SIDE PROCESSES IN THE REDUCTION OF THE ETHYL ESTER OF p-NITROBENZOIC ACID

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The reduction of the ethyl ester of p-nitrobenzoic acid (I) is one of the basic methods of producing anesthesin. The conditions of the reduction appreciably influence the quality of the final product, in a number of cases contaminating it with colored impurities. A study and elimination of the conditions of formation of the colored impurities are therefore of practical importance.

It might have been assumed that in the reduction of I by cast iron shavings in aqueous medium in the presence of ammonium chloride, processes of incomplete reduction of the nitro compound with doubling of the molecule might take place. Actually, we have isolated and briefly characterized the diethyl ester of p-azoxybenzoic acid (II), the diethyl ester of p-azobenzoic acid (III), the disodium salt of p-azobenzoic acid (IV), and the diethyl ester of p-hydrazobenzoic acid (V).

The side process can be prevented by using an excess of the cast iron shavings and by fractional introduction of I into the reaction sphere. Conducting the process in the opposite manner (excess of I and deficiency of cast iron shavings) permits the production of up to 6% of the azoxy derivative.

EXPERIMENTAL SECTION

The synthesis of side products was accomplished by conducting the reduction of I with cast iron shavings in the presence of ammonium chloride according to the following procedure: 50 g of I and 0.5 g of ammonium chloride were placed in a three-necked flask with mixer, thermometer, and funnel for powders, 200 ml of water was added, the mixture was heated to 90-98°, and at this temperature cast iron shavings (30 g) were added in small portions (5 g at a time). The portions were added at 30 min intervals. After the addition of the entire amount of shavings the reaction mixture was kept at the same temperature for 1 h, then cooled to room temperature and filtered on a Buchner funnel. The filtrate was discarded, and the residue extracted with 200 ml of alcohol. The alcohol extract was diluted with an equal volume of water, and the mixture of anesthesin I, and II, that precipitated was filtered off. The mixture of products was treated with a 10% solution of hydrochloric acid to remove the anesthesin. The insoluble precipitate of I and II remaining was crystallized several times from alcohol. Since II dissolves with difficulty in alcohol, it is readily separated from I. The orange-yellow needles thus obtained, with mp 117-118° (according to the literature data, 117-188° [1]), are soluble in hot alcohol and acetone, and extremely soluble in water. Yield 6%.

Further reduction of II with cast iron shavings in an aqueous alcohol mixture in the presence of ammonium chloride led to the formation of III. Orange crystals with a silky luster, with mp 146-147° (according to the literature data 145.5° [2]), difficultly soluble in alcohol and acetone, almost insoluble in water.

After boiling of III with a 10% alcohol solution of sodium hydroxide for 2 h, followed by filtration and recrystallization from water, we obtained IV. Found, %: Na 15.15, 15.47. $C_{14}H_8Na_2O_4$. Calculated, %: Na 15.02.

Prolonged boiling (13 h) of III in an aqueous alcohol mixture with an addition of a triple excess of cast iron shavings and a small quantity of ammonium chloride yielded V. This was in the form of white needles, difficultly soluble in water, and readily soluble in alcohol and acetone. After repeated recrystallization from alcohol, the product melts at 132° (according to the literature data, 118° [3]). During storage, it slowly acquires a rose color, being oxidized to III.

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