8. A. Zhunke, Nuclear Magnetic Resonance in Organic Chemistry [Russian translation], Mir, Moscow (1974), p. 40.
9. Sh. A. Samsoniya, M. V. Trapaidze, N. N. Suvorov, and I. M. Gverdtsiteli, Soobshch. Akad. Nauk Gruz. SSR, 91, No. 2, 361 (1978).

ELECTROCHEMICAL SYNTHESIS OF 2,2,6,6-TETRAMETHYLPIPERIDINE

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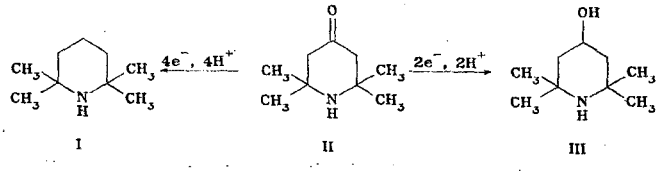
A preparative method for the production of 2,2,6,6-tetramethylpiperidine based on the electrochemical reduction of 4-oxo-2,2,6,6-tetramethylpiperidine in 30% sulfuric acid on cadmium or lead electrodes was developed.

2,2,6,6-Tetramethylpiperidine (I) is used for the synthesis of the medicinal preparation pempidine [1] and the corresponding nitroxyl radical, which is widely used as a spin probe [2], for the stabilization of polymers [3, 4], and for the inhibition of radical polymerization [4, 5].

The known method for the preparation of 2,2,6,6-tetramethylpiperidine (I), which is based on the reduction of 4-oxo-2,2-6,6-tetramethylpiperidine (II) (triacetonamine) with hydrazine, is rather complex, and this limits its use [1].

We have established that two compounds viz, 2,2,6,6-tetramethylpiperidine (I) and 4-hydroxy-2,2,6,6-tetramethylpiperidine (III), are simultaneously formed in the electrochemical reduction of triacetoneamine in an acidic medium on cathodes with high hydrogen overvoltages (cadmium and lead):



Compound III is an important intermediate in the synthesis of stabilizers for polymeric materials [4, 6].

The ratio of the products of electrochemical reduction of triacetonamine concentration stantially on its concentration and the amount of free sulfuric acid in the electrolyte. When the electrolysis is carried out in 30% sulfuric acid at a triacetonamine concentration of 0.65 mole/liter, the yield of 2,2,6,6-tetramethylpiperidine (I) exceeds 65%, and the yield of 4-hydroxy-2,2,6,6-tetramethylpiperidine (III) is 20%. When the triacetonamine concentration is increased to 1.3 moles/liter, the yield of alcohol III increases to 25-27%, and the yield of 2,2,6,6-tetramethylpiperidine (I) decreases correspondingly.

Alcohol III was obtained in virtually quantitative yield by the electrochemical reduction of triacetonamine in an alkaline medium (4% sodium hydroxide solution at a triacetonamine concentration of 0.25 mole/liter [7].

No substantial effect on the yields of the reaction products was observed when the temperature was varied from 25 to 65°C and the current density was varied from 0.05 to 0.01 A/cm^2.

The separation of I and III does not present any difficulties and can be achieved by removal of I from nonvolatile alcohol III by distillation.

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The method for the preparation of 2,2,6,6-tetramethylpiperidine described in this paper is simpler and more efficient than the known method for its synthesis [1] and is the first example of the preparative electrochemical reduction of a piperidone to the corresponding piperidine.

EXPERIMENTAL

Triacetonamine produced by the All-Union Scientific-Research Institute of Glass Fibers in Kalinin (TU 6-06-32-323-79; this product contained 97.9% of the principal substance and had mp 36°C) was used. Thin-layer chromatography (TLC) was carried out on activity II aluminum oxide with elution by chloroform–ethanol (15:1) and development with iodine vapors. The IR spectra were recorded with a Specord 75 IR spectrometer.

