[Contribution from the Chemical Laboratories of Montana State University]

PINACOL REDUCTION OF KETONES AT PLATED COPPER GAUZE CATHODES

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Reduction of ketones to pinacols electrolytically as an alternative to the use of metallic reducing agents such as aluminum and magnesium amalgams has been known for many years (1). In general, electrolytic reduction has the advantages of requiring a smaller volume of solution and giving a reaction mixture easier to work up.

The purpose of this problem was to study the reduction at copper gauze cathodes plated with various other metals. Sheet lead, pure and plated (1–3), and mercury (4) have been used most often as cathode materials in this reaction. Lead electrodes are troublesome to make and are more difficult to support in the reaction vessel than copper gauze electrodes. Pure sheet lead is not as readily available as copper gauze and impurities present in ordinary lead may diminish current efficiency. The area of mercury cathodes is limited by the shape of the reaction vessel and, in alkaline medium, sodium ion is reduced, thus obscuring visible evidence of the end of the reaction. Copper electrodes (sheet and gauze) have been used previously for reducing nitro compounds (5), aromatic acids (6), and Michler's ketone (7) (to a pinacol) but no systematic study has been made of their reducing properties with ketones. It is necessary to plate the copper with other metals because the overvoltage of the pure copper is too low to bring about the pinacol reduction of most ketones.

p-Hydroxypropiophenone was the compound used in most of the reductions because it forms two isomeric pinacols which can readily be separated and because it is easily soluble in a variety of media. This ketone has previously been reduced by aluminum amalgam (8, 9) and electrolytically at a lead cathode (2, 3). The pinacol was first made by Dodds (8) as an intermediate in the synthesis of dienestrol. Adler (9) separated and purified two isomers of the pinacol, using the diacetates as intermediates. The α (meso) isomer comprised 58% of the mixture (m.p. 217–219°). The more soluble β (racemic) isomer melted at 212–214°. Hobday and Short (3), reducing the ketone in alkaline medium at a lead cathode obtained a 20% yield of material melting at 204–206°. Another isomer, to which the *dl* configuration was assigned, was isolated which was reported to melt at 95°. In this work, no compound corresponding to the 95° isomer of Hobday and Short was isolated, the two isomeric pinacols and their diacetates giving melting points similar to those reported by Adler.

The reaction variables studied were the mesh of the gauze, plating material and density of coating on the cathode, current density, and temperature and *p*H of the reaction medium.

Copper gauze having meshes of 20 (0.0155 in.-diam. wire), 40 (0.009 in.-

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[1] Taken from the M.A. thesis of W. J. Sullivan, Montana State University, 1953.

diam. wire), 60 (0.007 in.-diam. wire), and 100 (0.0045 in.-diam. wire) was used. It was found that the mesh of the gauze had no effect on the products formed but that current efficiency decreased as the mesh grew larger. Current efficiency was low enough with #20 gauze to obscure the end point of the reaction which was marked by vigorous evolution of hydrogen with cathodes giving high current efficiency. For this reason most runs were made using #40 and finer mesh gauzes. Quantitative measurements of the variation of current efficiency with mesh are shown in Table I.

Current efficiency and product yield were found to vary widely with the plating material. Lead and mercury were the only platings which gave high enough current efficiencies in alkaline medium to warrant extensive study. In acid medium platings of mercury, lead, bismith, cadmium, arsenic, antimony, and thallium were studied. Lead and mercury platings were again found to give the highest current efficiencies as well as the best yields of pinacols. Lower efficiencies and yields were obtained with bismuth, cadmium, and thallium. Antimony and arsenic were found to be ineffective. The gauze was also given a heavy plating of nickel or silver followed by mercury. These electrodes gave lower yields compared with electrodes plated directly with mercury. Yields from mercury plated cathodes in alkaline medium and cathodes, plated lightly with lead, in acid medium were about the same as the yields obtained from the mercury cathode and copper plated lead cathode in the same solution, but higher current efficiencies were obtained with the plated copper gauze cathodes.

Although a pure copper cathode produces only hydrogen under the conditions of the reaction, very little mercury need be added to cause reduction. The minimum amount found to be effective was 0.02 mg./cm.^{2} on #60 gauze in acid medium. No effect was noted on yield and current efficiency by changes in the plating density of the mercury. With lead, a light plating where the copper was plainly visible gave better yields of pinacol in acid medium than heavily plated cathodes. In alkaline medium, only the heavily plated cathodes gave high enough current efficiencies to be effective.

