ELECTROCHEMICAL SYNTHESIS OF NICOTINIC ACID AND OF N-ACETYL-1,2,3,4-TETRAHYDROQUINOLINE FROM QUINOLINE

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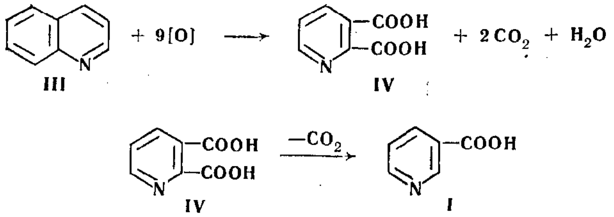
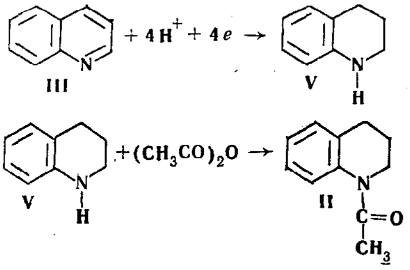
A description is given of a method of synthesizing electrochemically nicotinic acid and N-acetyl-1, 2, 3, 4-tetrahydroquinoline from quinoline, the yield of the former being 40–43% and that of the latter 70–75%.

Nicotinic acid (I) and N-acetyl-1,2,3,4-tetrahydroquinoline (II) are of great practical interest, I being an important vitamin (RR), used to vitaminize flour and fodder, and widely used in medicine, while II is used as the highly effective repellent "kyuzol" [1].

The present paper describes a method [2] for simultaneous synthesis of I and II, unlike previously described methods [3–6] of separate electrochemical synthesis of them. At the anode quinoline (III) is oxidized to quinolinic acid (IV), and this by decarboxylation readily gives I:



At the same time III is reduced at the cathode, to 1,2,3,4-tetrahydroquinoline (V) which is readily acetylated to II.



In previous papers [3,4] anodic oxidation involved evolution of hydrogen at the cathode, and in papers [5,6] cathodic reduction of quinoline involved evolution of oxygen at the anode.

The method of carrying out the electrolysis described here considerably cuts expenditure of electrical energy, technologically, and with respect to production space and equipment required, it is more satisfactory than methods previously described.

EXPERIMENTAL

In the work use was made of pure III, prepared by recrystallizing the phosphate from water as described in [7]. Pure III had the following properties: bp 104–106° (9–9.5 mm), 108–109° (11 mm), 114–115° (17 mm), n_D^{20} 1.6258; phosphate mp 161–162°; picrate mp 202–203°.

The **electrolysis** was carried out in a "viniplast" electrolyzer, with a ceramic or "miplast" diaphragm, separating cathode and anode spaces. The anode was a preformed lead one, previously coated with a layer of lead dioxide, while the cathode was also of lead. The working anolyte volume was 100 ml, that of the catholyte 250 ml.

Anolyte composition (g/*l*): quinoline–100, $(NH_4)_2SO_4$–152, V_2O_5–1; catholyte composition (g/*l*): quinoline–200, H_2SO_4–750. Conditions of electrolysis: anolyte temperature 75 ± 3°; catholyte temperature 20–70°; anode current density 5 amp/sq. dm; cathode current density 15–50 amp/sq dm; quantity of electricity passed 46–47 amp-hr.

Nicotinic acid (I). After electrolysis the anolyte was neutralized with 25% ammonia, and brought to pH 2. IV was isolated from this solution by extracting with n-BuOH at 90–95°, and on distilling off the solvent IV is decarboxylated to I. The butanol is distilled off till the volume is small, and on cooling I separates. Yield 4.2–4.5 g I containing 90–95% of the main component, equal to a 40–43% yield.

N-acetyl-1, 2, 3, 4-tetrahydroquinoline (II). After electrolysis the catholyte was made alkaline, when V separated out, along with dihydroquinoline polymers and unreacted III. Compounds V and III were steam-distilled off, and were extracted from the distillate with benzene, which was then distilled off. A small excess of Ac_2O was added to the residue, the mixture boiled for 1 hr, and the products vacuum-distilled, when II distilled over at 144–147° (6 mm), 156–159° (9 mm), 169–172° (16 mm), yield 47–50 g II, i.e. 70–75%. Found: C 75.30; 75.75; H 7.32; 7.26; N 8.07; 8.09%. Calculated for $C_{11}H_{13}NO$: C 75.39; H 7.47; N 7.99%.

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