2,2,6,6-Tetramethylpiperidine (I) and 4-Hydroxy-2,2,6,6-tetramethylpiperidine (III). A) The synthesis was carried out in the diaphragm electrolyzer described in [8]. The cathode was prepared from analytical-grade cadmium. Prior to electrolysis, the cathode was treated for 3-5 min in 10-12% sulfuric acid, washed with water, purified with soda crystals, and washed again with water. The cathode space of the electrolyzer was charged with 300 ml of 30% sulfuric acid and 31.1 g (0.2 mole) of triacetonamine. The anode space was filled with 30% sulfuric acid. The electrolysis was carried out at a current strength of 15 A (at a current density of 0.11 A/cm^2) at 25-30°C with stirring. The electrolysis time was 3-4 h [the end of the reaction was determined from the disappearance of the triacetonamine, which was determined by means of TLC (R_f 0.83)]. At the end of the electrolysis, the colorless and transparent catholyte was neutralized with 40% sodium hydroxide solution to pH 10. The solution was extracted while still warm (30-40°C) with chloroform (four 150-ml portions), the extract was dried with anhydrous sodium sulfate, and the solvent was removed with a water bath. The residue was subjected to vacuum distillation. The fraction with bp 40-43°C (3 mm), which was identified as 2,2,6,6-tetramethylpiperidine, was collected to give 18.7 g (66.1%) of a product with n_D^{20} 1.4458 (according to the data in [1], this compound was obtained in 51% yield and had bp 151-155°C and n_D^{20} 1.4455). The IR spectra of a sample of I and a genuine sample [1] were identical. Alcohol III, with mp 131-133°C (from n-heptane), the yield of which was 6.3 g (20%), remained in the distilling flask after removal of I by distillation. According to the data in [9], III had mp 131-133°C. No melting-point depression was observed for a mixture of III and a genuine sample [9].

B) Electrolysis of a solution of 31.1 g (0.2 mole) of triacetonamine in 150 ml of 30% sulfuric acid by method A gave 7.84 g (27.7%) of I and 17.2 g (54.6%) of III.

C) The cathode was prepared from C–O grade lead. Prior to electrolysis, the cathode was treated for 5 min in 10% nitric acid, washed with tap water, purified with soda crystals, and washed with distilled water. Electrolysis of a solution of 31.1 g (0.2 mole) of triacetonamine in 300 ml of 30% sulfuric acid by method A gave 16.8 g (60%) of I and 3.12 g (9.9%) of III.

LITERATURE CITED

1. M. V. Rubtsov and A. G. Baichikov, Synthetic Pharmaceutical-Chemical Preparations [in Russian], Meditsina, Moscow (1971), p. 194.
2. A. N. Kuznetsov, The Spin-Probe Method [in Russian], Nauka, Moscow (1976), p. 210.
3. B. Ranby and J. Rabek, Photodegradation, Photooxidation, and Photostabilization of Polymers, Wiley (1975).
4. M. Dagonneau, V. B. Ivanov, E. G. Rozantsev, V. D. Sholle, and E. S. Kagan, J. Mol. Sci. Rev. Macromol. Chem. Phys., 22, 169 (1982).
5. H. C. Bailey, British Patent No. 1346774; Ref. Zh. Khim., 8N71P (1975).
6. A. R. Patel and J. J. Usilton, Stabilization and Degradation of Polymers, Washington (1978), p. 116.
7. T. G. Tsar'kova, V. T. Novikov, I. A. Avrutskaya, and M. Ya. Fioshin, in: News in the Electrochemistry of Organic Compounds. Summaries of Papers [in Russian], Novocherkassk (1980), p. 67.
8. A. P. Tomilov, V. A. Smirnov, and E. Sh. Kagan, Electrochemical Syntheses of Organic Preparations [in Russian], Izd. Orstovsk. Univ., Rostov-on-Don (1981), p. 11.
9. W. Lutz, S. Lazarus, and R. Meltzer, J. Org. Chem., 27, 1695 (1962).