale yellow or green oil separates as a bottom layer. The oil is removed, and the aqueous layer is washed with methylene chloride. The washings are added to the oil, and the combined product is dried with anhydrous magnesium sulfate. Methylene chloride is removed by distillation, and the residual oil is distilled under reduced pressure through a 6-in. Vigreux column (Note 5). The fraction boiling at 125–135° (0.9–1.5 mm.) amounts to 217–225 g. (79–82%) and is a colorless oil that crystallizes on standing or when seeded to give a solid with a melting point of approximately 35–45°. This fraction is redistilled through a 24-in. spinning-band column and gives 166–180 g. (60–65%) of colorless 4-methyl-4-nitrovaleric acid, b.p. 122–124°/0.70–0.90 mm., m.p. 45–46° (Note 6).

B. *2,7-Dimethyl-2,7-dinitroöctane*. A 200-mm. desiccator is adapted for use as an electrolysis cell. A lid is prepared from a glass plate ground to fit the desiccator; holes are bored in the lid to accommodate electrodes, a thermometer, and a stirrer, and to provide an opening for making additions to the cathode compartment. The cathode (Note 7) is placed in a porous ceramic cup having outside dimensions 4 in. deep, 6 in. long, and 2 in. wide (Note 8). This cup is placed on the glazed ceramic plate

of the desiccator under the holes cut in the lid for the cathode and for making additions. The glazed ceramic plate is notched so that it can be slipped down over the supports in the bottom of the desiccator. The notches should be large enough for the ceramic plate to be about halfway between its normal position and the bottom of the desiccator (Note 9). The cathode is a 26-gauge stainless-steel plate 3 in. square (Note 10), and the anode consists of two platinum plates each 0.01 in. thick and 3 in. square (Note 11) placed as close as possible, one on either side, to the ceramic cup without touching the sides of the cup.

A solution made by dissolving 161 g. (1 mole) of 4-methyl-4-nitrovaleric acid and 33.0 g. (0.5 mole) of potassium hydroxide in 2.7 l. of methanol is added to the cell. The ceramic cup is filled with 200 ml. of 2N potassium hydroxide in methanol. The cell contents are cooled to 20° (Note 12), and current is passed through the solution (Note 13). When the current is turned on, vigorous evolution of hydrogen takes place inside the porous cup. Potassium hydroxide (2N) in methanol is added as needed to maintain the original volume inside the cup (Note 14). Carbon dioxide is evolved at the anodes. After about 5 hours, white crystals of the dinitroöctane form in the anode solution. As electrolysis proceeds, the resistance of the cell increases, and after several hours the cell is operated at 3–5 amperes and 60–80 volts. If a current of 3–5 amperes cannot be maintained, it is desirable to add 2N potassium hydroxide in methanol to the anode compartment (Note 15) and (Note 16). After 8 hours of operation, the current is shut off, the ceramic cup removed and cleaned, and the anode solution cooled to about −30°. The anode solution is filtered to remove crystals of 2,7-dimethyl-2,7-dinitroöctane. The yield of dry product, m.p. 98–100°, amounts to 50–65.5 g. (43–56%), which is sufficiently pure for most uses (Note 17). One recrystallization from methanol (Note 18) gives pure 2,7-dimethyl-2,7-dinitroöctane, m.p. 100–101° (lit.[3] 101.5–102°).

2. Notes

1. If stirring is not used, hydrolysis does not start until the reaction mixture is heated almost to the reflux temperature. Under these conditions the reaction, which is exothermic, proceeds so rapidly that the reflux condenser is flooded.
2. Although no explosions have yet occurred, it is advisable to conduct this reaction behind a shield. The hydrolysis, once started, proceeds quite rapidly.
3. The time required varies with the initial temperature of the hydrolysis solution. With warm solutions, e.g., freshly made potassium hydroxide solution, external heating is not needed. With such a solution, the checkers found that a cloudy mixture having an initial internal temperature of 40° became clear within 2–5 minutes of mixing and during this time the temperature rose to 70°. Stirring was continued for 20 minutes to ensure complete hydrolysis.
4. Addition of potassium permanganate removes colored impurities that otherwise persist through subsequent distillations of the acid. The maximum concentration of potassium permanganate in water at room temperature is about 5%. It may be more convenient to use a concentrated solution of sodium permanganate, which is very soluble in water. However, the end point is difficult to observe with sodium permanganate.
5. During this first distillation, nitrogen oxides are evolved in appreciable amounts. It is suggested this operation be done behind a shield in a well-ventilated area. A trap cooled with a mixture of solid carbon dioxide and acetone or with liquid air should be inserted between the column and the vacuum pump. Pumps used in this distillation did not appear to suffer corrosion damage. A dry oil was used and changed after each distillation.
6. It may be necessary in this second distillation to apply a source of heat to the fraction-collecting system to prevent crystallization of the product prior to entry of the distillate into the receivers.
7. The cathode is the electrode connected to the negative terminal of the current source.
8. A satisfactory alumina cup may be purchased from the Norton Company, Worcester, Mass., Catalog No. 44805, RA-98.
9. This is necessary because the top of the porous cup must be below the lip of the desiccator. The volume of the desiccator up to the top of the porous cup should be 4 l.
10. The considerable heat generated inside the cup leads to rapid evaporation of the methanol with which the cup is filled. The cell can be operated by constant replenishment of methanol. However, loss of methanol can be minimized by use of a water-cooled cathode. Such an electrode is conveniently prepared from two 3-in.-square stainless-steel plates and a strip of stainless steel about 0.25 in. wide,

