The product so prepared melted at 231–233°. It was insoluble in ether, chloroform, ethyl acetate and benzene. It crystallized from hot 95% ethyl alcohol in beautiful lemon yellow needles having a final melting point of 288.5°.

Anal. Qualitative: C, H, N, +; S, Cl, −. Calcd. for $C_{12}H_{11}O_3N$: C, 66.35; H, 5.07. Found: C, 66.32; H, 5.00.

The yield of the product melting at 231–233°, as shown in three separate runs, averaged slightly below 20%. The yield of the product melting at 288.5° was approximately 12% of the theoretical. This low yield was believed to be due to the retention of much of the product in the precipitated chromium hydroxide, which was difficult to filter out, and almost impossible to wash.

Summary.—Optochin has been oxidized with chromic oxide in an acid solution. The analysis of the product, and its method of preparation, indicated that it was 6-ethoxyquinoline-carboxylic acid-4.

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COMMUNICATIONS TO THE EDITOR

THE POTENTIAL OF THE Ag(s), AgCl(s), KCl(aq), AgCl(s), Ag(s) CELL, SHOWING THE EFFECT OF FLOWING THE ELECTROLYTE OVER ONE ELECTRODE ONLY

Sir:

Carmody, in a recent note [THIS JOURNAL, **52**, 210 (1932)], states that when the electrloyte is flowing over a Ag(s), AgCl(s) electrode, there is a difference of 0.006 volt positive to a Ag(s), AgCl(s) electrode at equilibrium with the cell solution [p. 191]. This note was written because the value obtained for the Pb, Pb^{++} potential by Randall and Cann [THIS JOURNAL, **52**, 589 (1930)] was 0.1203 v. whereas Carmody [THIS JOURNAL **51**, 2905 (1929)] had obtained the value 0.1263 v. The difference in values was attributed by Carmody to the fact that Randall and Cann had allowed the electrolyte to flow over the Ag(s)–AgCl(s) electrode.

Because of this apparent discrepancy the authors investigated the cell Ag(s), AgCl(s), KCl(aq), AgCl(s), Ag(s), using an H-cell, set up according to Fig. 1, keeping the electrolyte on one side stationary, and allowing it on the other side to be in motion, entering the cell at I and leaving it at II. The Ag(s)–AgCl(s) electrodes were prepared in precisely the same way as had been done previously by Randall and Cann, care being taken to free them from adsorbed gas. The electrodes were white because they were protected from all light. Every operation was performed in containers painted black on the outside. Two cells were made, one containing 0.025 *M* KCl and the other 0.05 *M* KCl. All measurements were made with a Type K potentiometer, using an oil-bath regulated at 25°.

Analysis of the results reveals the following facts. First, readings were always taken with the electrolyte on both sides of the cell stationary. In each case a period of at least twenty-four hours was allowed for this equilibrium to be obtained. After the flow of the electrolyte was started, a period of about twenty minutes was allowed to elapse before any readings were taken, in order to permit the cell to come to equilibrium under the new conditions. When the electrolyte was flowing, the potentials were always negative to those obtained when the electrolyte was stationary.

More than forty readings were taken on Cell A and about fifteen on Cell B. With Cell A the readings varied from the lowest values of -0.00023 v. to the highest of -0.00162 v. With Cell B the lowest reading was -0.00072 v. and the highest -0.00190 v. The average of the differences from the mean in Cell A was 0.00038, and the average deviation of the average differences was 0.000078. The average of the differences from the mean in Cell B was 0.00031 and the average deviation of the average differences was 0.0001.

It might seem that the greater the rate of flow the more negative the difference becomes. A large variety of different rates of flow was examined, but apparently no definite relationship exists between rate of flow and difference of potential. Also, readings of the barometer were invariably taken, but the variations in this value, a maximum of eight millimeters, appeared to have no effect. The average difference in potential due to the flowing of the electrolyte in Cell A was -0.00074 v., and that in Cell B was -0.00100 v.

Fig. 1.

These results indicate that Carmody is correct in his contention that there is a drop of potential when electrolyte is flowing over the Ag(s), AgCl(s) electrode. But the value obtained by us, using potassium chloride as the electrolyte, is much less than that suggested by Carmody, who used hydrochloric acid as the electrolyte. Our values of -0.00074 and
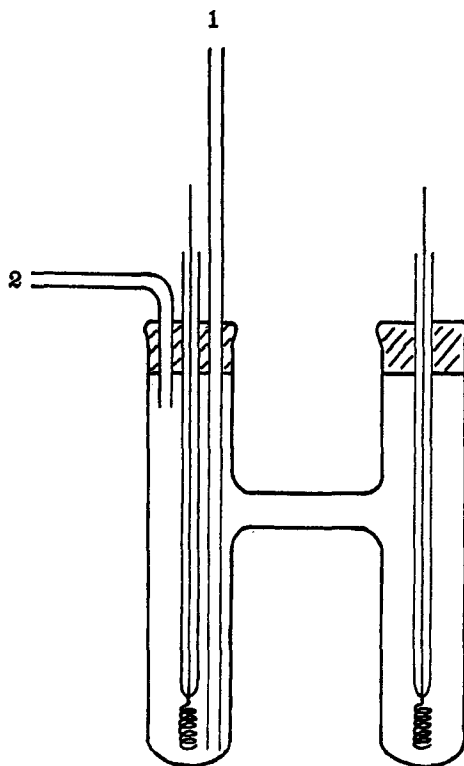
−0.00100 are not sufficient to account for the discrepancy between the values of 0.1203 v. for the Pb, Pb^{++} electrode as obtained by Randall and Cann and the value of 0.1263 v. as obtained by Carmody.

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THE CONSTITUTION OF BORNYL ANILINE

Sir:

In a recent publication, P. Lipp and G. Stutzinger [*Ber.*, **65**, 241 (1932)] presented evidence purporting to establish the identity of the so-called "bornyl aniline" of Ullmann and Schmidt [*ibid.*, **43**, 3202 (1910)] with the secondary amine obtained by the condensation of aniline with camphene in the presence of aniline hydrochloride and also with the amine resulting from the reduction of camphor anil with hydrogen and platinum. These findings have duplicated in part investigations well under way in this Laboratory, on which a preliminary report was presented by the authors at the recent Fall Meeting of the American Chemical Society at Buffalo, N. Y., under the title "The Fixation of Aniline by Hydrocarbons of the Terpene Series." The results of our experiments confirm the statement of L. and S. as to the identity of the camphene-aniline condensate with "bornyl aniline," but appear to be at variance with regard to the amine obtained from camphor anil by reduction. We performed the reduction of the anil with sodium and aniline as the reducing medium, obtaining a secondary amine whose acetyl derivative melted at 112–113° while L. and S. report 123° as the melting point of their product. The behavior of these amines, and also one obtained by the condensation of aniline with α-pinene in the presence of aniline hydrochloride are under investigation in this Laboratory in a further attempt to establish their structures by exhaustive methylation. The bornyl aniline of Ullmann and Schmidt and also that obtained from camphene have been found to yield camphene nearly quantatively, while those obtained from α-pinene and reduced camphor anil exhibit behavior on exhaustive methylation which is similar to that of bornyl amine.

We expect to publish a complete account of this investigation in the near future.

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