Reduction of Acetophenone by an Electrolytic Method Using Raney Nickel as Catalyst

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The electrolytic reduction of ketones has been studied with many compounds, and its reduction proceeds to the formation of hydrocarbon, alcohol, and pinacol or a mixture of both alcohol and pinacol. These reductions depend upon the electrode materials, electrolyte, temperature, and the concentration of ketones. Concerning acetophenone, Elbs and Brand[1] found that in alkaline or acid solution at lead cathode, it was reduced to a mixture of acetophenonepinacol and methylphenylcarbinol. Swann[2], Kauffler[3], and Müller[4] prepared acetophenonepinacol by using many electrode materials in alkaline or acid solution. Futaki[5] prepared methylphenylcarbinol with a better yield in the solution of sodium sulfate at mercury cathode and lead anode. By the chemical method, acetophenone[6] was hydrogenated to methylphenylcarbinol at room temperature under the pressure of 15 to 45 lb./sq.in. using Raney nickel as catalyst.

Raney nickel, however, has not been used for electrolytic reduction. The author tried to prepare methylphenylcarbinol from acetophenone by the electrolytic method with Raney nickel and found a way to produce it with a satisfactory result by using lead cathode in weak alkaline electrolyte with Raney nickel suspended.

Experiment and Discussion

In acid or alkaline solutions using lead, copper, and zinc amalgam electrode, the reduction of acetophenone by electrolytic method was not suitable for the synthesis of methylphenylcarbinol.

Then Raney nickel was suspended in cathodic solution,—Wako Pure Chemical Industries Ltd.'s Raney nickel was used. By this method, in acid solution the resinous material formed in electrolysis mixed with nickel, adhered to the cathode plate, and in consequence the electrolysis was not conducted well. In alkaline electrolyte with Raney nickel which corresponded from about 5 to 10% by weight of the ketone, the reduction was confirmed to be the most favorable for the purpose. The electrolysis was conducted under following conditions;

Cathode: lead plate 100 cm^2; Cathodic solution: 25 g. of acetophenone and 2 g. of Raney nickel suspended in a mixture of 70 ml. of 5% sodium hydroxide and 70 ml. of alcohol was placed in a porous pot;

Anode: carbon plate; Anodic solution: 5% sodium hydroxide;

Temperature: 25°C average; Time of electrolysis: 17 hours.

The electrolysis was carried out by cooling the electrolytic bath in cold water and by vigorously stirring the cathodic solution to which 2 g. of Raney nickel was added at the same time.

The completion of electrolysis is recognized when a small quantity of cathodic solution, after acidifying, gave a negative ketone test with sensitive 2,4-dinitrophenylhydrazine reagent.

After the finishing of electrolysis, the alcohol was evaporated on a water bath and the residue was made slightly acidic by addition of diluted sulfuric acid and had the nickel therein filtered off after cooling. Then it was extracted repeatedly with ether, and the combined ether extracts were dried over anhydrous potassium carbonate.

The ether was removed and the residue distilled. The fraction distilling at 98°–100°C/18 mm Hg was collected. Its yield was about 18.5 g., corresponding to 74% of the theoretical amount. This substance was colorless, and gave a negative test with 2,4-dinitrophenylhydrazine reagent, but it smelled like acetophenone when oxidized with potassium chromate and sulfuric acid, and formed 2,4-dinitrophenylhydrazone melting at 246°–247°C (uncorr).

Moreover, the reduced material was mixed with phenyl isocyanate and then the crystal formed was recrystallized from alcohol, m.p. 92°–93°C. This corresponds to the reported value of 94°C for methylphenylcarbinol.

The average yield of reduction was calculated to correspond to 73% of the theoretical amount. The yield was not affected by ketone concentration from 1 to 3 molar, but in higher concentrations the yield was decreased, and it resulted in the formation of tarry materials. Sodium acetate in cathodic solution which was used for a pinacol formation was not favorable in this experiment.

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1) K. Elbs and K. Brand, *Z. Electrochem.*, **8**, 784 (1902).

2) S. Swann and C. Herson, *Electrochem., Spec.*, reprint, **67**, 49 (1935).

3) F. Kauffler, *Z. Electrochem.*, **13**, 633 (1907).

4) E. Müller, *Z. Electrochem.*, **16**, 236 (1910).

5) Zenji Futaki (present address: Shiono Chemical Industrial Co.), *Japan. P.* 174, 272 Dec. 10 (1946).

6) H. Adkins and H. Billica, *J. Am. Chem. Soc.*, **70**, 659 (1948).

The temperature was found not to influence the reduction result from 20°C to 50°C, but the yield was lowered above 80°C in a water bath.

It was also found that the current density had no effect between 4 and 7 amps./cm^2.

In this method, it was thought that the electrode material was of little significance as Raney nickel was suspended in electrolyte, therefore copper cathode was used instead of lead, and the electrolysis was conducted under the same condition as before.

Consequently, the same reduction product and similar yield was obtained.

This was regarded as a catalytic reduction by electrolysis, that is, the electrolysis was used only for the evolution of hydrogen.

Up to the present, the electrolysis using the catalyst has been attempted in different methods, but these have not been carried out well, because the catalyst reacted on the acid of electrolyte generally, except that platinum electrode was used.

In our experiment, however, as electrolysis was conducted in alkaline solution, the catalyst was not changed, so that this case was thought to be very favorable.

In the experiments related above, ethylbenzene was not prepared from acetophenone, and therefore the reduction of methylphenylcarbinol obtained was carried out in acid electrolyte. The electrolysis was conducted by using zinc amalgam cathode in the mixture of 50% sulfuric acid and ethyl alcohol, and it seemed that only benzene ring was partially hydrogenated, but the identification of the reduction product was not investigated further.

Summary

The catalytic reduction of acetophenone by electrolysis using Raney nickel in weak alkaline solution with lead or copper cathode was studied and methylphenylcarbinol was prepared.

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