In acid medium current densities ranged from 0.003 to 0.03 amp./cm.^{2} and in alkaline medium from 0.0009 to 0.24 amp./cm.^{2}. No effect was noted except for a decrease in yield for low current densities, and a slight decrease in current efficiencies at high current density.

Temperature appeared to have no effect on yield and current efficiency from 15–40° in acid medium, but the yield dropped by 50% between 40 and 50°. No temperature effect was noted in alkaline medium between 15 and 35°.

The electrolyte concentration and *p*H of the medium were found to be important in determining current efficiency, yield, and proportion of isomers present in the product. The acid medium consisted of methanol, water, and varying amounts of acid. Phosphoric acid was found to be ineffective in any concentration used. With sulfuric acid, the current efficiency dropped when the acid concentration was less than 3 g./100 ml. of catholyte. When the concentration exceeded 7 g./100 ml. there was a reduction in yield of pinacol but not in current efficiency. In alkaline medium, concentration had no effect on current efficiency

TABLE I

CURRENT EFFICIENCIES OF MERCURY-PLATED COPPER CATHODES

Cathode	Efficiency—per cent		
	Battery current		Rectifier current, acid soln.
	Acid. soln.	Alk. soln.	
100 mesh	78	77	63
60 mesh	69	79	55
40 mesh	68	69	—
20 mesh	48	64	—
Foil	44	57	—

within the ranges studied, but yields of pinacol dropped from 60–70% in 8–10% sodium hydroxide to 50% in 5% solution and 10% in 2.5% solution. No advantage was to be gained in using solutions stronger than 10% as the sodium salt of the α isomer precipitated out and clogged the cathode. A few runs were made with a buffered catholyte of sodium acetate, acetic acid in water, and methanol. Some product was obtained but yield and current efficiency were low even with mercury plated cathodes.

Rectifier and ripple-free direct current were both used. The only difference noted was that rectifier current gave lower current efficiency (Table I).

The α and β isomers could be separated in a fairly pure state on the basis of the solubility of their sodium salts in 20% salt solution. Lead and mercury plated cathodes gave the same proportion of isomers but the *p*H of the medium was found to have some effect. Acid and alkaline media gave 60–70% of the α isomer while buffered medium gave only 45%.

In addition to the isomeric pinacols a viscous liquid product was formed in acid, buffered, and, to a lesser extent, in alkaline media. It appeared to be polymeric as no volatile product could be obtained by methylating it, or by dehydrating the methylated product. Since the amount formed was not increased by prolonging the time of the electrolysis, the pinacols apparently were not intermediates.

A few runs were made with *p*-methoxypropiophenone in acid, alkaline, and buffered media using mercury plated cathodes. Current efficiency was good and fair yields of one of the isomers was obtained in acid and buffered media. However, the other isomer was an oil and the solid isomer was so insoluble that it coated both the diaphragm and cathode before the reaction was complete. Methylation of the α-*p*-hydroxy- isomer produced the insoluble pinacol, while the product from the methylation of the β-*p*-hydroxy isomer was an oil.

EXPERIMENTAL[2]

p-Hydroxypropiophenone. The Dow product was decolorized and recrystallized twice from reagent acetone to give a light tan product melting at 148–150°.

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[2] Melting points in this paper are uncorrected.

p-Methoxypropiophenone. The Dow product was used without further purification.

Apparatus. The reductions were carried out using a modification of the apparatus used by Swann (10). A 300-ml. Berzelius beaker was equipped with a rubber stopper drilled with holes to accept a 22 x 80 mm. alundum extraction thimble, used as anode compartment, propeller type stirrer, thermometer, and cathode tab. A platinum mesh anode was used in all runs. In alkaline medium, 40% potassium carbonate (10) and in acid medium, methanol, water, and a small amount of the acid. The current passing through the cell was measured with an ammeter. Two sources of direct current were used, a 55 volt rectifier and a motor generator passing its output through a battery bank, with the current for the electrolysis being taken off the battery terminals.

Cathodes. The *copper gauze* was cut to proper shape and sewn together with fine copper wire. The area of the cathode was estimated from the diameter of the wire and the mesh number, taking into account the sinusoidal curve of the wire but ignoring irregularities in shape and contact points between the wires.