which are welded to form a stainless-steel box. Nipples serving as water inlet and outlet are welded to the top of the box.

11. The 3-in.-square platinum plates are welded to a heavy platinum wire that protrudes through one of the holes cut in the glass lid. Heavy copper wire (No. 10) is used to connect the electrodes to the source of current.

12. This temperature is easily maintained by surrounding the cell with a methanol bath cooled with solid carbon dioxide. About 100 lb. of solid carbon dioxide is required for 8 hours' operation. Yields are severely reduced if the methanol is allowed to boil. Temperatures lower than 20° can be used but are less satisfactory.

13. The initial current is usually 6–8 amperes at 50–60 volts. The resistance of the cell constantly changes because of depletion of electrolyte and deposition of potassium methoxide in the pores of the ceramic cup. The preferred source of current is a rectifier capable of delivering 10–15 amperes at 30–90 volts. Lead storage batteries connected in series are also satisfactory but require frequent recharging.

14. In a typical run, 30 ml. of 2*N* potassium hydroxide in methanol was added at the end of each hour of operation. Total addition was 210 ml.

15. The amount added must be less than that required to bring the pH to 7. When the pH of the anode solution is greater than 7, undesirable reactions occur.

16. The checkers found that after 5.5 hours the current dropped below 3 amperes at 75 volts. Addition of 25 ml. of 2*N* potassium hydroxide in methanol to the anode solution increased the current to 6 amperes. Subsequent additions of 10–15 ml. of base were made approximately every 30 minutes. The total volume of base added was 80 ml.

17. Some unchanged 4-methyl-4-nitrovaleric acid can be recovered from the spent electrolysis solution by alkaline extraction followed by acidification and distillation of the water-insoluble oil. However, under ordinary circumstances, recovery of this material is not worth the effort expended.

18. About 500 ml. of refluxing methanol and 58 g. of crude product afford about 53 g. (95% recovery) of recrystallized material.

3. Discussion

2,7-Dimethyl-2,7-dinitroöctane has been prepared by nitration of 2,7-dimethyloctane.[3]

4. Merits of Preparation

Kolbe electrolysis is generally useful for the formation of hydrocarbons from monocarboxylic acids and for the preparation of many difunctional compounds as well. A specific illustration is the synthesis of esters of long-chain dicarboxylic acids from monoesters of appropriate dicarboxylic acids (see p. 463). A number of these syntheses are discussed by Fichter.[4] In the present preparation, a two-compartment cell is employed to avoid, or at least greatly reduce, undesired reduction of the nitro group at the cathode. It seems likely that the procedure could be adapted to the preparation of other difunctional compounds containing groups that are easily reduced.

References and Notes

1. Contribution No. 516 from the Central Research Department, Experimental station, E. I. du Pont de Nemours and Co., Wilmington, Del.
2. R. B. Moffett, *Org. Syntheses*, Coll. Vol. **4**, 652 (1963).
3. M. Konowalow, *J. Russ. Phys-Chem. Soc.*, **38**, 124 (1906) [*Chem. Zentr.*, 1906, **II**, 314].
4. F. Fichter, *Organische Elektrochemie*, p. 17, Theodor Steinkopff, Dresden and Leipzig, 1942.

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

hydrochloric acid (7647-01-0)

methanol (67-56-1)

hydrogen (1333-74-0)

potassium permanganate (7722-64-7)

carbon dioxide (124-38-9)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

manganese dioxide (1313-13-9)

methylene chloride (75-09-2)

magnesium sulfate (7487-88-9)

potassium methoxide (865-33-8)

2,7-dimethyloctane (1072-16-8)

Octane, 2,7-dimethyl-2,7-dinitro-,
2,7-Dimethyl-2,7-dinitrooctane (53684-51-8)

4-Methyl-4-nitrovaleric acid (32827-16-0)

sodium permanganate (10101-50-5)

methyl 4-methyl-4-nitrovalerate (16507-02-1)