Mercury cathodes were made by covering the bottom of the beaker with mercury and connecting the pool to the current source with an iron wire lead inside a glass tube.

The *lead cathode* was made by welding 2-mm. lead tubing into a cylindrical shape and drilling a grid of 3-mm. holes 8 mm. apart in order to aid mixing.

Platings. The copper cathodes were first cleaned by dipping in 40% nitric acid followed by a water wash and a bath in concentrated hydrochloric acid.

Mercury was plated on the cleaned cathode by dipping in a 5% solution of mercuric chloride for a few seconds, followed by a wash with concentrated hydrochloric acid to give a shiny coating. The cathode then was washed with water and used immediately. For light mercury platings, the cleaned cathode was allowed to stand for 15 minutes in a water solution containing the desired amount of mercuric chloride, with occasional stirring. The cathode then was rinsed with water and used immediately.

Lead was plated on the cleaned cathode by electrolysis with a 1 amp. current of a 5% solution of lead fluoborate using lead anodes. Where light platings were desired the process was stopped while the copper was still visible.

Bismuth was plated using the method outlined by Harbaugh (11) and Swann (10) using bismuth perchlorate solution and a platinum anode.

Cadmium and *thallium* were also electroplated from perchloric acid solutions.

Antimony and *arsenic* were electroplated from a solution of the trioxide in hydrochloric acid.

Nickel was electroplated from an ammoniacal nickelous sulfate solution and *silver* from a cyanide solution. Platinum anodes were used for all platings but lead.

Lead electrodes were electroplated with copper by adding a small amount of copper sulfate to the catholyte used in the reduction of the ketone.

Pinacol reductions. (*a*). *Acid medium.* The appropriate amount of ketone (5–15 g.) was dissolved in 160–180 ml. of methanol and placed in the reaction beaker. A solution of the acid to be used (usually 4–6 ml. of conc'd sulfuric) in 60 ml. of water was added. The beaker was set in a cooling bath, and the solution was stirred while the current was passed through. Current was passed until a vigorous evolution of hydrogen was noted and then for an additional 20–30 minutes. Prolonged passage of current appeared to have no significant effect on the yield. When cathodes of low current efficiency were used, 2–300% excess current was passed through the cell as the end point of the reaction could not be determined. The maximum current was limited to 5 amp. as the cell would otherwise heat excessively. Where high current density was desired, small cathodes were used. Most reactions were run with a current density of 0.05–0.07 amp./cm.^{2} The reaction product was neutralized with 28% ammonia, filtered, and evaporated *in vacuo* until all methanol was removed. The gummy residue was washed twice with water and transferred to a 50-ml. flask with the aid of 10–20 ml. of warm glacial acetic acid. The solution then was chilled overnight in the refrigerator. The product was filtered, washed to colorless with glacial acetic acid, and suspended in a little water. Reagent sodium bicarbonate was added with stirring until the suspension tested alkaline. The product then was filtered, washed with water, and dried. If no starting material were present, the product melted at 180–195°, otherwise melting might start at about 150°. Under optimum conditions of temperature and acid concentration (15–25°; 3–6 g. of sulfuric acid per 100 ml. of catholyte) lead- and mercury-plated cathodes gave yields of 35–40% of the mixture of isomers. Cadmium- and bismuth-plated cathodes gave yields of about 25% and thallium 20%. Antimony and arsenic coatings were not effective.

(*b*). *Alkaline medium.* The appropriate amount of ketone (10–15 g.) was dissolved in a solution of 16–20 g. of sodium hydroxide in 180 ml. of water. The solution was cooled and stirred while the current was passed through. The reaction was interrupted 15–20 minutes after a vigorous evolution of hydrogen started. The reaction mixture was acidified with acetic acid and heated until the gummy residue solidified. The product then was filtered, washed with water, and suspended and stirred in a small amount of glacial acetic acid for 5 minutes. The product was filtered and washed with a small amount of acetic acid and water. It was suspended in water and treated with sodium bicarbonate as previously outlined. The product then was filtered, washed with water, and dried. The melting point of the product was the same as for the acid-reduced product. Mercury- and lead-plated copper gauze cathodes and the mercury cathode all gave similar yields running from 60–70%. The current efficiency of the lead electrode was too low to be effective.

(*c*). *Buffered medium.* The solution was similar to that used in acid runs except that 13 ml. of acetic acid and 6 g. of sodium acetate were added as electrolyte. The product was worked up in the manner outlined for an acid medium except that ammonia was not added. Using mercury-plated cathodes the yield of product was about 15–20%.

Separation of isomers. The crude product was suspended in 14 times its weight of water, a 10% excess of sodium hydroxide was added, and the mixture was warmed until the solid dissolved. Enough reagent sodium chloride to make a 20% solution was added with stirring. The solution was seeded or scratched until crystallization ensued, then allowed to stand in a cool spot for 2 hours, with occasional stirring. The solid was filtered by suction on a sintered glass funnel and the precipitate washed with 20% brine. The filtrate was acidified with acetic acid, heated to boiling, cooled, and filtered. The above precipitate was dissolved in 50–100 ml. of water, acidified with acetic acid, heated to boiling, cooled, and filtered. The melting points of the insoluble (α) isomer were from 190–195° to 200–207°, and for the soluble (β) isomer from 195–200° to 207–212°. Handling losses ran from 3 to 9% of starting material. If desired, the wash with glacial acetic acid outlined previously, followed by neutralization with sodium bicarbonate could be repeated to give a somewhat purer product. The best sample of α-isomer isolated under these circumstances melted at 206–209° and the purest sample of β-isomer at 208–212°. To obtain the isomers in the pure state, the method of Adler (9) was used starting with the products of the first separation. The purified α-diacetate melted at 205–208.5° [208–210° (9)]. The pinacol recovered from hydrolysis of the diacetate was recrystallized from reagent acetone, m.p. 220.5–222° [217–219° (9)]. The diacetate of the β-isomer melted at 78–82° [83–84°(9)] and the pinacol at 212–215.5° [212–214° (9)].

Current efficiency. Quantitative measurements and comparisons of current efficiencies between various meshes of copper gauze were made in a cell different from that used in the preparations. The cathode compartment was an inverted 8-in. test tube with a 2 in. length from a 6-in. test tube sealed on the bottom. The cathodes were 2.5-cm. wide and cut to length so each would have an area of about 42 cm.^{2} The cathode was soldered to a copper lead and set in a U tube with wax. The cathode was cleaned and plated with mercury as previously outlined. A current of 0.8 amp. (ammeter) was passed for 2 minutes or until about 10 ml. of gas was collected, the time being measured by a stop watch. The cathode compartment was set in a 250-ml. beaker which served as an anode compartment, with a platinum anode. The acid and alkaline solutions used were the same as those outlined previously and contained 10 g. of ketone. The results obtained are summarized in Table I. The volume of gas generated was measured (corrected to standard conditions) and used to calculate the efficiency.

By-products. The oily material from several acid runs was methylated with dimethyl sulfate and sodium hydroxide and an attempt was made to distill the product *in vacuo*. No distillate was obtained to a bath temperature of 200°. Attempts to produce a volatile product by boiling with acetic anhydride were also unsuccessful.

Reduction of p-methoxypropiophenone. A solution of 16 g. of ketone in 180 ml. of methanol, 5 ml. of sulfuric acid, and 50 ml. of water was electrolyzed at 25° with a 60 mesh, 280 cm.^{2} copper gauze cathode plated with mercury. The current of 2.4 amp. was passed for 66 minutes. The anode was platinum and the anolyte consisted of methanol, water, and sulfuric acid. The current dropped near the end of the reaction as the diaphragm and cathode became coated with product. The mixture was worked up as previously described for an acid medium. The crude product was washed with isopropyl ether to remove the oil and was recrystallized from an acetone-isopropyl ether solution to give 3.6 g. of product, m.p. 192–194° [194° (3)]. Methylation of the α-*p*-hydroxy isomer with dimethyl sulfate and sodium hydroxide produced the same compound.

Reduction of the ketone in alkaline medium, with methanol added as solvent, did not give rise to a solid product.

Reduction in buffered medium gave about the same yield of solid product as in acid medium.

SUMMARY

p-Hydroxy- and *p*-methoxy-propiophenone have been reduced at plated copper gauze cathodes under a variety of conditions. Best results were obtained with mercury and lead platings. The cathodes were convenient to prepare and meshes of 40 and finer gave very high current efficiencies.

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